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The Chemistry of
SYNTHETIC DYES

VOLUME V

Edited by

K. VENKATARAMAN

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PREFACE

For a few years I considered writing an entirely new edition of "The Chemistry of Synthetic Dyes." As a result of discussions with many friends and colleagues who are familiar with the two volumes, I decided that the urgent need was not for a revision, because very little of the material had become obsolete, but for the addition of supplementary material covering the developments from 1950.

The progress made in the chemistry of synthetic dyes in the last twenty years is amazing. The discovery of reactive dyes is one major advance. There has also been extensive research on intermediates, disperse dyes, cationic dyes, cyanine dyes, and pigments, which has led to much new chemical knowledge. Consequently I realized that it was no longer possible for a single author to give accurate and authoritative accounts of the progress made in each specialized area of synthetic dyes. I have been very fortunate in the response I have had to my invitations to contribute to the additional volumes. The chapters have been written by acknowledged authorities who have worked for many years on the topics they have covered; their names have been associated with many patents and papers.

The additional volumes not only cover synthetic dyes of nearly all types, but also raw materials, intermediates, and such fundamental topics as color and electronic states of organic molecules, measurement of color, photochemistry of dyes, and physical chemistry of dyeing. A separate chapter on fluorescent brightening agents has also been included because of their close relationship to synthetic dyes.

These volumes are intended primarily for chemists and technologists who are concerned with the synthesis of dyes and their applications, but since most of the chapters constitute essays in synthetic organic chemistry, they should be of interest to organic chemists in general. An important feature is the very thorough coverage and critical assessment of patent literature as well as publications in scientific journals. The record of achievement presented in these volumes also indicates the direction of future research.

I am deeply indebted to the authors for accepting my invitation. I must also thank the companies who made it possible for their leading scientists to spare the necessary time. The plan for this multiauthor effort took concrete shape during ten days I spent in the Research Department of Farbenfabriken Bayer; I am greatly indebted to Professor Petersen, Dr. Delfs, and their colleagues for valuable suggestions. I am grateful to Dr. R. R. Davies of the Research Department, Imperial Chemical Industries (Dyestuffs Division), Manchester, who has helped me in many ways. My thanks are also due to Dr. R. B. Mitra, Mr. J. V. Rajan, Dr. N. R. Ayyangar, and Mr. V. Parameswaran for assistance in the editorial work. Academic Press has handled production of the volumes with its usual efficiency, and it is a pleasure to thank the staff for their cooperation. Finally, I wish to make grateful acknowledgment of the hospitality of the National Chemical Laboratory provided by the Director, Dr. B. D. Tilak, and the Director-General of Scientific and Industrial Research, Dr. Atma Ram, without which I could not have undertaken this project.

K. VENKATARAMAN

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VOLUME II

VOLUME III

VOLUME IV

VOLUME VI

VOLUME VII (*Tentative*)

LIST OF ABBREVIATIONS

Manufacturing companies (CI abbreviations have generally been followed):

AAP	Koppers Co. Inc., Pittsburgh, Pennsylvania (American Aniline Products Inc.)
ACC	Augusta Chemical Co., Augusta, Georgia
Acna	Aziende Colori Nazionali Affini A.C.N.A., Milan, Italy
B & BASF	Badische Anilin- und Soda-Fabrik A.G., Ludwigshafen a. Rhein, Germany
BrC	British Celanese Ltd., Spondon, England
CCC	American Cyanamid Co., Bound Brook, New Jersey
CFM	Cassella Farbwerke Mainkur A.G., Frankfurt a. Main, Germany
Chinoin	Chinoin Gyogyszer-es Vegyeszeti Termelek Gyara, RT, Budapest, Hungary
CIBA	CIBA Ltd., Basle, Switzerland
CL	Celanese Corporation of America, New York
CN	Compagnie Nationale de Matières Colorantes et de Produits Chimiques du Nord réunies Etablissements Kuhlmann, Paris, France
DGS	Deutsche Gold- und Silber Scheideanstalt vormals Roessler, Frankfurt, Germany
DH	Durand & Huguenin S. A., Basle, Switzerland
Dow	Dow Chemical Co., Midland, Michigan
DuP	E. I. Du Pont de Nemours & Co., Wilmington, Delaware
EKCo	Eastman Kodak Co., Rochester, New York
Ethicon	Ethicon Inc., Somerville, New Jersey
FBy	Farbenfabriken Bayer A.G., Leverkusen, Germany
FH	Farbwerke Hoechst A.G., Frankfurt/Main-Hoechst, Germany
Filature Provoust	Filature de Laine Provoust, Roubaix, France
Fran	Compagnie Française des Matières Colorantes, Paris, France
FW	Farbenfabrik Wolfen, Kr., Bitterfeld, Germany
G	General Aniline & Film Corporation, New York
Gy	J. R. Geigy S. A., Basle, Switzerland
HCC	Hodogaya Chemical Co. Ltd., Tokyo, Japan
HH	Hardman and Holden Ltd., Manchester, England
HWL	Hickson & Welch Ltd., Castleford, England

IC	Interchemical Corporation, Hawthorne, New Jersey
ICI	Imperial Chemical Industries Ltd., Manchester, England
IG	I. G. Farbenindustrie A.G., Frankfurt a. Main, Germany
K	Kalle & Co., A.G., Biebrich, a. Rhein, Germany
Kewanee	Kewanee Oil Co., Bryn Mawr, Pennsylvania
KYK	Nippon Kayaku Co. Ltd., Tokyo, Japan
LBH	L. B. Holliday & Co., Huddersfield, England
MCI	Mitsubishi Chemical Industries Ltd., Tokyo, Japan
MDW	Mitsui Chemical Industry Co. Ltd., Tokyo, Japan
MLB	Farbwerke vorm. Meister, Lucius & Brüning, Hoechst a. Main, Germany
NAC	Allied Chemical Corporation, New York, New York
Nepera	Nepera Chemical Co., Inc., Harriman, New York
NSK	Sumitomo Chemical Co., Ltd., Osaka, Japan
OBM	Otto B. May, Inc., Newark, New Jersey
PCC	Peerless Color Co., Passaic, New Jersey
PHO	Phoenix Color & Chemical Co., Paterson, New Jersey
Pitt	Pittsburgh Coke & Chemical Co., Pittsburgh, Pennsylvania
RL	Rohner Ltd., Pratteln, Switzerland
S	Sandoz Ltd., Basle, Switzerland
TE	Eastman Chemical Products (Eastman Kodak Co.), Kingsport, Tennessee
Ube-Ditto	Ube-Ditto Kasai Ltd., Osaka, Japan
UCC	Union Carbide Corporation, New York, New York
VGF	Vereinigte Glanzstoff-Fabriken A.G., Wuppertal-Elberfeld, Germany
Vond	N. V. Fabriek van Chemische Producten, Vondelingenplaat, Holland
Whitten	H. A. Whitten Co., New York, New York
YDC	Yorkshire Dyeware & Chemical Co. Ltd., Leeds, England

Journals, Reports, and Books:

1961 *Chemical Abstracts List of Abbreviations* has been generally followed. The following special abbreviations have also been used.

BIOS	British Intelligence Objectives Sub-Committee Final Report
CA	Chemical Abstracts
CI	Colour Index, 2nd edition, 1956
CIOS	Combined Intelligence Objectives Sub-Committee Report
CIS	Colour Index, 2nd edition, Supplement 1963
CSD	The Chemistry of Synthetic Dyes, Academic Press, 1952

FIAT	Field Intelligence Agency Technical Report
PB	Technical Report of the Office of the Publication Board, Office of the Technical Services of the U.S. Department of Commerce
Ullmann	Ullmanns Encyclopädie der Technischen Chemie

Patents:

AustP	Austrian Patent
BeP	Belgian Patent
BP	British Patent
CP	Canadian Patent
CzechP	Czechoslovakian Patent
DAS	Deutsche Auslegeschrift
DBP	Deutsche Bundespatente
DP	Dutch Patent
DRP	Deutsche Reichspatente
EGP	East German Patent
FP	French Patent
IP	Indian Patent
JP	Japanese Patent
PolP	Polish Patent
RP	Russian Patent
SAP	South African Patent
USP	United States Patent

CHAPTER I

NAPHTHOQUINONOID DYES AND PIGMENTS

B. D. Tilak

NATIONAL CHEMICAL LABORATORY
POONA, INDIA

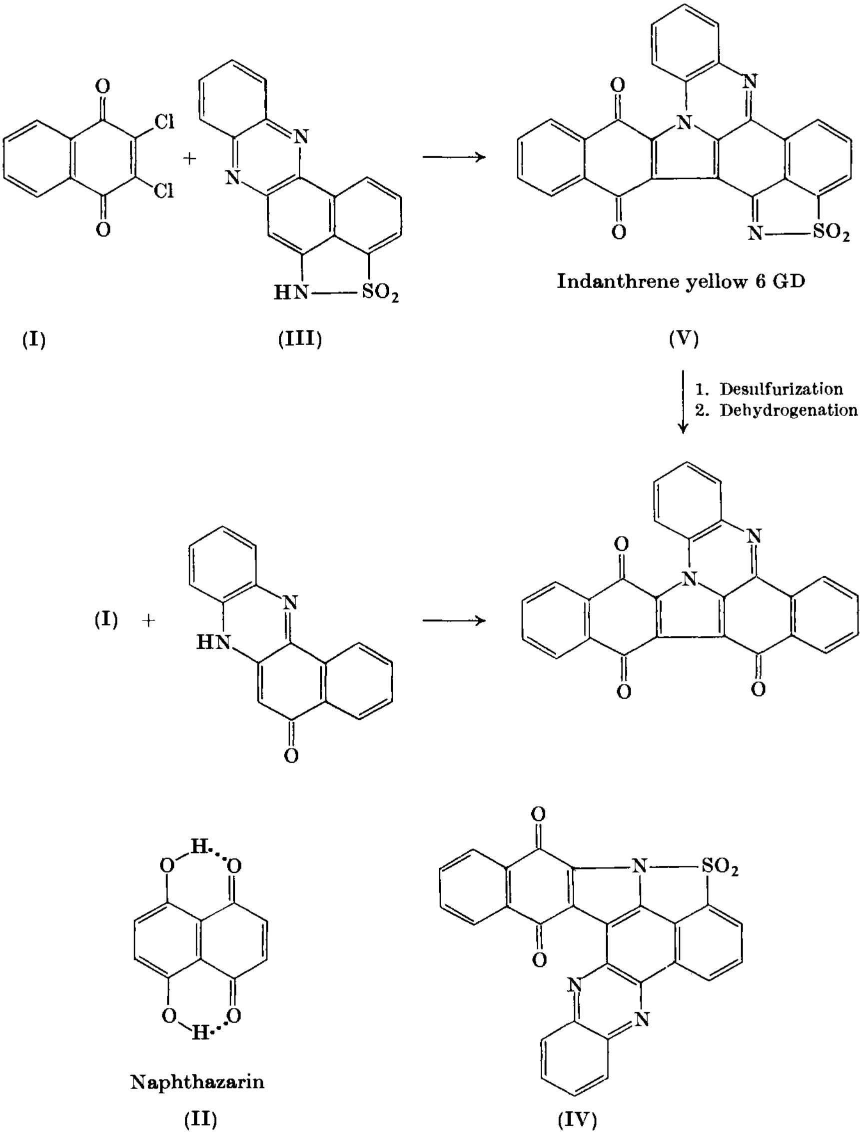
I. Introduction

Whereas several pigments related to 1,4-naphthoquinone have been isolated from vegetable and animal sources, synthetic naphthoquinone dyes are mainly derived from 1,4-naphthoquinone and its 2,3-dichloro derivative. 2,3-Dichloro-1,4-naphthoquinone (I) is more commonly used because of its ease of preparation and its high chemical reactivity.

Among dyes derived from 1,4-naphthoquinone and (I), Naphthazarin (Brilliant Alizarin Black B) (II), its derivatives, and Indanthrene Yellow 6GD, a vat dye, are the only ones used for dyeing textiles. Indanthrene Yellow 6GD is nontendering and possesses good lightfastness (4–5). It is synthesized by condensing (I) with the azine (III) obtained by condensation of nitrosoated naphthosultam with *o*-phenylenediamine.

CHART 1

Evidence for Structure (V)

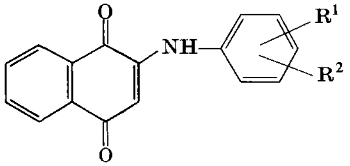


The structure (IV) assigned earlier[1] to Indanthrene Yellow 6GD has been found to be incorrect and it has now been shown to possess the structure (V).[2] The evidence in support of the structure (V) is outlined in Chart 1.

Interest in naphthoquinonoid dyes increased over the last few years when the excellent tinctorial properties of furanonaphthoquinones and the 2,3-phthaloylpyrrocolines were revealed. In this chapter, apart from describing these dyes, the several interesting reactions which are involved in the synthesis of naphthoquinone dyes are also discussed. The influence of coplanarity on the affinity of naphthoquinonoid dyes for cellulosic and synthetic fibers is also discussed.

II. Dyes Derived from 1,4-Naphthoquinone

1,4-Naphthoquinone readily reacts with aromatic amines in boiling methanol to give 2-arylamino-1,4-naphthoquinones (VI), which are brightly colored. The dyes containing fluorine atoms dye wool and polyester fibers red, yellow, orange, and violet shades with good fastness to light, wet treatment, and rubbing.[3]



(VI)

$R^1 = p\text{-F}, m\text{-CF}_3, p\text{-OCF}_3, p\text{-SCF}_3, p\text{-SO}_2\text{CF}_3$

$R^2 = \text{H, Cl}$

III. Dyes Derived from 2,3-Dichloro-1,4-naphthoquinone (I)

2,3-Dichloro-1,4-naphthoquinone (I) is the most commonly used starting material for the synthesis of naphthoquinonoid dyes and pigments. Because of the two keto groups, a carbonium ion is readily created at the 2- or 3-position which is the site of attack by nucleophilic reagents.

---

[1] *CSD II*, p. 800.

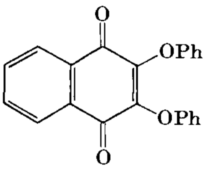
[2] K. H. Shah and S. H. Gole, *Indian J. Chem.* **6**, 173 (1968).

[3] L. Kh. Vinograd, S. M. Shein, A. P. Cherepivskaya, and G. V. Shalimova, *Zh. Prikl. Khim.* **38**, 208 (1965); cf. *J. Soc. Dyers Colourists* **81**, 226 (1965).

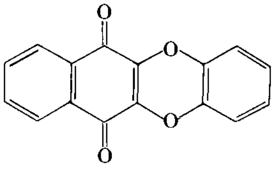
With the elimination of a chloride anion, a monosubstituted derivative is obtained. The second chlorine atom can also be replaced to yield 2,3-disubstituted or heterocyclic derivatives of 1,4-naphthoquinone. The chemistry of (I) and its derivatives has recently been reviewed.[4–6] Because of their intense color and substantivity to cellulosic and hydrophobic fibers, the heterocyclic quinones derived from (I) have been gaining in importance as dyes and pigments. The dyes obtained by interaction of (I) with different nucleophilic reagents are discussed below. Some of the characteristic reactions of (I) are summarized in Chart 2.

A. REACTION OF (I) WITH PHENOLS: FURANONAPHTHOQUINONES

When (I) is warmed with potassium phenoxide, 2,3-diphenoxy-1,4-naphthoquinone (VII) is obtained.[7] Interaction of (I) with catechol in presence of diethylamine gives the dioxine derivative (VIII). Resorcinol and other *m*-substituted phenols react with (I) to yield 3-substituted benzonaphthofurandiones [e.g., (IX)] which are also referred to as brazanquinones.[8, 9] The mechanism of formation of 3-hydroxybrazanquinones is illustrated in Chart 3.



(VII)



(VIII)

Although the brazanquinone structure was assigned to the product of reaction of (I) and resorcinol by Liebermann[8] in 1899, proof for this structure was afforded only in 1954 by Chatterjea[9] when he obtained 3-methoxybrazanquinone by reacting 6-methoxycoumarandione with phenacyl bromide and showed it to be identical with the product obtained by methylation of the compound obtained by Liebermann. The

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[4] B. D. Tilak, *In* "Recent Progress in the Chemistry of Natural and Synthetic Colouring Matters" (T. S. Gore, B. S. Joshi, S. V. Sunthankar and B. D. Tilak, eds.), p. 537. Academic Press, New York, 1962.

[5] M. F. Sartori, *Chem. Rev.* **63**, 279 (1963).

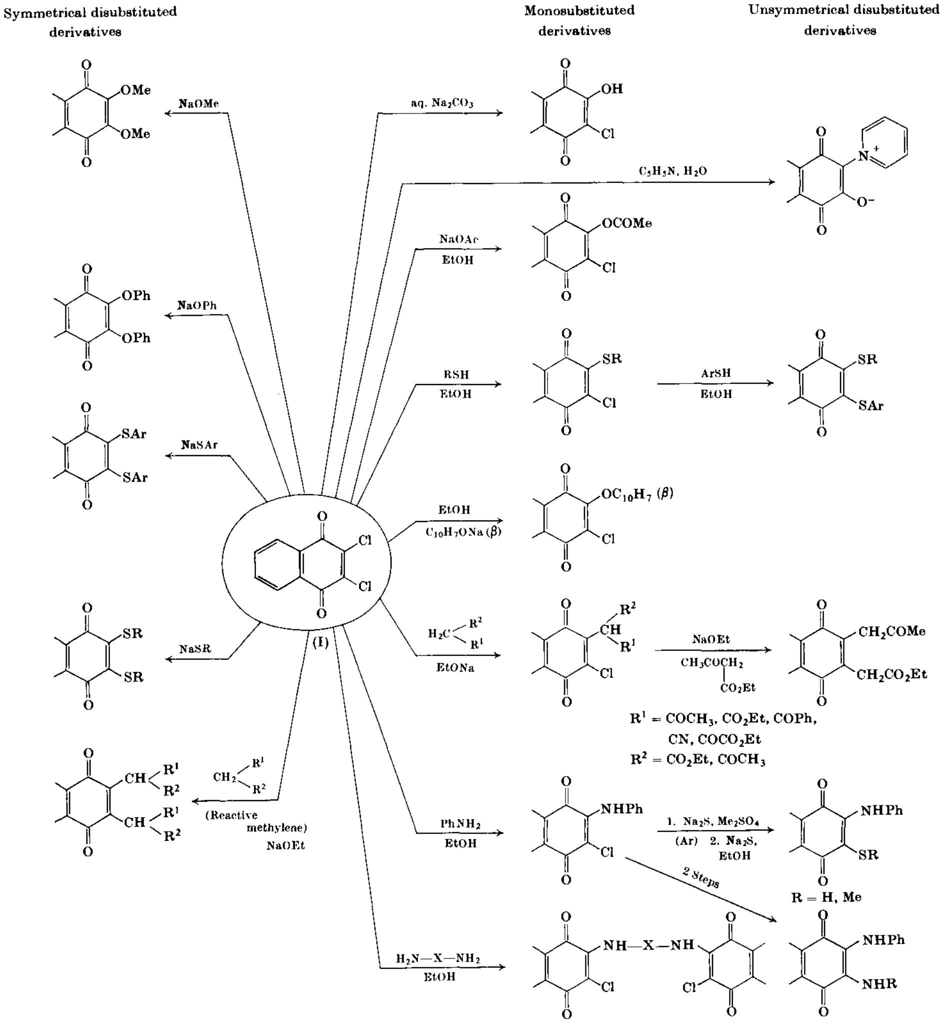
[6] P. R. Venkateswaran, Ph.D.(Tech.) Thesis, University of Bombay (1967).

[7] F. Ullmann and M. Ettisch, *Ber. Deut. Chem. Ges.*, **54**, 259 (1921).

[8] C. Liebermann, *Ber. Deut. Chem. Ges.* **32**, 923 (1899).

[9] J. N. Chatterjea, *J. Indian Chem. Soc.* **31**, 101 (1954).

CHART 2



use of brazanquinones as vat dyes was first studied by Eistert,[10] who condensed various meta-substituted phenols with (I) to obtain a series of 3-substituted brazanquinones. Other hydroxy compounds and enolizable heterocyclic compounds such as 3-methyl-1-phenyl-5-pyrazolone, 4-hydroxy-1-methyl-3-picolone, and 3-hydroxythionaphthene, have been used in place of *m*-substituted phenols to give the brazanquinones (X)-(XII).

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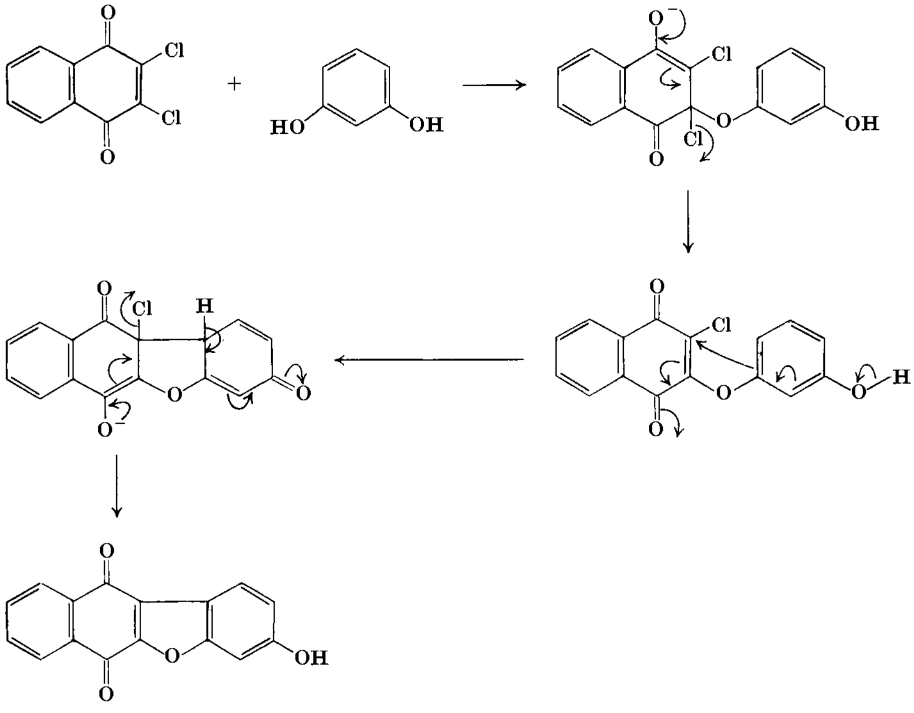
[10] B. Eistert, *Chem. Ber.* **80,** 47 (1947).

CHART 3

Mechanism of 3-Hydroxybrazanquinone Formation



(IX)

The above brazanquinones had very poor affinity to cotton. When brazanquinones are subjected to electrophilic substitution, the substituents enter the benzene moiety. Dyes containing substituents in the naphthalene part of the brazanquinone ring system are obtained by reacting phenols with appropriately substituted 2,3-dichloro-1,4-naphthoquinone derivatives. Thus, nitration of 3-methoxybrazanquinone gives the mono and dinitro derivatives (XIII) and (XIV), respectively. Interaction of 5-nitro-2,3-dichloro-1,4-naphthoquinone with *m*-methoxyphenol gives a mixture of 7- and 10-nitro-3-methoxybrazanquinones[11] [(XV) and (XVI)], which have been reported as vat dyes.

Condensation of (I) with α- and β-naphthols in the presence of an acid-binding agent such as pyridine leads to the formation of dinaph-

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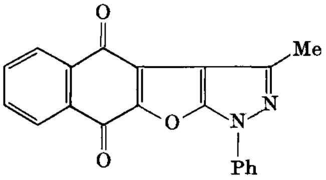
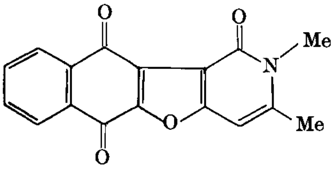
[11] M. F. Sartori, *J. Org. Chem.* **26**, 3152 (1961).



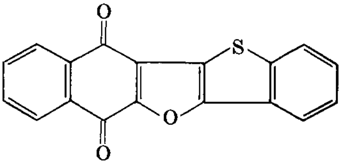
Red

(X)



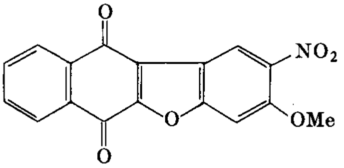
Reddish orange

(XI)

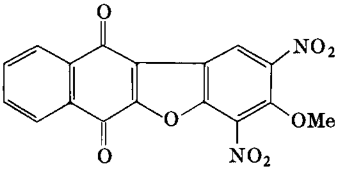


Blue

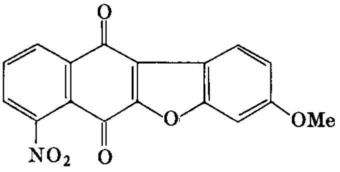
(XII)



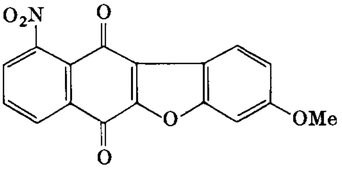
(XIII)



(XIV)



(XV)



(XVI)

thofurandiones, which are also referred to as benzobrazanquinones [(XVII) and (XVIII)].[10, 12–14]

The condensation of (I) with α-naphthol to give (XVII) takes place at the free 2-position in α-naphthol. In the case of formation of (XVIII) from (I) and β-naphthol, the 1-position in β-naphthol is involved in the reaction. Thus when (I) was reacted with 1-bromo-2-naphthol in the presence of pyridine, a bromine-free product was obtained which was

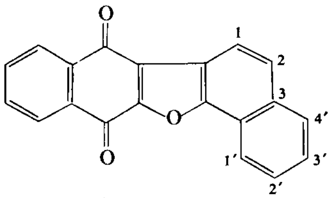
---

[12] N. P. Buu Hoi, *J. Chem. Soc.* p. 489 (1952).

[13] L. F. Fieser and R. H. Brown, *J. Am. Chem. Soc.* **71**, 3609 (1949).

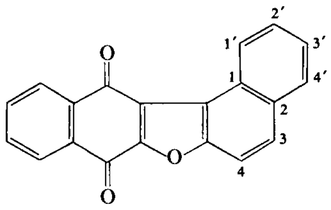
[14] B. D. Tilak and B. Suryanarayana, *Proc. Indian Acad. Sci.* **37A**, 81 (1953).

identical with the dye obtained by condensation of (I) with β-naphthol. The mechanism of formation of (XVIII) from (I) and β-naphthol in the presence of pyridine or sodium ethoxide[15b] is shown in Chart 4. The formation of (XVIII) by adding β-naphthol to the intermediate 2-chloro-1,4-naphthoquinone-3-pyridinium chloride (XIX) prepared *in situ* by reacting (I) with pyridine shows that it proceeds through the 2-β-naphthoxy-1,4-naphthoquinone-3-pyridinium chloride. The formation of (XVIII) by adding (I) to a mixture of β-naphthol and pyridine proceeds through 2-chloro-1,4-naphthoquinone-3-pyridinium chloride (XIX) and/or 2-chloro-3-β-naphthoxy-1,4-naphthoquinone. 2-Chloro-3-β-naphthoxy-1,4-naphthoquinone obtained by reacting (I) with β-naphthol in presence of sodium ethoxide, when reacted with pyridine or sodium β-naphtholate, undergoes cyclization to yield (XVIII), (XX), and β-naphthol.



(XVII)

2 = H, Br, COPh, CO—NHPh
2′ = OH, OMe
4′ = OH, OMe



(XVIII)

2′ = OH, OMe
3′ = Br, CO—NHPh
4′ = OMe, CO—NHPh

The pyridinium betaine (XX) obtained in the above reactions is removed by extraction with hot water. Both 1,2-benzobrazanquinone (XVII) and 3,4-benzobrazanquinone (XVIII) are weakly substantive to cotton.

When substituted α- and β-naphthol derivatives such as bromo,[14] benzoyl,[15] and benzamido[14, 15] are used, the resulting benzobrazanquinones are substantive to cotton. In the case of (XVIII), the introduction of a carboxyanilide group at the 4′-position gives a dye[14] which is more substantive to cotton than the isomeric dye in which the same group is in the 3″-position.[15a] These observations are analogous to 2-hydroxy-3-naphthanilide (Naphtol AS), which is substantive, whereas

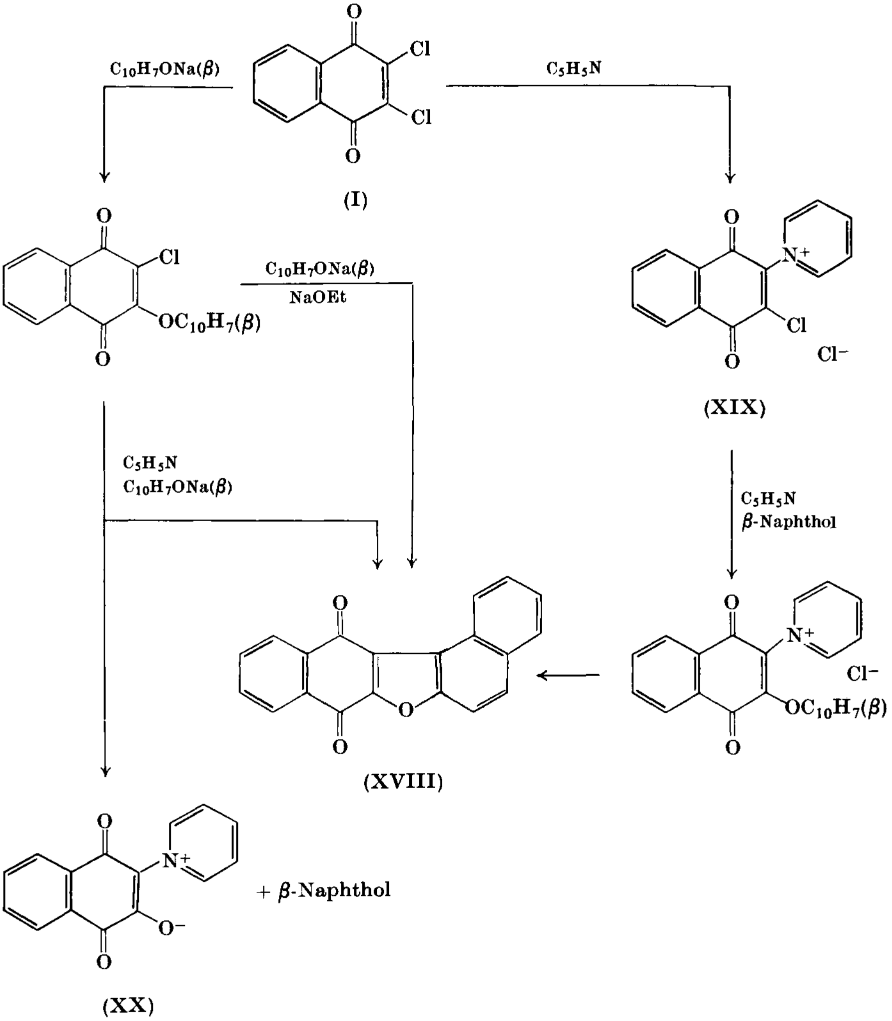
---

[15a] B. D. Tilak, R. V. Acharya, and M. R. Venkiteswaran, *J. Sci. Ind. Res.* (*India*) **14B**, 250 (1955).

[15b] Ibid, **16B**, 400 (1957).

CHART 4

Formation of (XVIII) from (I) and β-Naphthol



2-hydroxy-6-naphthanilide is nonsubstantive to cotton.[16] The benzobrazanquinone obtained by condensing (I) with Naphtol-AS gives a bright yellow shade on cotton, possessing good fastness properties to all agencies excepting chlorine. Condensation of (I) with a series of more complex naphthols of the Naphtol AS series, such as Naphtol AS-E,

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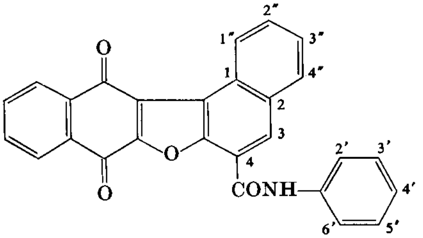
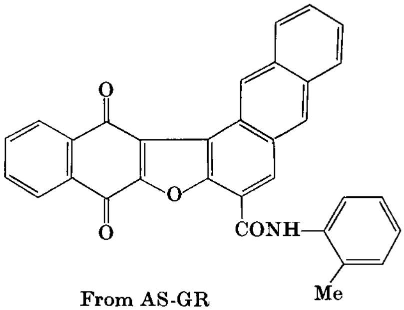
[16] *CSD I*, p. 673.

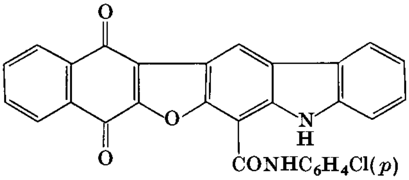
AS-TR, AS-OL, AS-RL, AS-BG,[17, 18] AS-BO, AS-SW, AS-LB, and AS-GR[17, 18] yields brazanquinone derivatives possessing satisfactory substantivity to cotton. Whereas the vat dyes derived from 2-hydroxy-3-naphthoic arylides give yellow to orange shades, Naphtols AS-LB, AS-GR, and AS-SG[19] give brown shades. Dyes derived from 2-hydroxy-3-naphthoic arylides are applicable in electrophoretic color-copying



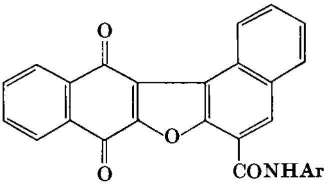


From AS-GR

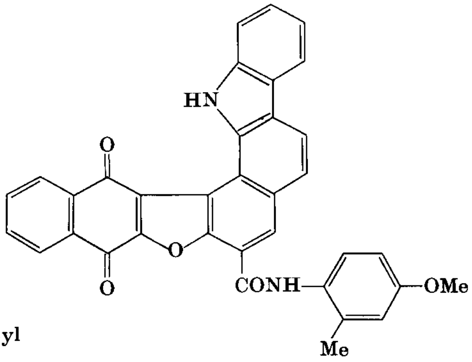
AS-E → 4'-Cl
4'-Br
3''-Br
AS-D → 2'-Me
AS-TR → 2'-Me, 4'-Cl
AS-RL → 4'-OMe
AS-OL → 2'-OMe
AS-BG → 2',5'-di$(OMe)_2$
AS-BS → 3'-$NO_2(NH_2OH$ fiber)



From AS-LB



AS-BO → Ar = α-naphthyl
AS-SW → Ar = β-naphthyl
AS-S → Ar = 2'-methoxydibenzofuran-3'-yl



From AS-SG

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[17] B. D. Tilak, V. K. Dikshit, and B. Suryanarayana, *Proc. Indian Acad. Sci.* **37A**, 92 (1953).

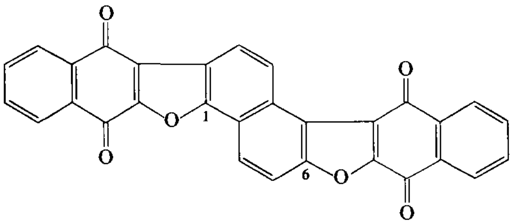
[18] B. D. Tilak and B. Suryanarayana, *Proc. Indian Acad. Sci.* **37A**, 99 (1953).

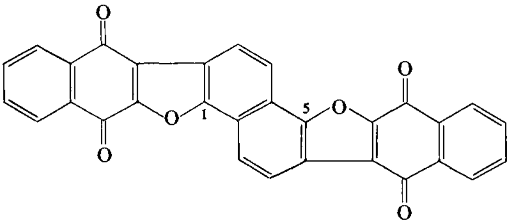
[19] B. D. Tilak and S. S. Rao, unpublished work.

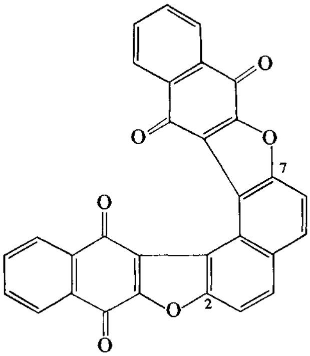
materials and in xerography of both the conventional and the frost-deformation type.[20]

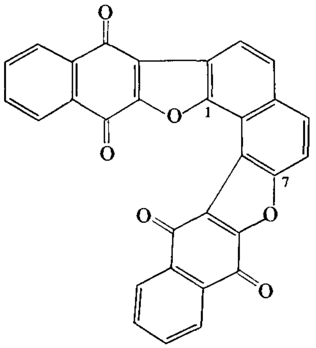
Dihydroxynaphthalenes react with (I) to yield a series of dibrazanquinones containing two naphthoquinone residues[21] which dye cotton attractive fast brown shades.

Brazanquinones are also reported from 1- and 2-anthrols,[22] 1,5- and 1,8-anthradiols,[22] hydroxybenzocoumarin,[23] and 3′-hydroxybenzocar-









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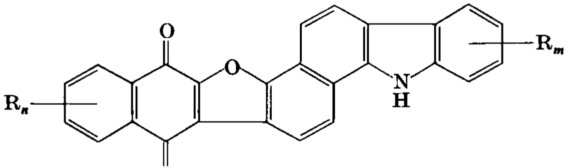
[20] Rank Xerox Ltd., *FP* 1,467,288.

[21] B. D. Tilak, R. V. Acharya, and M. R. Venkiteswaran, *J. Sci. Ind. Res.* (*India*) **16B**, 554 (1957).

[22] IG, *BP* 300,407.

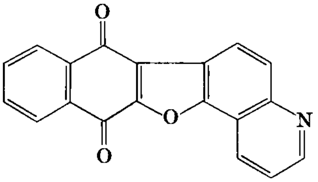
[23] N. P. Buu Hoi and D. Lavit, *J. Chem. Soc.* p. 1743 (1956).

bazole.[24] Reddish brown vat dyes of the general formula (XXI) possessing good all-around fastness properties to cotton have been reported.

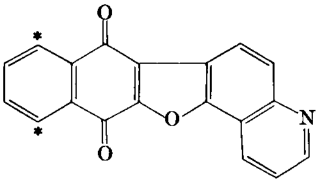


(XXI)

$n = 0–1$ and $m = 0–3$
$R = NO_2, NH_2$, Hal, or lower alkyl



(XXII)



(XXIII)

Condensation of (I) with 5-hydroxyquinoline yields a naphthofuroquinolinedione (XXII), indicating a higher reactivity of the chlorine for the phenolic hydroxyl group than the heterocyclic nitrogen atom.[5] Naphthofuroquinolinediones are also obtained from 6- and 7-quinolinols. Naphthofuroquinolinediones (XXIII) with amino groups at the starred positions are used as disperse dyes and the quaternary amino derivatives as dyes for synthetic fibers containing acidic groups, modified polyester fibers, and polycyclic fibers.[25] These dyes are obtained by condensing 5-nitro-2,3-dichloro-1,4-naphthoquinone with the appropriate hydroxyquinoline. Reduction of the nitro derivative to the amino derivative is achieved by alkaline hydrosulfite.

Investigations exploring the use of branzanquinones as vat dyes and dyes for synthetic fibers have been actively pursued. Most of the information covering these dyes is, however, confined to patent literature. Some of these dyes are discussed below. Dyes of the general formula (XXIV) are used as disperse dyes for Terylene.[26]

Whereas 7-bromo-3-methoxybrazanquinone dyes Terylene polyester

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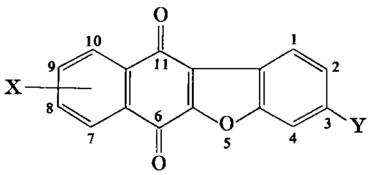
[24] G, *USP* 2,768,172.
[25] DuP, *USP* 3,121,086.
[26] DuP, *USP* 2,995,578.

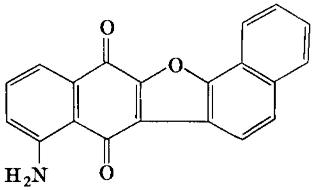


(XXIV)

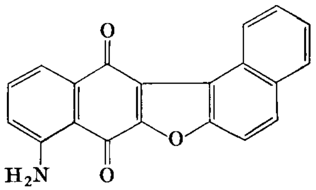
X = 7- or 10-NO_2, NH_2, Cl, or Br
Y = H, OH, or OMe

fiber a greenish yellow shade with excellent sublimation fastness, the 7-amino derivative dyes a fast bright red shade.

A series of interesting vat dyes has been reported wherein the dinaphthofurandione system is linked to other vat dye systems. These dyes are derived from aminodinaphthofurandiones (XXV) and (XXVI). When (XXV) is heated with dibromodibenzopyrenequinone in nitrobenzene



(XXV)



(XXVI)

at 200–205° for 2 hours in the presence of soda ash and copper, the resulting product dyes cotton a blackish brown shade from an alkaline hydrosulfite bath.[26] The shades are fast to washing, chlorine, and light. When (XXVI) is used instead of (XXV) a black dye is obtained.[27] Reaction of (XXV) with dibromoanthanthrone under similar conditions yields a dye which gives a bluish gray shade on cotton. Interaction of tetrabromopyranthrone and (XXV) under these conditions yields a vat dye giving a neutral gray on cotton. A blue vat dye is obtained by the reaction of tribromoisoviolanthrone with (XXV). Condensation of (XXV) with aryl halides yields vat dyes giving tertiary shades on cotton. When (XXV) is heated with *p*-dibromobenzene in nitrobenzene at 200–205° for 20 hours in the presence of potassium acetate and copper chloride, a gray vat dye is obtained. Similarly, interaction of (XXV)

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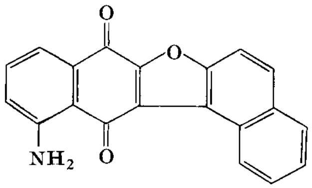
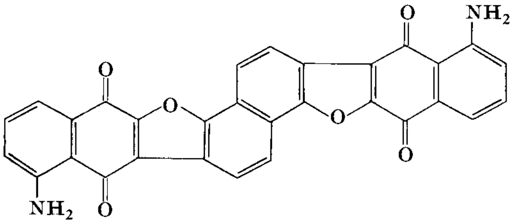
[27] G, *USP* 2,862,931.

with 4,4′-dibromodiphenyl yields a bluish gray vat dye. 1,3,5-Tribromobenzene when reacted with (XXV) gives a violet-gray vat dye. Whereas the reaction product obtained by condensation of (XXV) and 1,2,4-tribromobenzene gives brownish gray shades, the condensation product resulting from the interaction of 2,4-dibromotoluene and (XXV) gives a neutral gray shade. All the above dyes dye cotton from an alkaline hydrosulfite bath, giving shades which possess good to excellent fastness properties as regards washing, chlorine, and light. Condensation of 5-nitro-2,3-dichloro-1,4-naphthoquinone with Naphtol AS in the presence of pyridine at 100–110° for 3 hours gives a mixture of benzobrazanquinones with the nitro group at the starred positions. The mixture of nitro compounds on reduction with alkaline hydrosulfite yields the corresponding amines. The latter dye cotton fast red shades from an alkaline hydrosulfite bath. Condensation of the amine mixture with 1-benzamido-4-chloroanthraquinone in the presence of copper acetate and sodium carbonate in nitrobenzene gives an anthrimide mixture. The anthrimide mixture on heating with aluminum chloride in nitrobenzene at 55–60° for half an hour is converted to a mixture of two carbazole derivatives.[28] This mixture gives a blue solution in sulfuric acid and an orange-brown alkaline vat from which cotton can be dyed to give brown shades of good fastness.

When the aminodinaphthofurandione derivative (XXVII) is reacted with terephthaloyl chloride in nitrobenzene, a bright orange-red vat



(XXVII)



(XXVIII)

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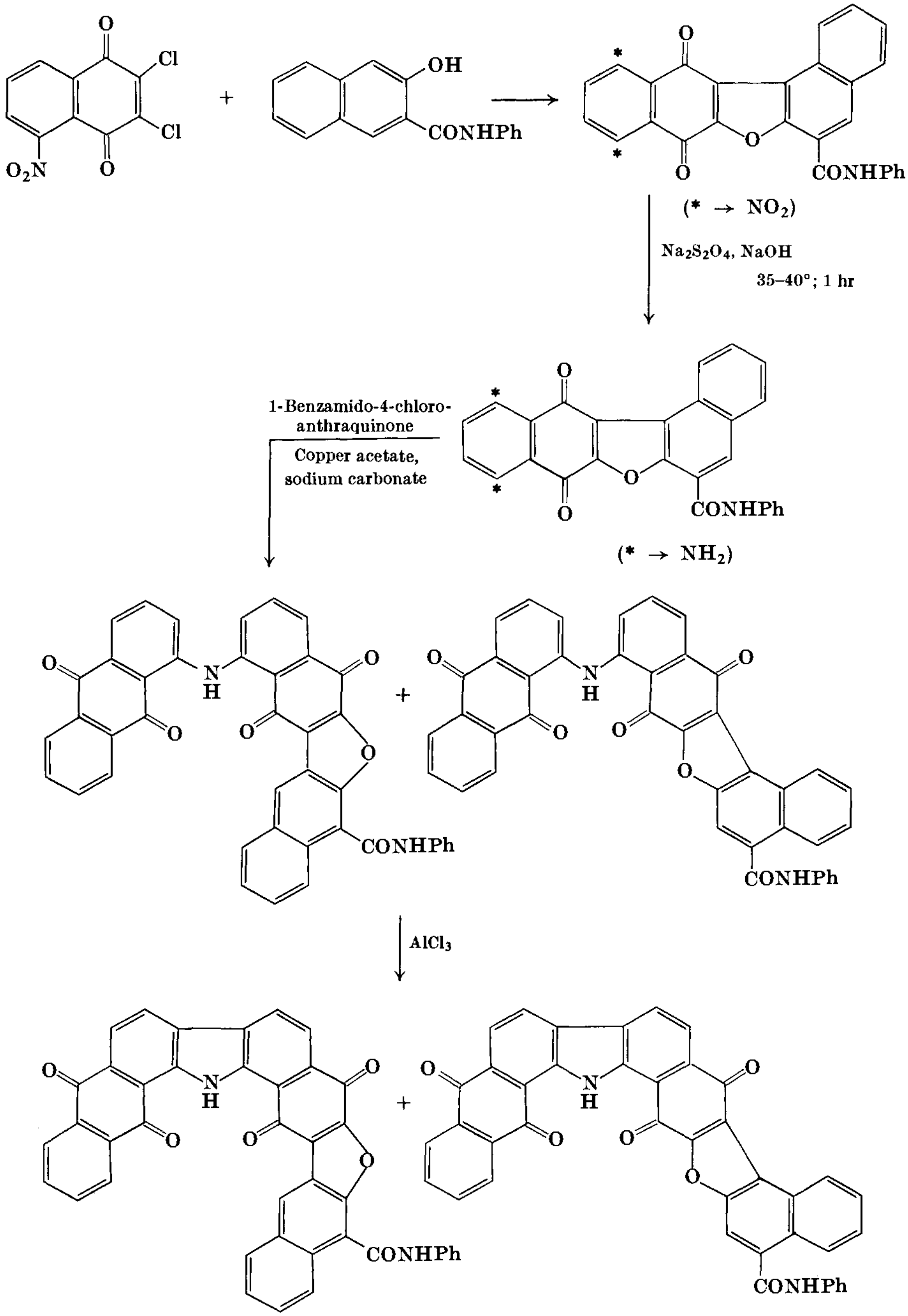
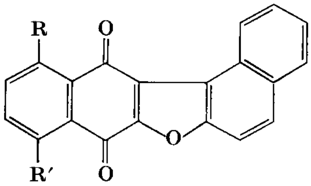
[28] DuP, *USP* 2,893,998.

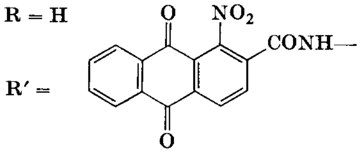

O
Cl
Cl
O_2N
O
+
OH
CONHPh
O
O
O
CONHPh
*
*
(* → NO_2)
$Na_2S_2O_4$, NaOH
35–40°; 1 hr
O
O
O
CONHPh
*
*
(* → NH_2)
1-Benzamido-4-chloro-anthraquinone
Copper acetate, sodium carbonate
N
H
CONHPh
+
CONHPh
$AlCl_3$
N
H
CONHPh
+
CONHPh

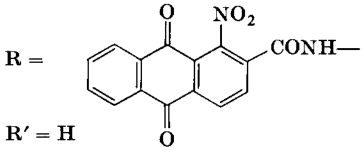
dye for cotton is obtained.[29] Similarly, the diaminodibrazanquinone (XXVIII) on heating with benzoyl chloride in nitrobenzene gives a brown vat dye.[29]

A mixture of 8- and 11-amino derivatives of dinaphtho[1,2*b*:2′,3′*d*]-furan-7,12-dione on interaction with 1-nitro-2-anthraquinone carbonyl chloride yields the red dye (XXIX) which has good general fastness, particularly to chlorine.



(XXIX)





B. Reaction of (I) with Reactive Methylene Compounds: 2,3-Phthaloylpyrrocolines

Reaction of (I) with ethyl acetoacetate in the presence of sodium ethoxide is reported to yield ethyl 3-(2-chloro-1,4-naphthoquinonyl)-acetoacetate (XXX) and a red product to which the structure (XXXI) was assigned.[30] Assignment of structure (XXXI) to the red product was considered unlikely since (XXXI) may be expected to be yellow and not red. Structure (XXXII) was therefore proposed for the red compound.[31]

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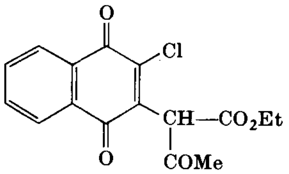
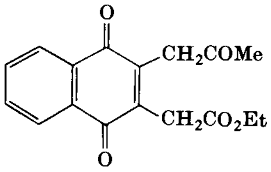
[29] G, *USP* 2,870,168.

[30] F. Michel, *Ber. Deut. Chem. Ges.* **33**, 2404 (1900).

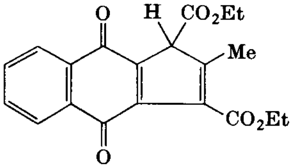
[31] B. D. Tilak and B. Suryanarayana, *Proc. Indian Acad. Sci.* **38A**, 534 (1953).



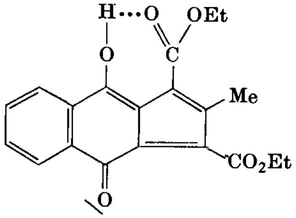
(XXX)



(XXXI)



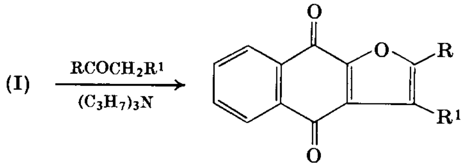
(XXXII)



(XXXIII)

Van Allan, Reynolds, and Adel,[32] however, concluded that the above red product should be represented by structure (XXXIII), on the basis of NMR, UV, and mass spectral data. The NMR spectrum showed a singlet at $-6.4\ \tau$ which was attributed to the strongly hydrogen-bonded hydroxyl group. The absorption spectrum was not affected by change of concentration and this peak vanished on deuterium exchange, thereby showing that the singlet was due to intramolecular hydrogen bonding.

In the course of a reaction of (I) with reactive methylene compounds in the presence of tributylamine, Pratt and Rice [33] observed the formation of the furanonaphthoquinone derivative (XXXIV). The general method of preparation of these compounds consists in reacting (I) with compounds containing a reactive methylene group, whereby 2-chloro-3-(disubstituted)methyl-1,4-naphthoquinone are obtained. The latter on



(XXXIV)

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[32] J. A. Van Allan, G. A. Reynolds, and R. E. Adel, *J. Org. Chem.* **30**, 3819 (1965).

[33] E. F. Pratt and R. G. Rice, *J. Am. Chem. Soc.* **79**, 5489 (1957).

base-catalyzed cyclization yield furanonaphthoquinone derivatives. Acetylacetone, ethyl acetoacetate, benzoylacetone, benzoylacetonitrile and dibenzoylmethane are among the reactive methylene compounds used for preparation of furanonaphthoquinone derivatives starting from (I).

1. *2,3-Phthaloylpyrrocolines*

With a view to the synthesis of furanonaphthoquinones, Tilak and Suryanarayana[34] reacted (I) with ethyl acetoacetate in the presence of pyridine. A nitrogen-containing quinonoid orange compound was obtained to which the structure (XXXV) was assigned.[34] Pratt, Luckenbaugh, and Erickson[35] regarded the orange compound as 1-carbethoxy-2,3-phthaloylpyrrocoline (XXXVI). In support, they cited the formation of phthalic acid by oxidation of the orange compound with concentrated nitric acid, although the fate of the pyridine half of the molecule was not investigated. Tilak, Acharya, and Suryanarayana[36] found that both the orange quinonoid compound and the pyridinium betaine (XX) gave phthalic acid and pyridine under similar conditions. It was also observed that α-picoline is converted to pyridine since picolinic acid which is formed *in situ* is decarboxylated. It is therefore difficult to distinguish between structures (XXXV) and (XXXVI) by an oxidative degradation procedure involving use of nitric acid (Chart 5). Conclusive proof that the compound had the 2,3-phthaloylpyrrocoline structure (XXXVI) was given by Tilak, Acharya, and Suryanarayana[36] by degradation of the compound with alkaline potassium permanganate, which leads to formation of both phthalic acid and picolinic acid. Final confirmation of the structure of the compound as (XXXVI) was provided by the synthesis of the parent 2,3-phthaloylpyrrocoline (XXXVII) starting from α-picoline and (I) and, alternately, by conversion of (XXXVI) to (XXXVII) by hydrolysis and decarboxylation (Chart 5).

The mechanism for formation of 1-carbethoxy-2,3-phthaloyl pyrrocoline from (I) and ethyl acetoacetate is represented in Chart 6.

As in the preparation of the brazanquinones, the pyridinium betaine (XX) is formed in the reaction and this is removed by extraction with water. Since the reaction of (I) with ethyl acetoacetate and pyridine in boiling ethanol does not give the 1-carbethoxy-2,3-phthaloylpyrrocoline in yields satisfactory enough for commercial exploitation, the process

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[34] B. D. Tilak and B. Suryanarayana, *Current Sci.* (*India*) **22**, 171 (1953).

[35] E. F. Pratt, R. W. Luckenbaugh, and R. L. Erickson, *J. Org. Chem.* **19**, 176 (1954).

[36] B. D. Tilak, R. V. Acharya, and B. Suryanarayana, *J. Sci. Ind. Res.* (*India*) **14B**, 394 (1955).

CHART 5

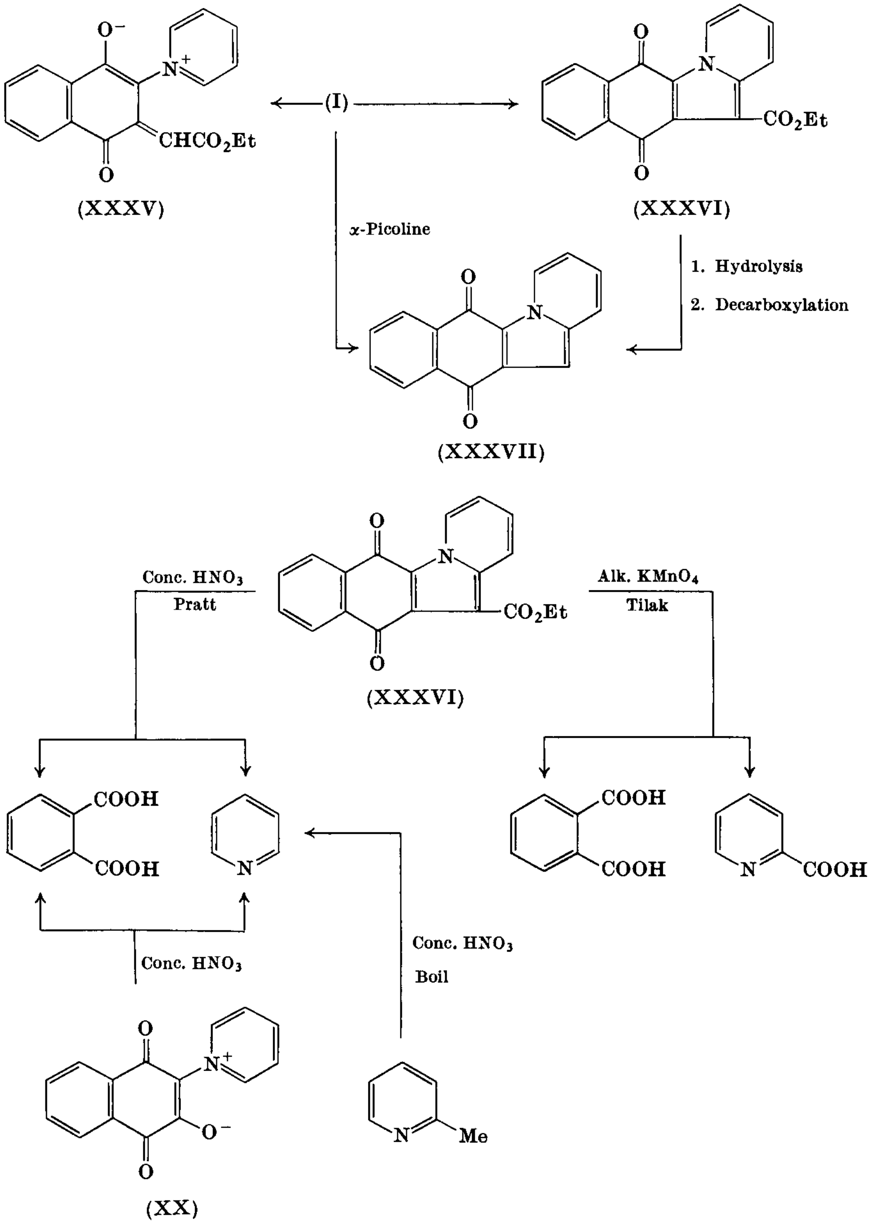
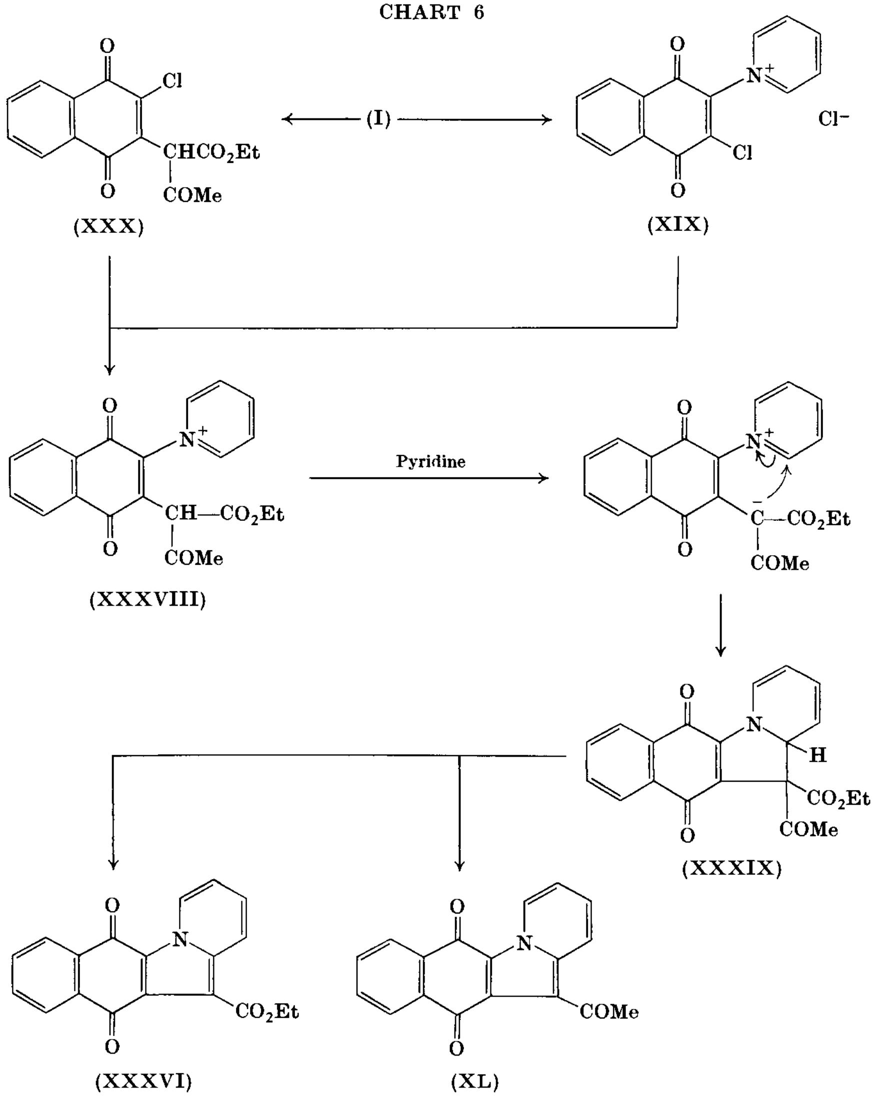

(XXXV)
(I)
(XXXVI)
α-Picoline
1. Hydrolysis
2. Decarboxylation
(XXXVII)
Conc. HNO₃
Pratt
(XXXVI)
Alk. KMnO₄
Tilak
COOH
COOH
COOH
COOH
COOH
Conc. HNO₃
Conc. HNO₃
Boil
Me
(XX)

CHART 6



has been improved by the use of ethyl chloroacetate instead of ethyl acetoacetate.[37] The reaction consists in heating (I), ethyl chloroacetate, and pyridine in a solvent such as dimethylformamide or dioxane at 100–110° for 2 hours. 1-Carbethoxy-2,3-phthaloylpyrrocoline (XXXVI) is obtained in high yield. The mechanism of formation of 1-carbethoxy-2,3-phthaloylpyrrocoline by this method is illustrated in Chart 7.

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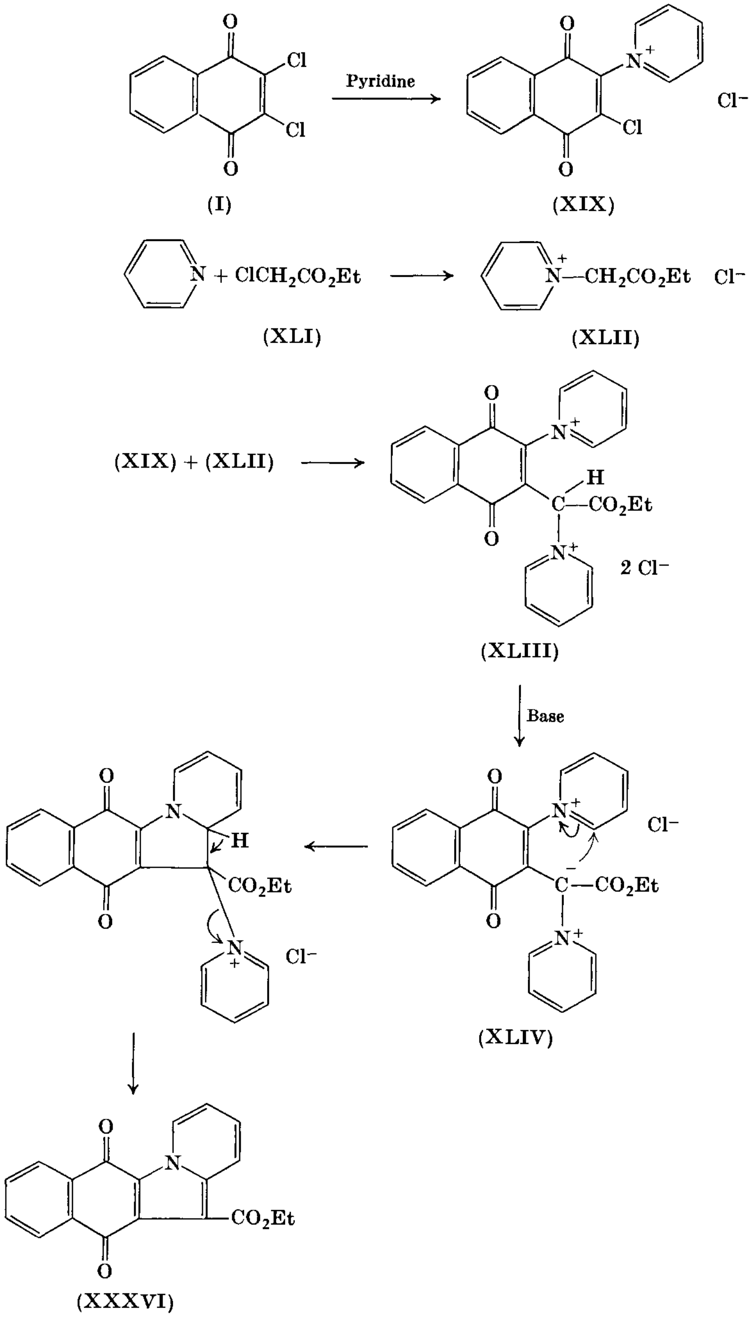
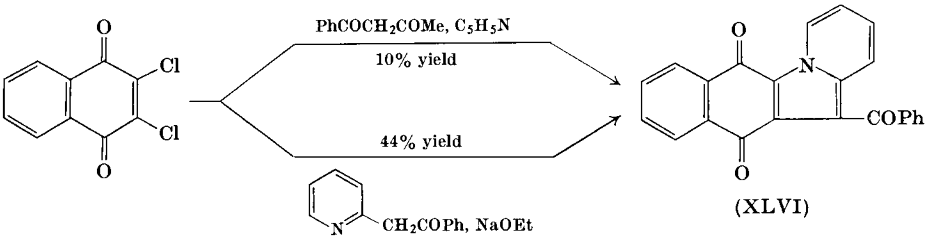
[37] CIBA, *BP* 1,046,643.

CHART 7


(I)
Pyridine
(XIX)
Cl⁻
+ ClCH₂CO₂Et
(XLI)
N—CH₂CO₂Et Cl⁻
(XLII)
(XIX) + (XLII)
2 Cl⁻
(XLIII)
Base
Cl⁻
(XLIV)
Cl⁻
(XXXVI)

In the above reactions pyridine reacts with ethyl chloroacetate to give the quaternary salt (XLII), which can readily form a reactive nitrogen ylid which reacts with the 2-chloro-1,4-naphthoquinone-3-pyridinium chloride (XIX). The formation of the carbanion (XLIV) is followed by cyclization and subsequent removal of pyridine, a very good leaving group. This method gives exclusively 1-carbethoxy-2,3-phthaloylpyrrocoline (XXXVI) as against the method using ethyl acetoacetate, in which both (XXXVI) and 1-acetyl-2,3-phthaloylpyrrocoline (XL) are formed.

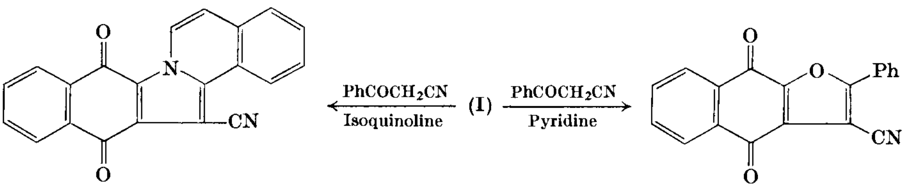
The synthesis of 1-carbethoxy-2,3-phthaloylpyrrocoline (XXXVI) led to an extensive study of the interaction of (I) with various reactive methylene compounds in the presence of pyridine. Cyanoacetic ester,[38] acetylacetone,[38] dibenzoylmethane,[36] and diethyl malonate[36] react with (I) in the presence of pyridine to yield the corresponding phthaloylpyrrocoline. Substituted 2,3-dichloro-1,4-naphthoquinones and also derivatives of pyridine such as 4-picoline,[36] phenylpyridine,[39] 4-carbethoxypyridine,[5] and collidines[5] have been used successfully in this reaction. When aryl α-picolinyl ketones (XLV) are used, better yields of the 1-aroyl-2,3-phthaloylpyrrocolines (XLVI) are obtained.



(XLV)

(XLVI)

Whereas quinoline does not react with (I) and compounds containing a reactive methylene group to give pyrrocolines, isoquinoline readily yields the corresponding phthaloylbenzopyrrocolines.



(XLVII)

(XLVIII)

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[38] E. F. Pratt, R. G. Rice, and R. W. Luckenbaugh, *J. Am. Chem. Soc.* **79**, 1212 (1957).

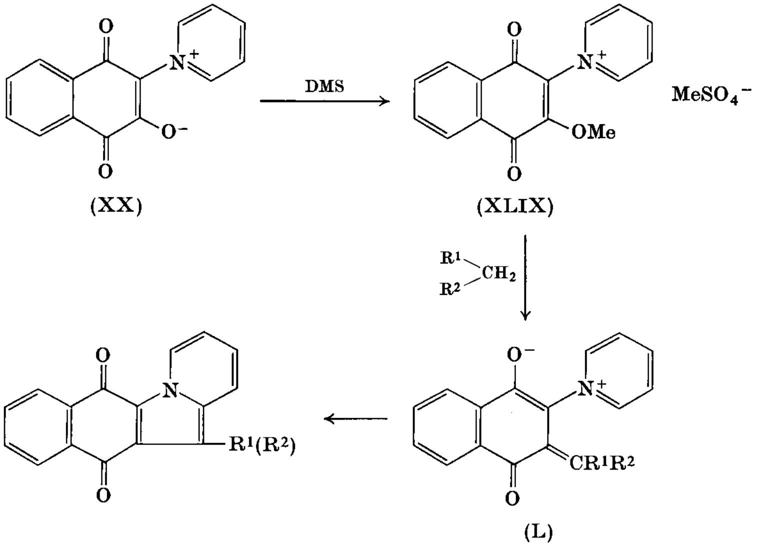
[39] B. D. Tilak and M. S. Mathur, *J. Sci. Ind. Res.* (*India*) **17B**, 33 (1958).

It is interesting to note that whereas benzoylacetonitrile reacts with (I) in the presence of isoquinoline to yield (XLVII), the reaction when carried out in presence of pyridine does not yield a pyrrocoline derivative, but gives 2-phenyl-3-cyano[2,3-*b*]naphthofuran-4,9-dione (XLVIII).[33]

2. *Synthesis of 2,3-Phthaloylpyrrocolines by Ring Closure of Ylidene–enol Betaines*

Methylation of the pyridinium betaine (XX) with dimethyl sulfate yields 3-(2-methoxy-1,4-naphthoquinonyl)pyridinium methosulfate (XLIX). The latter reacts with reactive methylene compounds to give the ylidene–enol betaines of the type (L), which cyclize to 2,3-phthaloylpyrrocolines on heating.[40] Whereas some reactive methylene compounds react with (XLIX) to yield directly 2,3-phthaloylpyrrocolines, others give the ylidene–enol betaines, which can be isolated and subsequently cyclized to yield phthaloylpyrrocolines. The formation of the ylidene–enol betaine as an intermediate in the reaction of (XLIX) with all reactive methylene compounds is indicated by a blue coloration which soon turns brown due to ring closure.

Several interesting reactions are observed in the cyclization of ylidene–enol betaines to phthaloylpyrrocolines.[40] These mainly involve interaction with the solvent used for cyclization. Thus the ylidene–enol



(XX)

(XLIX)

(L)

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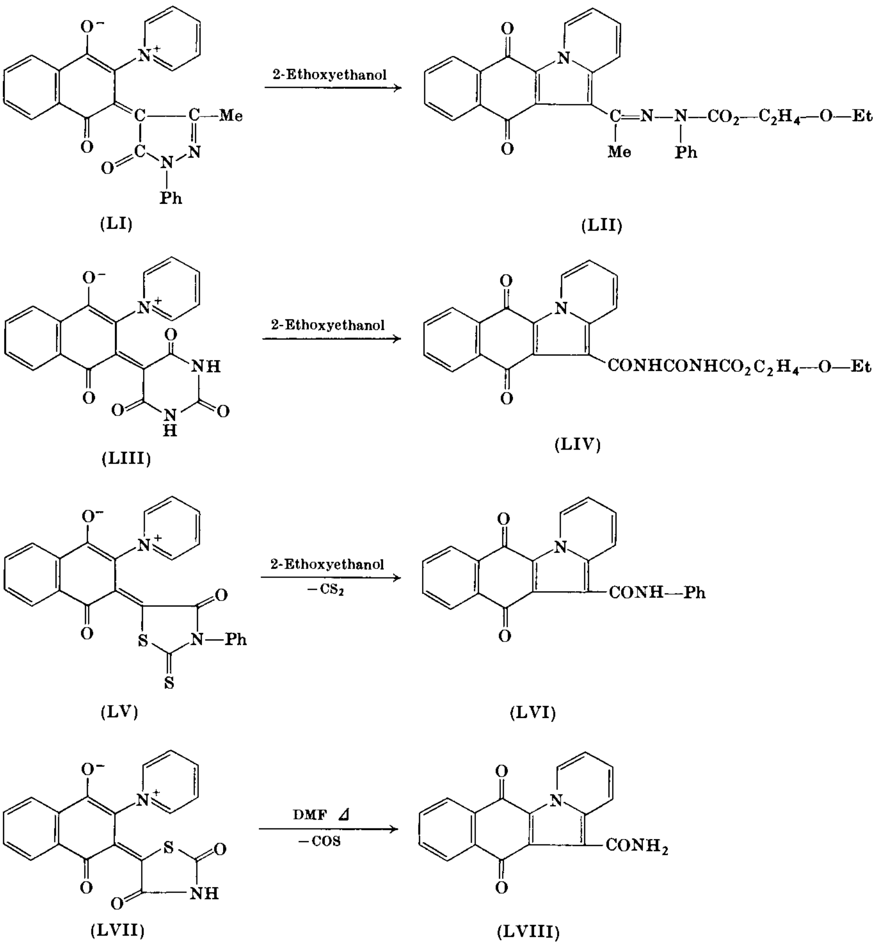
[40] J. A. Van Allan, G. A. Reynolds, and R. E. Adel, *J. Org. Chem.* **28**, 3502 (1963).

betaine (LI), obtained from (XLIX) and 1-phenyl-3-methyl-5-pyrazolone, yields (LII) when heated with 2-ethoxyethanol.

The ylidene–enol betaine (LIII) from barbituric acid and (XLIX) on heating in 2-ethoxyethanol gives the pyrrocoline derivative (LIV). Elimination of carbon disulfide and carbon oxysulfide accompanies the formation of the pyrrocolines (LVI) and (LVIII) from the corresponding ylidene–enol betaines (LV) and (LVII).

The phthaloylpyrrocolines were first synthesized by Tilak *et al.*[31, 34, 36] with a view to obtaining useful vat dyes for cotton. 1-Carbethoxy-, 1-acetyl-, and 1-benzoyl-2,3-phthaloylpyrrocolines, however, dye very



(LI) (LII)

(LIII) (LIV)

(LV) (LVI)

(LVII) (LVIII)

weak shades and therefore are of no interest as vat dyes.[40] To prepare useful vat dyes, 1-carbethoxy-2,3-phthaloylpyrrocoline was hydrolyzed by alcoholic alkali to the 1-carboxy derivative, which was then converted to the 1-carbonyl chloride. A series of carboxy arylamido derivatives were then synthesized by reacting the acid chloride with various arylamines, such as chloroanilines, toluidines, dehydrothio-*p*-toluidine, benzidine, and *o*-tolidine.[41, 42] These arylides, with the exception of those derived from benzidine and *o*-tolidine (LIX), are only weakly substantive to cotton. The dyes of type (LIX) dyed attractive fast violet shades on cotton.[42] An interesting dye obtained in this work is (LX) from (I) and Naphtol AS-LG and ASL3G.[36, 42, 43] It dyes an attractive reddish orange shade. Although 1-carbethoxy-2,3-phthaloylpyrrocoline was of no interest as a vat dye, it dyes an attractive golden yellow shade of moderate fastness on cellulose acetate.[39]

The 1-carboxyarylamido-2,3-phthaloylpyrrocolines have been the subject of recent patents as many of them have been found to be of use as vat dyes and particularly as pigments. Some of these derivatives merit inclusion in a range of pigments noted for their outstanding fastness characteristics to all agents. Many of these are used for mass coloring of high molecular weight synthetic fibers and possess good resistance to light, cross-lacquering, migration, heat, and solvents. They have been particularly useful for coloring polyvinyl chloride, polyethylene, rubber, and also printing inks. Compounds of the general formula (LXI) have been reported to possess good all-round fastness properties and are yellowish red to violet pigments.[44] A bright red pigment (LXIII) is obtained by reacting 2,3-phthaloylpyrrocoline-1-carbonyl chloride with 2-aminobenzoyl-3′,4′,5′-trichloroanilide (LXII) in boiling *o*-dichlorobenzene for 6 hours.[44] 2,3-Phthaloylpyrrocoline-1-carbonyl chloride on condensation with *p*-aminobenzoic acid in boiling *o*-dichlorobenzene gives the intermediate (LXIV). The acid chloride (LXV) derived from (LXIV) on interaction with arylamines yields a series of arylamides which are used in printing inks and for coloring polyvinyl chloride and lacquers.[45] Thus condensation of 3,4,5-trichloroaniline with (LXV) gives a bright red pigment (LXVI).

A red vat dye (LXVII) which is also useful as a pigment is obtained by condensing 2 moles of 2,3-phthaloylpyrrocoline-1-carbonyl chloride

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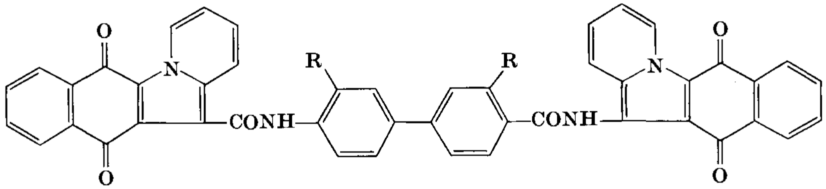
[41] B. Suryanarayana, Ph.D.(Tech.) Thesis, University of Bombay (1954).

[42] B. D. Tilak, R. V. Acharya, M. S. Mathur, B. Suryanarayana, and M. R. Venkiteswaran, *J. Sci. Ind. Res.* (*India*) **17B**, 483 (1958).

[43] G, *USP* 2,772,275.

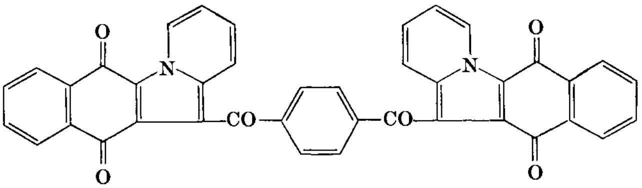
[44] Gy, *BP* 1,042,636.

[45] Gy, *Neth. Pat.* 6,410,993.

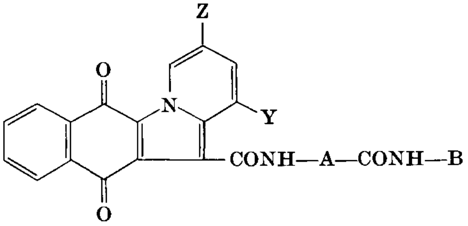


(LIX)

R = H, Me



(LX)

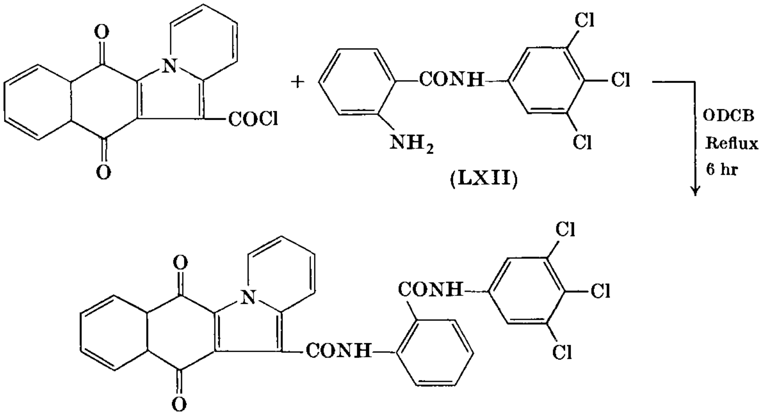


(LXI)

A = Substituted or unsubstituted arylene with hal, alk, O-Alk, O-Ar, or halogenated aryloxy groups.

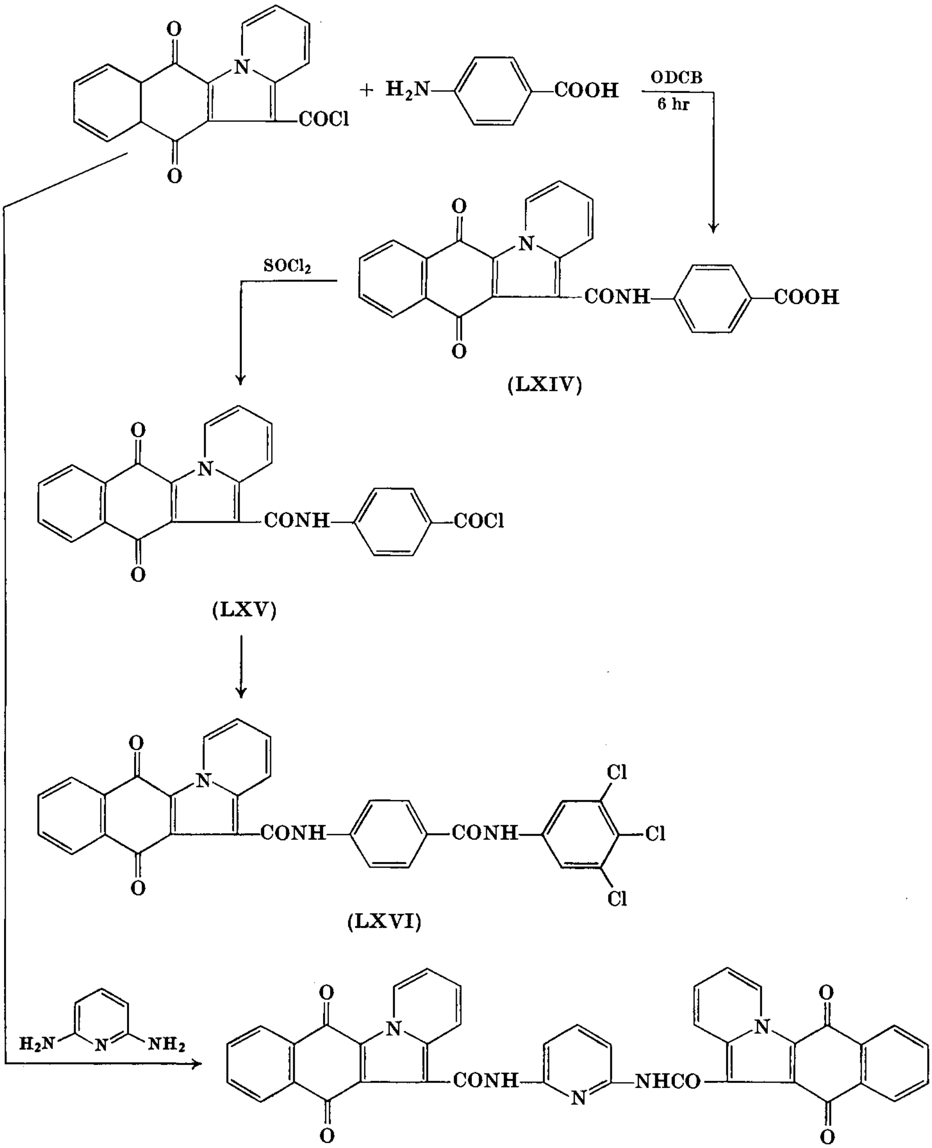
B = Ph, α-naphthyl, or β-naphthyl substituted with hal, alk, O-Alk, CF_3, CN, R-CO, Ar-CO, NO_2, CONH-Alk, SO_2NH-Alk, SO_2-Alk, SO_2-Ar

Y and Z = H or one is alkyl



(LXII)

(LXIII)



(LXIV)

(LXV)

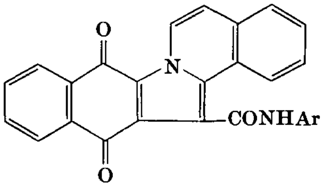
(LXVI)

(LXVII)

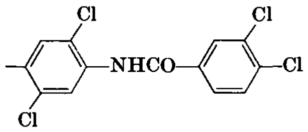
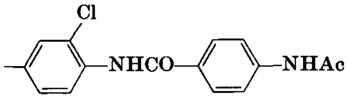
with 2,6-diaminopyridine.[46] Heterocyclic pigments of the general formula (LXVIII) are obtained by condensing the 2,3-phthaloylbenzopyrrocoline-1-carbonyl chloride with various amines.[47,48] Table I gives the shade and yield of the resulting pigments.

TABLE I

2,3-PHTHALOYLPYRROCOLINE ARYLAMIDE PIGMENTS



(LXVIII)

Ar	*Color*	% *yield*
3-Cl—C_6H_4	Red	94
3,4-Cl_2—C_6H_3	Orange	99
2,5-Cl_2—C_6H_3	Yellow	94
2,4,5-Cl_3—C_6H_2	Orange	73
3,4,5-Cl_3—C_6H_3	Orange-red	91
3,4-Cl(AcNH)—C_6H_3	Orange-yellow	80
3,4-Me(AcNH)—C_6H_3	Orange-yellow	99
4,3-AcNH(OMe)—C_6H_3	Orange-yellow	84
3,5-Cl_2—4(CN)—C_6H_2	Orange	71
3,5-Br_2—C_6H_3	Orange-red	74
3,4-Br(AcNH)—C_6H_3	Orange-yellow	68
3,5,4-Cl(Br)(AcNH)—C_6H_2	Orange	77
	Yellow	—
	Orange	—

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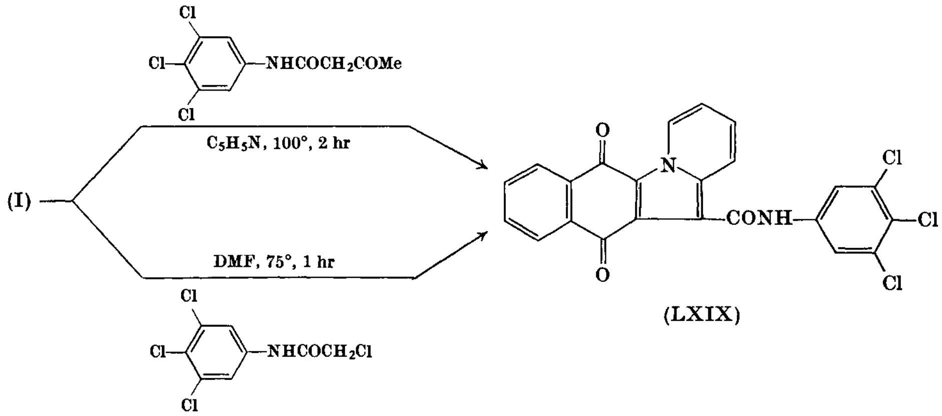
[46] CIBA, *BP* 969,309.

[47] Gy, *Neth. Pat.* 6,504,888.

[48] Gy, *Neth. Pat.* 6,514,409.

The arylamides derived from 2,3-phthaloylpyrrocolines have also been synthesized by reacting (I) with acetoacetarylides and pyridine.[45, 48, 49, 50] When (I) is reacted with acetoacet-3,4,5-trichloroanilide in the presence of pyridine or dimethyl formamide, a bright red pigment (LXIX) is obtained.



(LXIX)

Because of their excellent pigmentary properties, the arylamides of 2,3-phthaloylpyrrocolines continue to be intensively studied with a view to the discovery of better pigments.

C. Reaction of (I) with Amines

1. *2-Arylamino-3-chloro-1,4-naphthoquinones and* N:N′*-Di-3-(2-chloro-1,4-naphthoquinonyl)arylenediamines*

Compound (I) reacts readily with alkyl or aryl amines to give 2-alkyl or 2-aryl amino-3-chloro-1,4-naphthoquinones [(LXX) and (LXXI)]. The second chlorine atom is not replaced even if an excess of amine is used. The second chlorine atom in (I) can be replaced by an alkyl or aryl amine only if the monoarylamino derivative is nitrosoated or acetylated. The reaction of (I) with aromatic primary amines is influenced by steric and electronic effects. Aromatic amines such as *o*-chloroaniline, *o*-toluidine, and 2,4-dichloroaniline react with (I) to give very low yields of the 2-arylamino-3-chloro-1,4-naphthoquinones. An increase in basicity overcomes the limitations imposed by steric effects as observed in the reaction of *o*-anisidine and *o*-aminophenol[51] with (I), whereby

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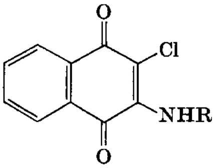
[49] Gy, *Neth. Pat.* 6,505,682.

[50] E. C. Inman and I. A. Macpherson, *BP* 1,076,482.

[51] J. A. Van Allan, G. A. Reynolds, and R. E. Adel, *J. Org. Chem.* 28, 2683 (1963).

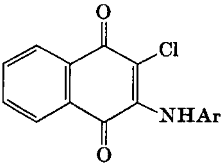
increased yields of 2-arylamino-3-chloro-1,4-naphthoquinone are obtained. Buu Hoi[52] has reported a series of 2-arylamino-3-chloro-1,4-naphthoquinones (LXXI) but none of these are useful as vat dyes. It has been found that these products are hydrolyzed to 2-arylamino-3-hydroxy-1,4-naphthoquinone and 2-chloro-3-hydroxy-1,4-naphthoquinone by the action of alkaline hydrosulfite at 60° (IN process of vat dyeing).[53] It is likely that the nonsubstantivity of these dyes may be due to degradation during dyeing. The dyes are found to be stable if the dyeing is carried out at lower temperature (IW process of vat dyeing).[53] Tilak *et al.* synthesized a series of mono- and dinaphthoquinonyl amines by reacting (I) with aromatic mono- and diamines. With the exception of dyes derived from dehydrothio-*p*-toluidine (brown-red shade) and primuline base (reddish brown shade), none of the 2-arylamino-3-chloro-1,4-naphthoquinones (LXXI) were substantive to cotton, although most of them dyed washfast shades on wool.

Interaction of (I) with diamines gives either the mono or the bis naphthoquinonylamines, depending on the quantity of the amine used.



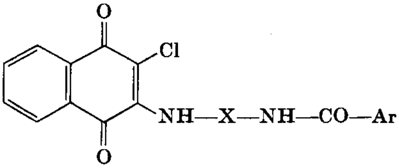
(LXX)

R = Alkyl

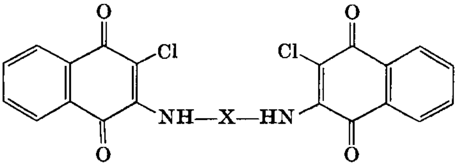


(LXXI)

Ar = Aryl



(LXXII)



(LXXIII)

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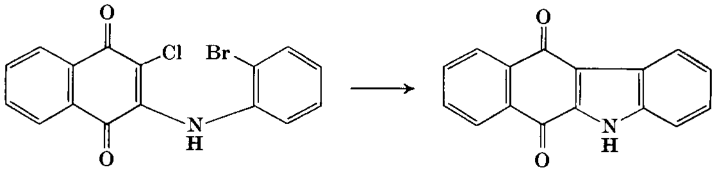
[52] N. P. Buu Hoi, *Bull. Soc. Chim. France* **11**, 578 (1944).

[53] B. D. Tilak and R. V. Acharya, *J. Sci. Ind. Res.* (*India*) **14B**, 219 (1954).

The mononaphthoquinonylamines are weakly substantive to cotton, although substantivity and fastness are improved by acylation of the free amino group with acid chlorides from benzoic, cinnamic, and azobenzene-4,4′-dicarboxylic acids to yield (LXXII). The bis naphthoquinonylamines (LXXIII) are, in general, more substantive to cotton and give fugitive violet shades.[54]

2. *2,3-Phthaloylindoles*

2-(*o*-Bromoarylamino)-3-chloro-1,4-naphthoquinones (LXXIV) when heated with copper powder in boiling nitrobenzene yield phthaloylindoles (LXXV).[55] Various substituted anilines, β-naphthylamine, and benzidine have been used in this reaction.



(LXXIV) (LXXV)

The phthaloylindoles give yellow shades when dyed on cotton as vat dyes. The parent phthaloylindole was used as a commercial vat dye for wool under the name of Helindone Yellow R (CI 56070).[56, 57] An alternative method for the preparation of 2,3-phthaloylindoles consists in the desulfurization of *lin*-naphthothiazinequinones (LXXVII) in boiling nitrobenzene in the presence of copper or an oxidizing agent like potassium ferricyanide.[58] The *lin*-naphthothiazinequinones are obtained by air oxidation of a boiling alcoholic solution of 2-arylamino-3-mercapto-1,4-naphthoquinones (LXXVI).[59] The probable reaction mechanism for the conversion of (LXXVI) to (LXXVII) is shown in Chart 8.

The *lin*-naphthothiazinequinones are deep blue, but have no substantivity to synthetic fibers as disperse dyes due to their noncoplanarity.[60]

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[54] B. D. Tilak and R. V. Acharya, *J. Sci. Ind. Res.* (*India*) **14B**, 390 (1955).

[55] IG, *DRP* 646,994.

[56] IG, *BP* 317,928; G, *USP* 1,763,216; IG, *DRP* 530,745.

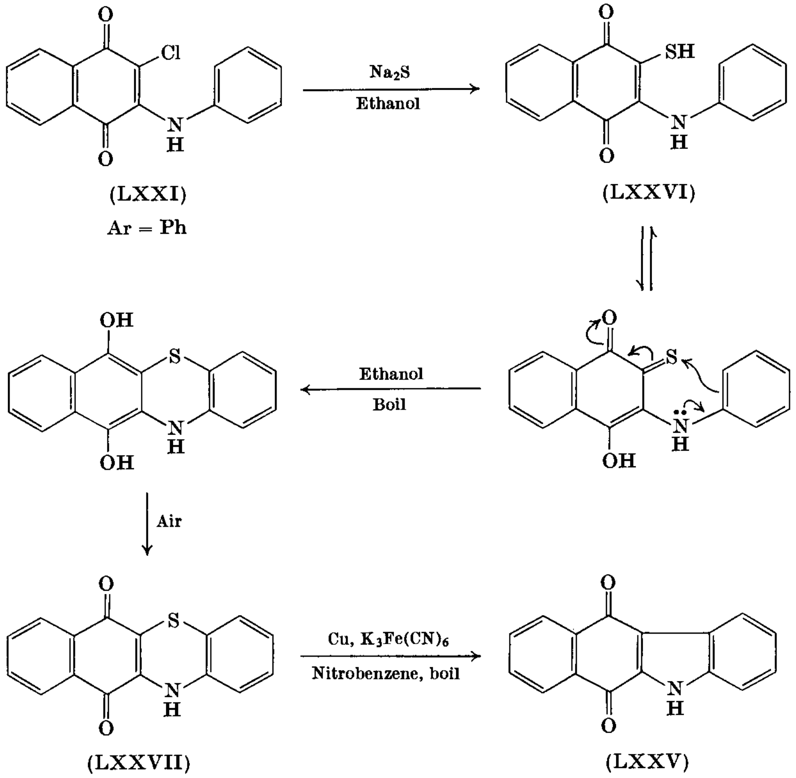
[57] von C. Graebe and W. Knecht, *Ann.* **202**, 13 (1880).

[58] G, *USP* 1,772,317.

[59] K. Fries and F. Kerkow, *Ann.* **427**, 288 (1922).

[60] B. D. Tilak and P. R. Venkateswaran, *Chimia* **22** (Suppl.) 95 (1968).

CHART 8



3. *Diazanaphthacenequinones*

Interaction of 2-arylamino-3-chloro-1,4-naphthoquinones (LXXI) sodium azide in dimethylformamide at 90–100° leads to the diazanaphthacenequinone (LXXXI).[61] Many substituted 2-arylamino-3-chloro-1,4-naphthoquinones are employed in this reaction. In no case has the intermediate 2-arylamino-3-azido-1,4-naphthoquinone (LXXVIII) been isolated, since temperatures which bring about the replacement of the chlorine atom are also high enough to bring about the cyclization by loss of nitrogen. In all examples cited, 2-amino-3-arylamino-1,4-naphthoquinone (LXXXII) has been obtained as a by-product. The cyclization of the intermediate azide (LXXVIII) has been assumed to proceed through the nitrene (LXXIX). Interaction of the nitrene with the benzene ring results in the formation of a dihydro intermediate (LXXX),

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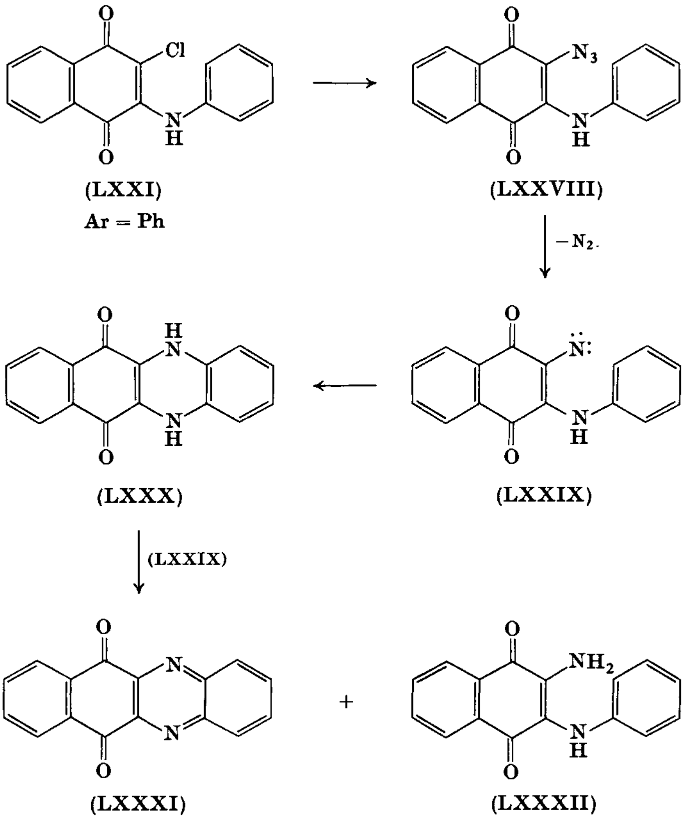
[61] J. A. Van Allan, G. A. Reynolds, and R. E. Adel, *J. Org. Chem.* **28**, 524 (1963).

which is then oxidized by the nitrene itself to the diazanaphthacenequinone (LXXXI) and 2-amino-3-arylamino-1,4-naphthoquinone (LXXXII). This mechanism is supported by the fact that in no case does the yield of (LXXXI) exceed 50%.



(LXXI)
Ar = Ph

(LXXVIII)

(LXXX)

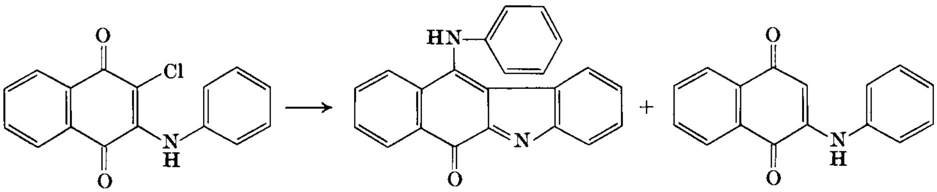
(LXXIX)

(LXXXI)

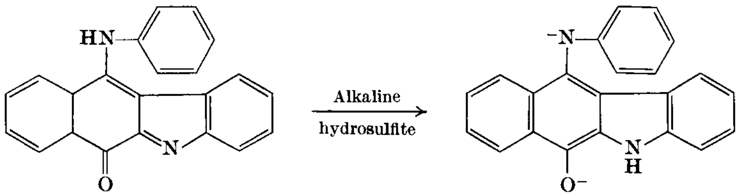
(LXXXII)

4. *11-Arylamino-6-ketonaphtho[b]indolenines*

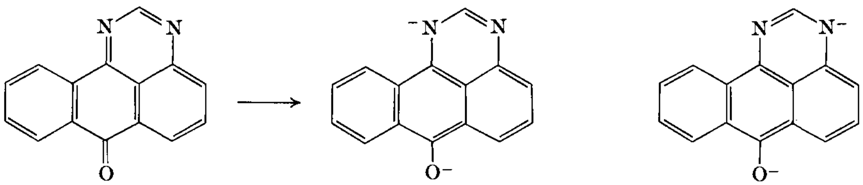
2-Anilino-3-chloro-1,4-naphthoquinone (LXXI) when heated with excess of zinc dust in a sealed tube at 240° for 4 hours gives mainly 2-anilino-1,4-naphthoquinone (LXXXIII) and a red product which has been shown to be 11-anilino-6-ketonaphtho[b]indolenine (LXXXIV) on the basis of its NMR, IR, and mass spectral data.[6,60] Compound (LXXXIV) has good affinity for Terylene polyester, which is dyed a red-brown shade. The shade on the dyed Terylene is not affected by acids, although the compound in substance dissolves in mineral acid, giving a yellow solution from which it is recovered unchanged on basification. The dye (LXXXIV) can be vatted by alkaline hydrosulfite and reoxidized without change. The vatting property of (LXXXIV) may be attributed to the formation of the leuco derivative (LXXXV), in analogy with the alkaline hydrosulfite reduction of pyrimidanthrone (LXXXVI) to its leuco derivative (LXXXVIIa,b).



(LXXI) (LXXXIV) (LXXXIII)

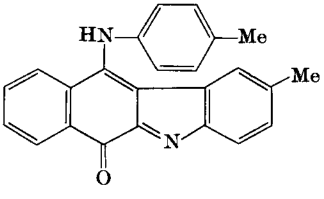


(LXXXIV) (LXXXV)



(LXXXVI) (LXXXVIIa) (LXXXVIIb)

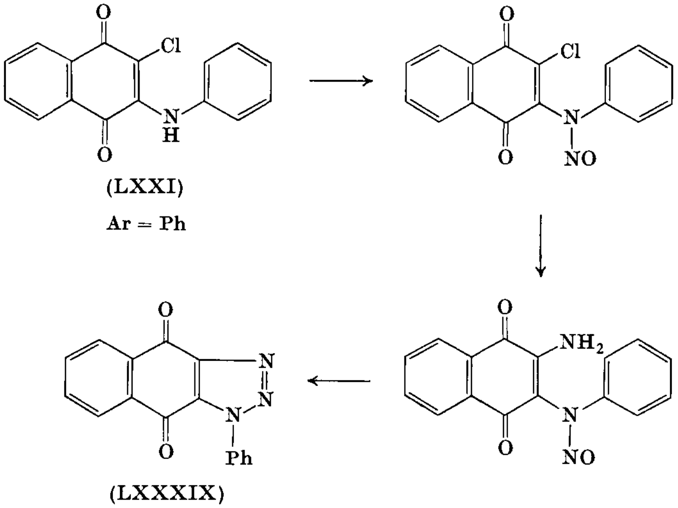
2-Chloro-3,*p*-toluidino-1,4-naphthoquinone on heating with zinc dust yields 2-methyl-6-keto-11-*p*-toluidinonaphtho[b]indolenine (LXXXVIII). 2-Chloro-3-(*o*-bromo-β-naphthylamino)-1,4-naphthoquinone and 2-carbazolylamino-3-chloro-1,4-naphthoquinone under these conditions, however, yield only the dehalogenated derivatives.[6, 60]



(LXXXVIII)

5. *Naphtho[2,3-d]triazole-4,9-diones*

Nitrosoation of 2-anilino-3-chloro-1,4-naphthoquinone (LXXI) followed by reaction with ammonia yields 2-amino-3-*N*-nitrosoanilino-1,4-naphthoquinone, which on heating in acetic acid readily cyclizes to give the naphthotriazoledione (LXXXIX). Nitro, amino, diamino, and aminobromo derivatives of 1-methyl, 1-ethyl, and 1-butyl naphthotriazolediones are reported as useful vat dye intermediates.[62, 63]



(LXXI)

Ar = Ph

(LXXXIX)

6. *Naphth[2′,3′;4,5]imidazo[1,2-a]pyridine-6,11-dione*

The condensation of (I) with 2-aminopyridine has been reported to yield an orange quinone which was constituted as the linear 1,4-naphthoquinone derivative (XC).[64] However, Mosby and Boyle[65] revised this structure to (XCI) since it gave a phenazine derivative on interaction with *o*-phenylenediamine. The compound was prepared by an alternative route starting from 2-aminopyridine and 3,4-dichloro-1,2-naphthoquinone and also by the interaction of 2-acetamido-3-chloro-1,4-naphthoquinone with 2-aminopyridine in methyl cellosolve.[65] The compound (XCI) has also been prepared by reaction of (I) with 2-amino-

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[62] CCC, *USP* 2,879,274.

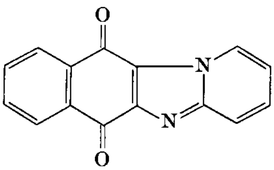
[63] CCC, *USP* 2,967,863.

[64] P. Truitt, H. E. Cooper, and F. M. Wood, *J. Am. Chem. Soc.* **79**, 5708 (1957).

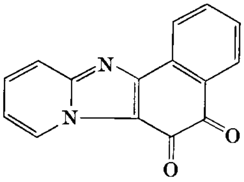
[65] W. L. Mosby and R. J. Boyle, *J. Org. Chem.* **24**, 374 (1959).

pyridine in 2-ethoxyethanol.[66] The mechanism of formation of (XCI) by the latter route is shown below.

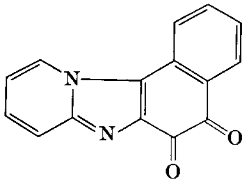
Various substituted 2-aminopyridines, such as methyl, chloro, ethoxy, 5-nitro, and 3,5-dinitro-2-aminopyridines have been used in this reaction to yield a series of naphthimidazopyridinediones with substituents in the pyridine ring. Derivatives of (I) containing nitro, halo, and hydroxy substituents have also been used in the reaction to give derivatives of (XCI) which have been reported as useful vat dyes and pigments.[5]



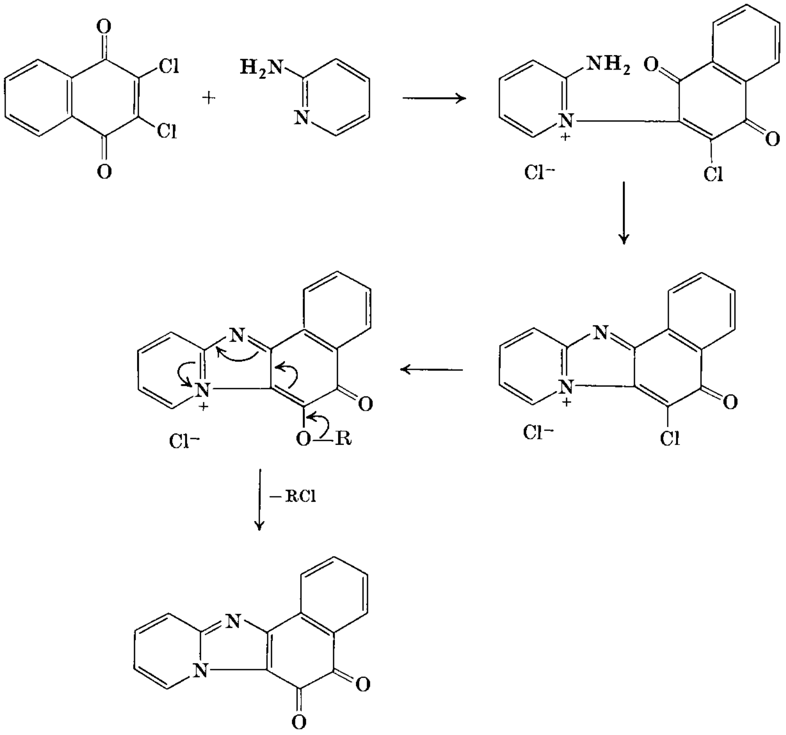
(XC)



(XCI)



(XCII)



(XCI)

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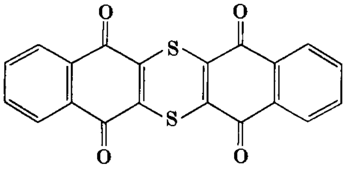
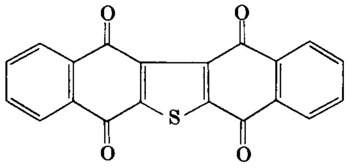
[66] J. A. Van Allan and G. A. Reynolds, *J. Org. Chem.* **28**, 1019 (1963).

D. REACTION OF (I) WITH MERCAPTANS: 3,4-PHTHALOYL-2-THIAQUINOLIZINES

Compound (I) is known to react with alkylmercaptans to give 2-alkylmercapto-3-chloro-1,4-naphthoquinone and with arylmercaptans to give 2,3-diarylmercapto-1,4-naphthoquinones. Interaction of (I) with sodium sulfide yields 2,3,5,6-diphthaloyl-1,4-dithiadiene (XCIII). The latter on desulfurization yields (XCIV).[5]

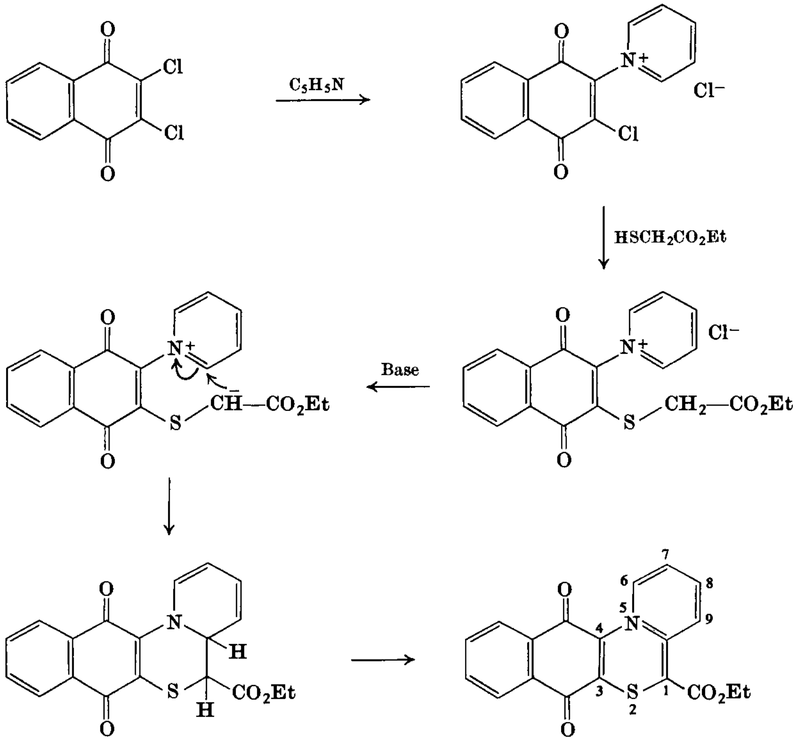


(XCIII)



(XCIV)

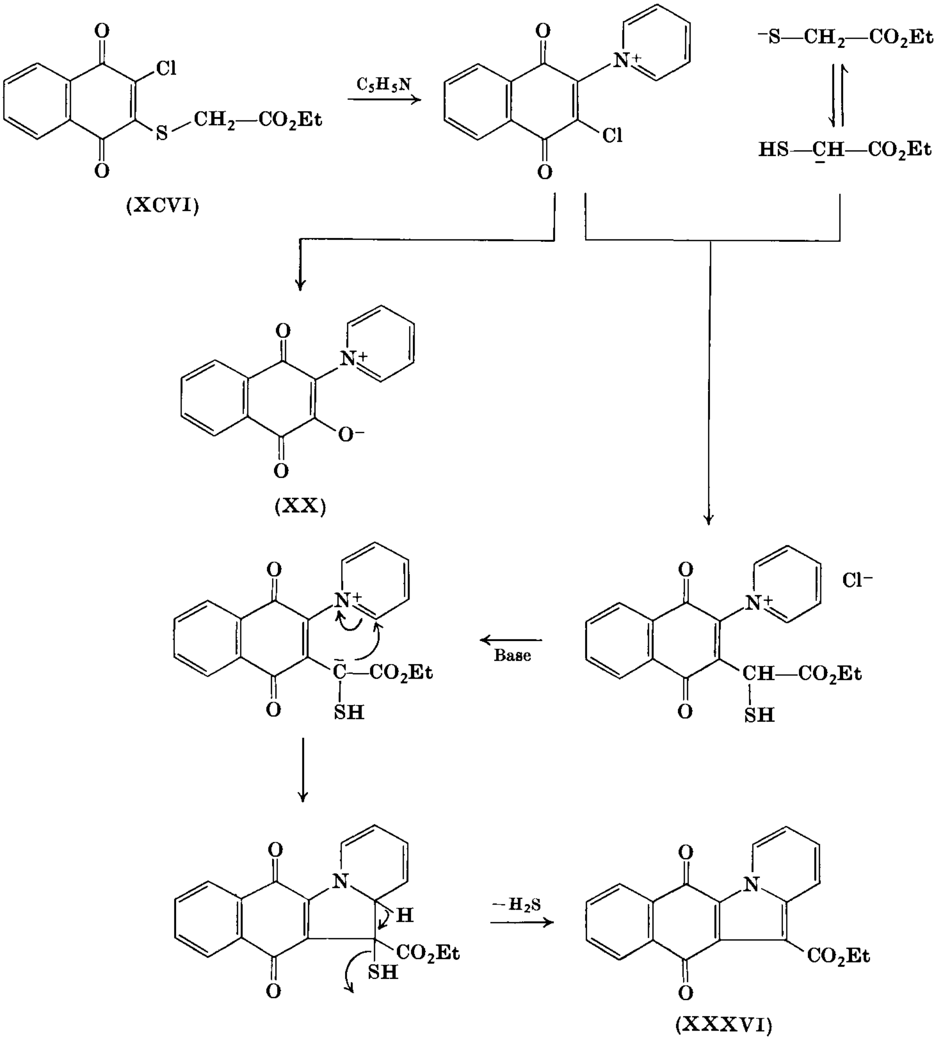
With a view to the synthesis of 1-carbethoxy-3,4-phthaloyl-2-thiaquinolizine (XCV), Tilak and Venkateswaran[6,60] reacted (I) with



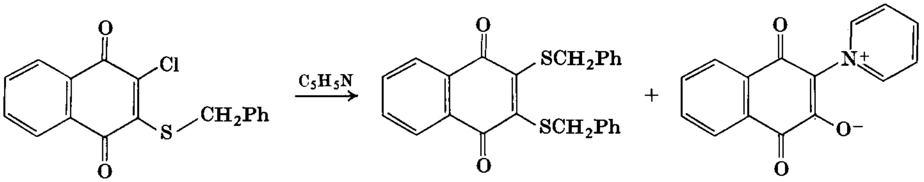
(XCV)

ethyl mercaptoacetate and pyridine in dimethylformamide. The reaction was expected to proceed in a manner analogous to the synthesis of 1-carbethoxy-2,3-phthaloylpyrrocoline (XXXVI). However, instead of (XCV), (XXXVI) and the betaine (XX) were obtained. Similarly, interaction of 2-carbethoxymethylmercapto-3-chloro-1,4-naphthoquinone (XCVI) with pyridine also yielded (XXXVI) instead of (XCV). The reactions taking place may be visualized as shown in Chart 9.

CHART 9

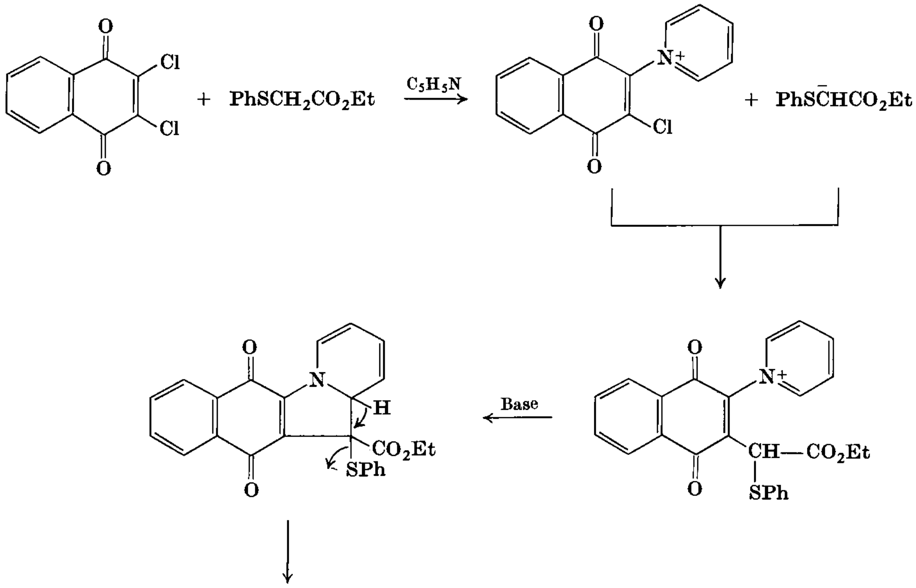


The above mechanism involves the elimination of the ethyl mercaptoacetate anion by pyridine. The mercaptide anion evolved in the reaction is then transformed to the carbanion which then takes part in the reaction. Subsequent ring closure takes place with the elimination of hydrogen sulfide, giving rise to (XXXVI). The elimination of the mercaptide side chain is supported by the observation that interaction of 2-benzylmercapto-3-chloro-1,4-naphthoquinone (XCVII) with pyridine yields 2,3-dibenzylmercapto-1,4-naphthoquinone (XCVIII) and the pyridinium betaine (XX).



(XCVII) (XCVIII) (XX)

The mechanism shown in Chart 9 is supported by the formation of (XXXVI) in small yield by the interaction of (I) with ethyl phenylmercaptoacetate in the presence of pyridine. Thiophenol, which would

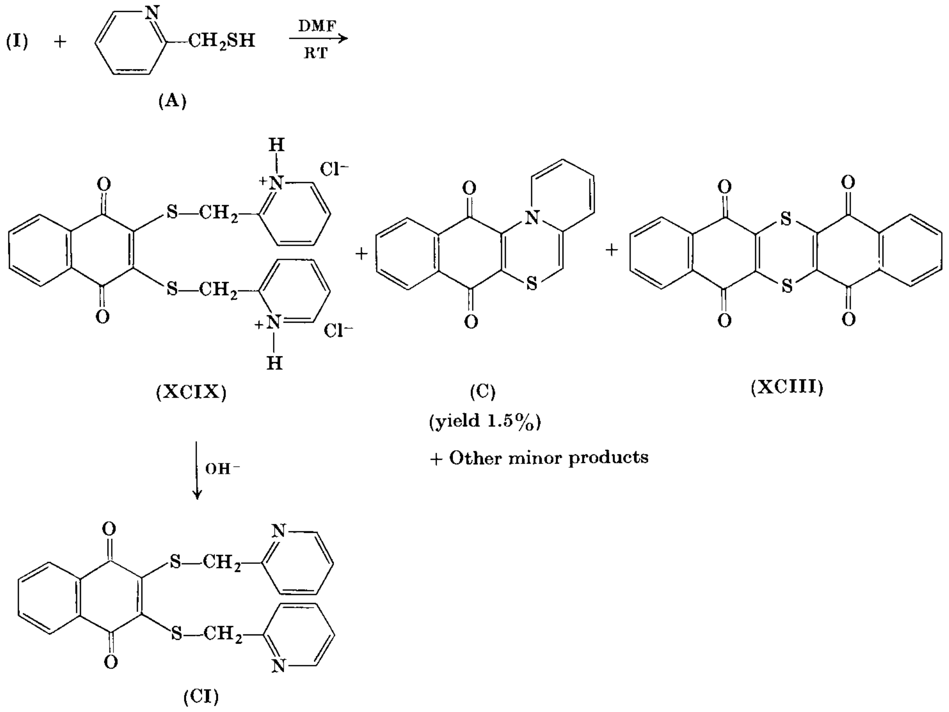


$$(XXXVI) + (PhSH) \longrightarrow PhSSPh$$

be eliminated in the reaction sequence, was detected as diphenyl disulfide, which was isolated and characterized.[67]

Interaction of (I) with 2-mercaptomethylpyridine (A) in dimethyl formamide at room temperature proceeded as shown in Chart 10, giving 3,4-phthaloyl-2-thiaquinolizine (C) in low yield along with unreacted (I) and other products.[67]

CHART 10



(A)

(XCIX)

(C)
(yield 1.5%)
+ Other minor products

(XCIII)

(CI)
(yield 28%)

When 2-mercaptomethylpyridine (A) was reacted with 2-chloro-1,4-naphthoquinone in methylene chloride the compounds shown in Chart 11 were obtained, of which (CII), when treated with dimethylformamide, yielded the desired 3,4-phthaloyl-2-thiaquinolizine (C) (yield 20%) along with 2,3-phthaloylpyrrocoline (XXXVII). A tentative mechanism of formation of the latter from (CII) is indicated.

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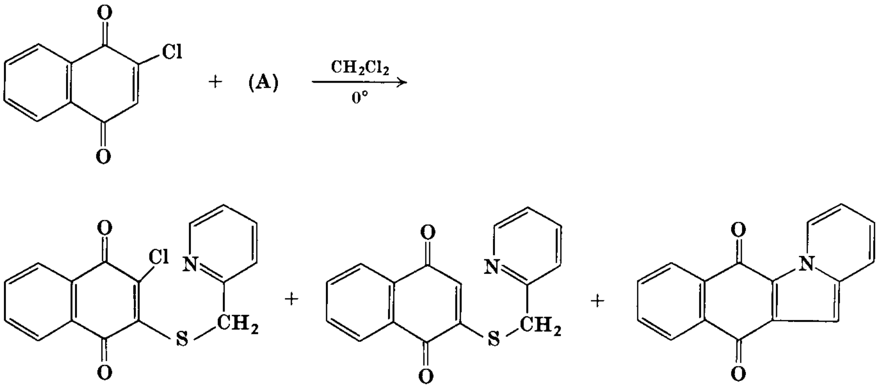
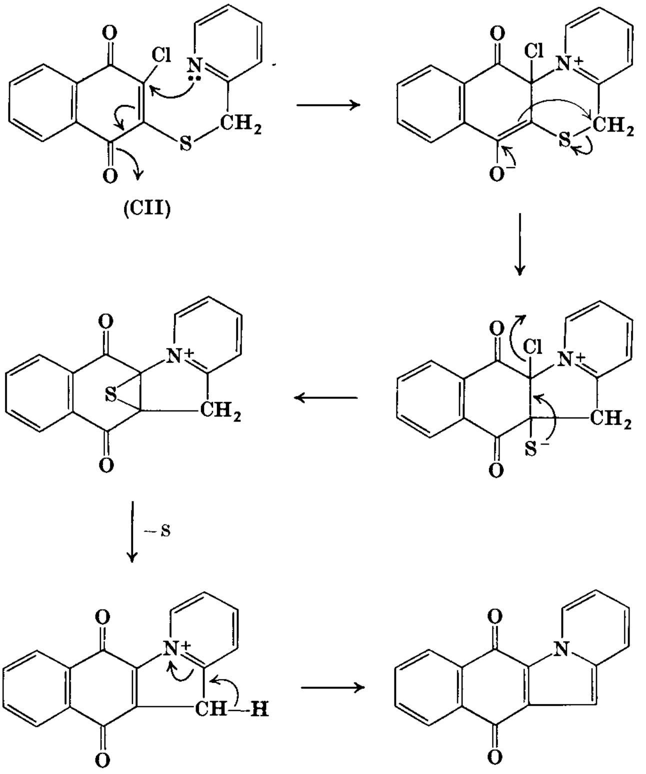
[67] J. N. Shah, Ph.D.(Tech.) Thesis, University of Bombay (1969).

CHART 11



(CII) (CIII) (XXXVII)

(yield, 31%) (3%) (< 1%)



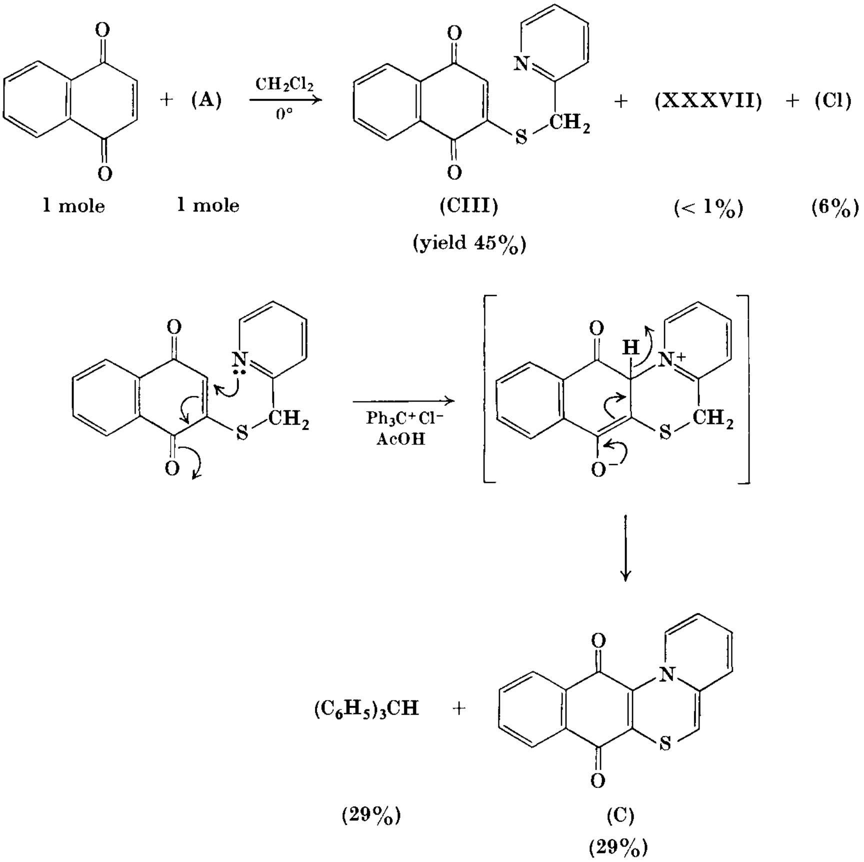
(CII)

(XXXVII)

The third route, developed by Shah and Tilak,[67] for the synthesis of (C) is outlined in Chart 12.

The compounds (CI), (CII), (CIII) on heating to their melting points or on sublimation yield 2,3-phthaloylpyrrocoline (XXXVII) (yield 10–15%) with the elimination of 2-mercaptomethylpyridine (identified as the disulfide), HCl and sulfur, and hydrogen sulfide, respectively.[67]

CHART 12

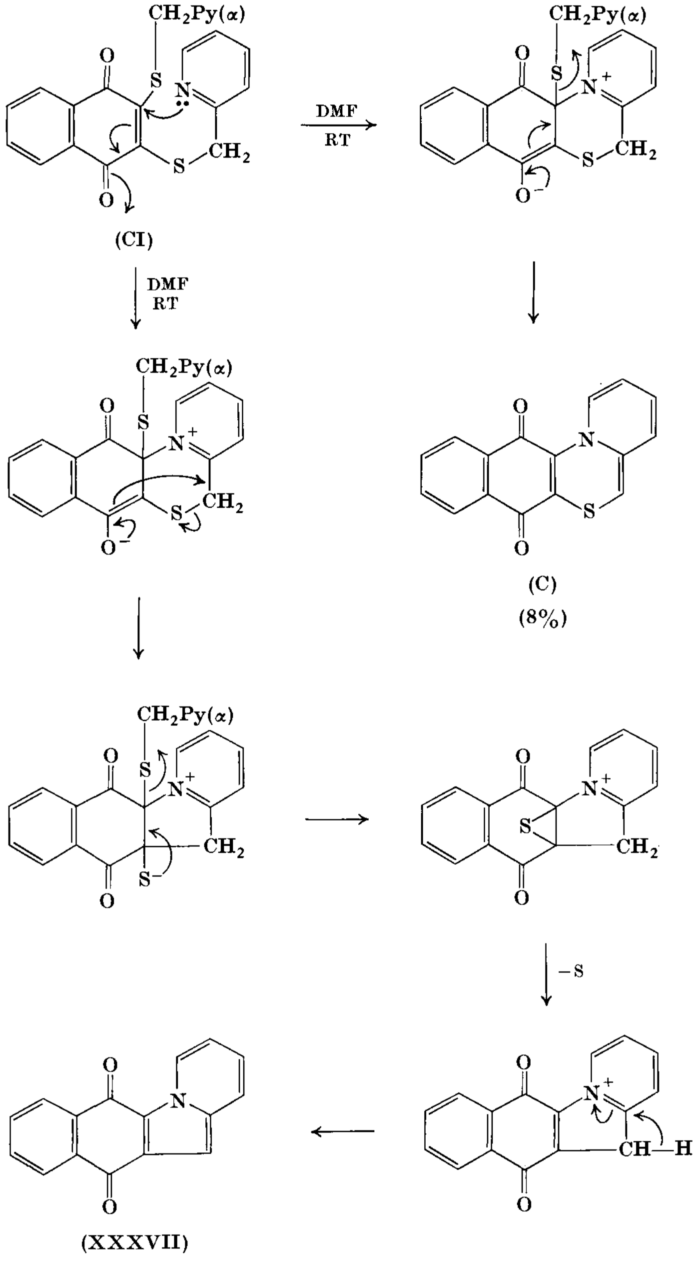


(CIII)
(yield 45%)

(C)

(CI) was also separately treated with dimethylformamide at room temperature or at the boil, whereby 3,4-phthaloylthiaquinolizine (C) was obtained along with (XXXVII) and several other products. The probable course of these reactions is outlined in Chart 13.

CHART 13



(CI)

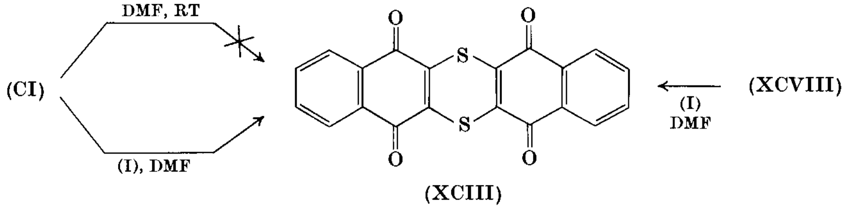
(C)

(8%)

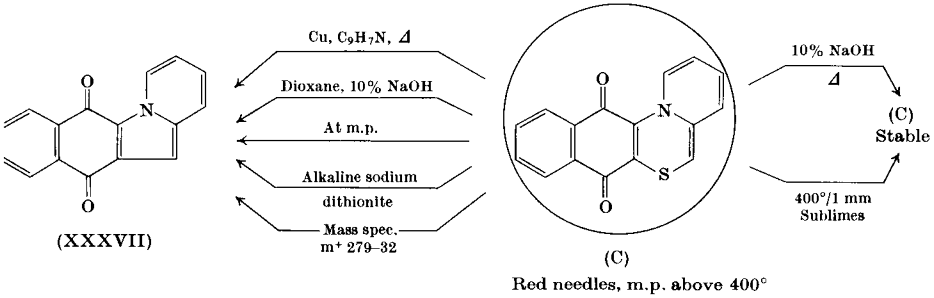
(XXXVII)

(< 1%)

Whereas (CI) does not give 2,3,5,6-diphthaloyl-1,4-dithiadiene (XCIII) on treatment with DMF, it gives the latter compound when interacted with 2,3-dichloro-1,4-naphthoquinone (I) in DMF at room temperature, albeit in low yield. 2,3-Dibenzylmercapto-1,4-naphthoquinone (XCVIII) when reacted with (I) in boiling naphthalene also yields (XCIII) in low yield.[67] These reactions give the genesis of (XCIII) in the reactions described in Chart 10.

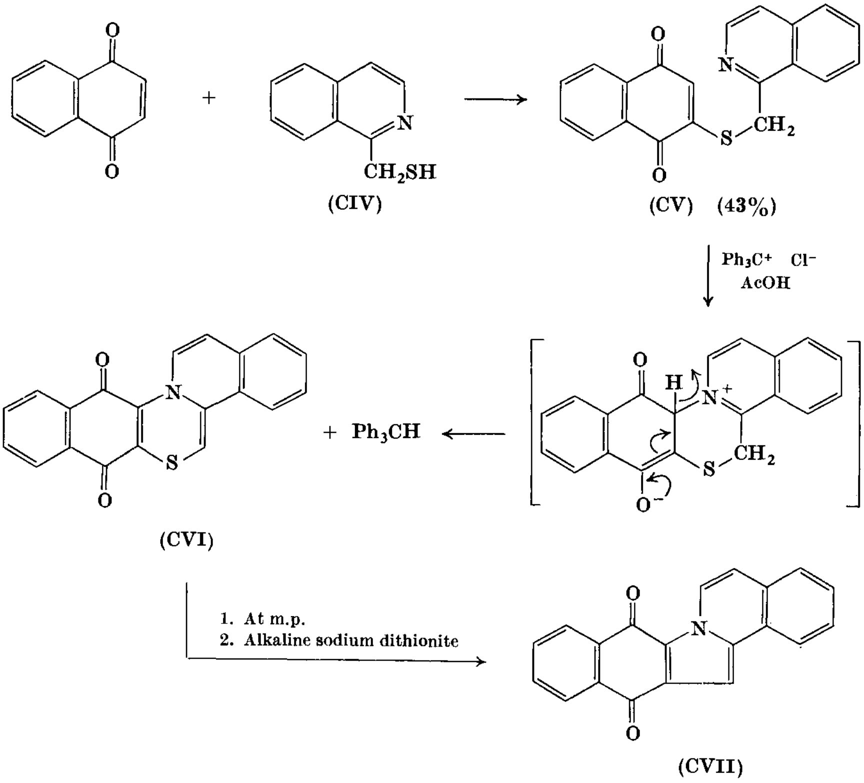


3,4-Phthaloyl-2-thiaquinolizine (C) appears to be an exceedingly interesting new chromophoric system which deserves further study. Its stability under various conditions is as follows:[67]



8,9-Benzo-3,4-phthaloyl-2-thiaquinolizine (CVI) was prepared starting from 1,4-naphthoquinone and 1-mercaptomethylisoquinoline (CIV) via 2-(1′-methylmercaptoisoquinolyl)-1,4-naphthoquinone (CV). The synthesis involves abstraction of a hydride ion by triphenylmethyl chloride.[67] Like (C), (CVI) also yields 7,8-benzo-2,3-phthaloylpyrrocoline (CVII) by heating or on alkaline hydrosulfite reduction.

Interaction of 2-mercaptomethylquinoline (CVIII) with 1,4-naphthoquinone gave the diol (CIX), which on oxidation yielded 2-(2-mercaptomethylquinonolyl)-1,4-naphthoquinone (CX). The latter, however, did not yield 6,7-benzo-3,4-phthaloyl-2-thiaquinolizine (CXI) on treatment with triphenylmethyl chloride and acetic acid, a failure which may be attributed to steric factors. When (CX) was heated to its melting



point, 5,6-benzo-2,3-phthaloylpyrrocoline (CXII) was obtained.[67] It may be recalled that the latter chromophoric system is not obtainable from (I) and quinaldine.

IV. Miscellaneous Dyes

2-Amino-3-chloro-1,4-naphthoquinone (CXIII) obtained by reacting (I) with aqueous ammonia in boiling ethanol is a useful intermediate for synthesis of a few vat dye systems.

A. 1-*H*-NAPHTHO[2,3-*d*]IMIDAZOLE-4,9-DIONE

When 2-acetylamino-3-amino-1,4-naphthoquinone is heated with ethyl orthoformate in sulfuric acid, it undergoes cyclization to yield 2-methyl-1-*H*-naphtho[2,3-*d*]imidazole-4,9-dione (CXIV).[68]

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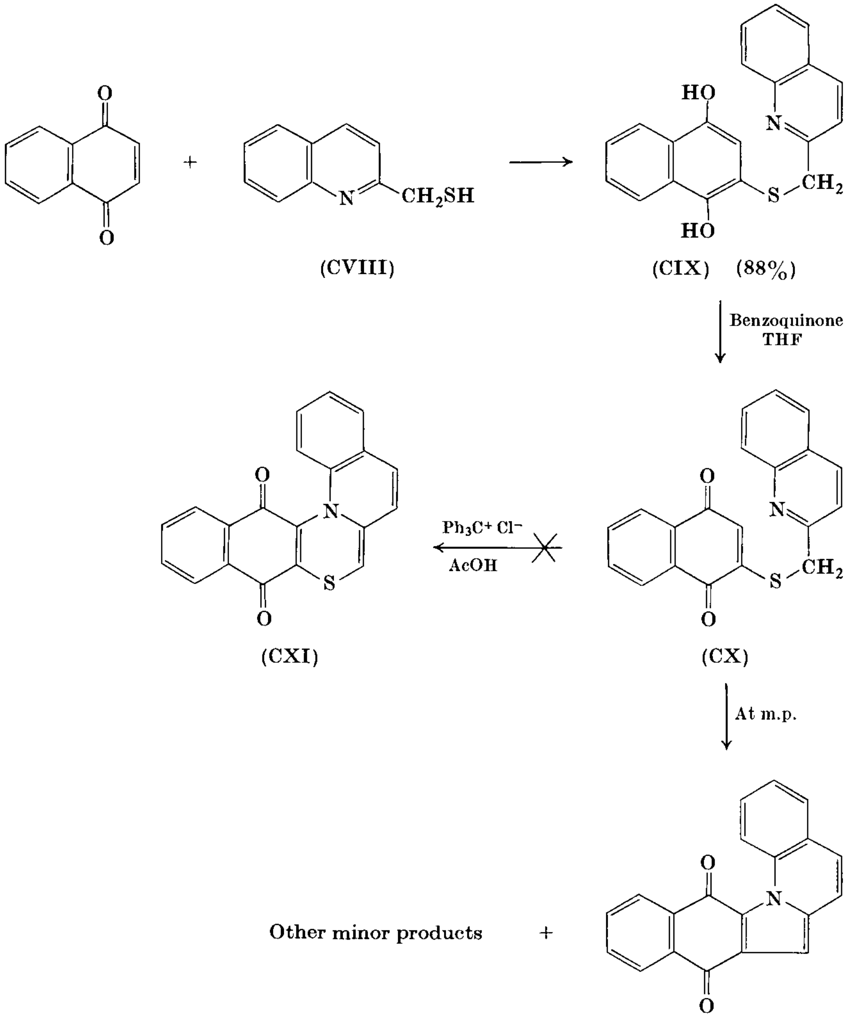
[68] J. R. E. Hoover and A. R. Day, *J. Am. Chem. Soc.* **76**, 4148 (1954).



(CXII)

Condensation of (CXIII) with terephthaloyl chloride gives the intermediate (CXV), which on condensation with an amine is converted to an intermediate of the type (CXVI). Ring closure of the latter leads to bis naphthimidazolediones of the type (CXVII).[69] Using the carbonyl chloride of naphthalene-1,4-dicarboxylic acid in the condensation reaction with (CXIII) and following the above steps, a bis naphthimidazoledione can be obtained in which the two naphthimidazolidione units are

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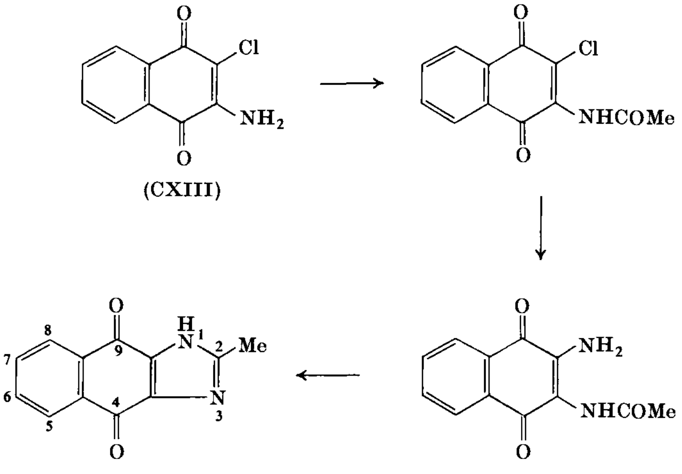
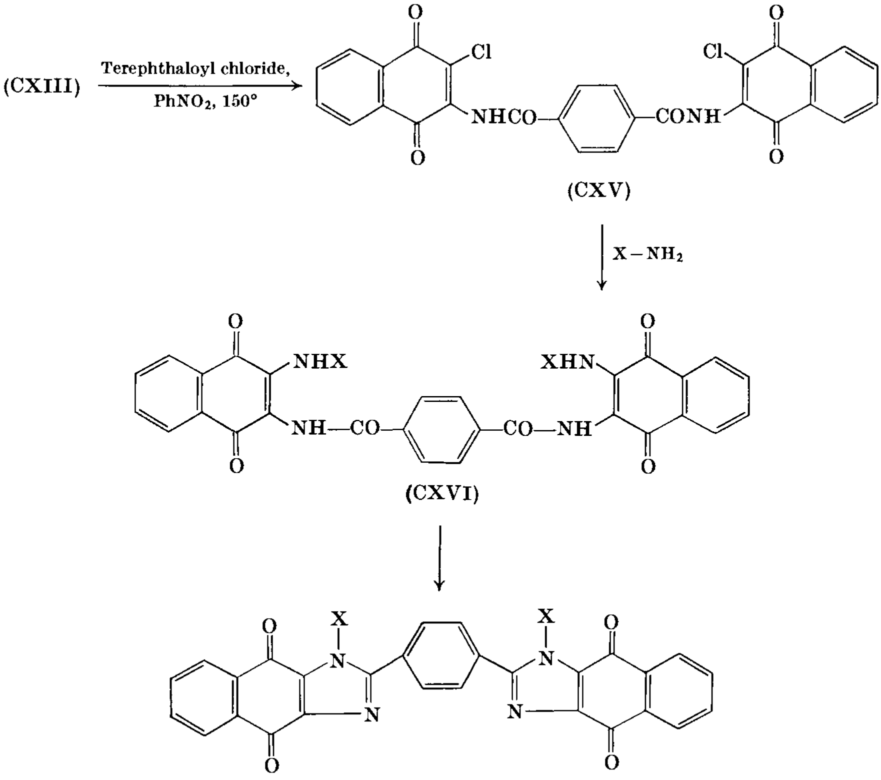
[69] IG, *DRP* 651,432.



(CXIII)

(CXIV)



(CXV)

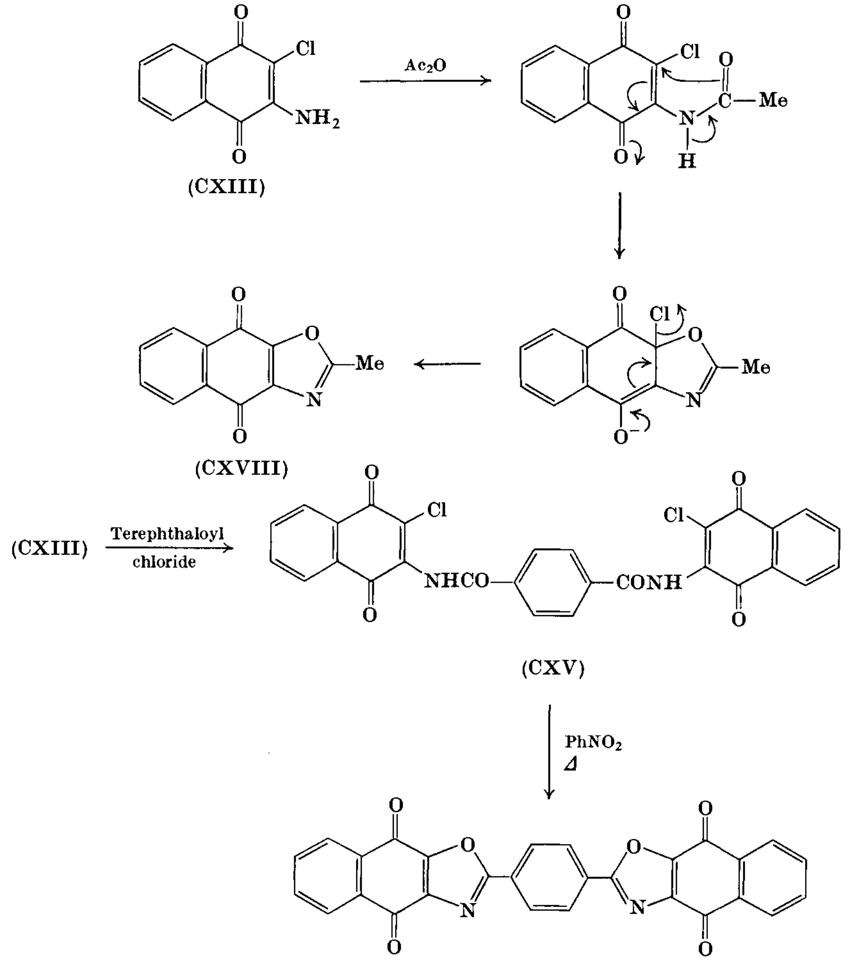
(CXVI)

(CXVII)

linked through a naphthalene bridge. The bis naphthimidazolediones are described as vat dyes.

B. NAPHTHOXAZOLEDIONES AND BISNAPHTHOXAZOLEDIONES

Interaction of 2-amino-3-chloro-1,4-naphthoquinone (CXIII) with acetic anhydride in the presence of sulfuric acid yields the naphthoxazoledione (CXVIII).[70] When (CXIII) is condensed with aryl dicarboxylic acid chlorides, such as terephthaloyl chloride, 4,4′-diphenyldicarboxyl



(CXIII)

(CXVIII)

(CXV)

(CXIX)

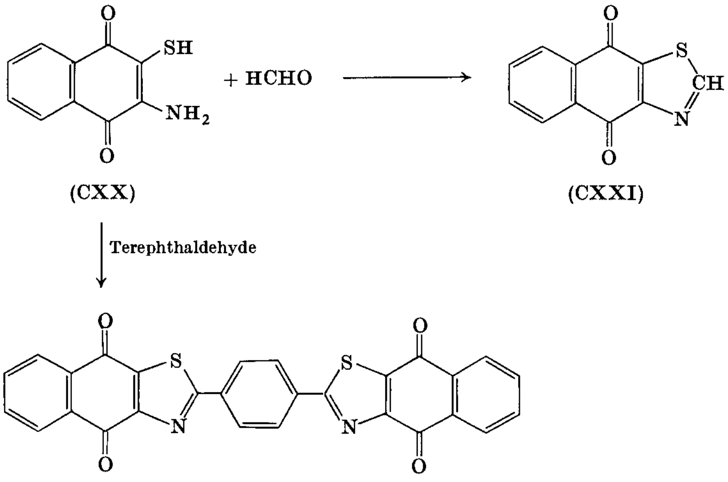
---

[70] K. Fries and P. Ochwat, *Ber. Deut. Chem. Ges.*, **56**, 1291 (1923).

chloride, or naphthalene-1,4-dicarboxyl chloride, and the intermediates of the type (CXV) are heated in nitrobenzene, bis naphthoxazolediones of the type (CXIX) are obtained, which are reported as useful vat dyes.[69]

C. NAPHTHOTHIAZOLEDIONES

Condensation of 2-amino-3-mercapto-1,4-naphthoquinone (CXX) with formaldehyde yields naphthothiazoledione (CXXI).[71,72] Substituted naphthothiazolediones are obtained by condensing (CXX) with other aldehydes such as glyoxal, acetaldehyde, benzaldehyde, and dimethylaminobenzaldehyde. When dialdehydes such as terephthaldehyde are condensed with (CXX), bis naphthothiazolediones of the type (CXXII) are formed. Bis naphthothiazolediones dye cotton from an alkaline hydrosulfite bath, giving yellow shades.



(CXX)

(CXXI)

(CXXII)

D. MEROCYANINES FROM 1,4-NAPHTHOQUINONE AND 2,3-DICHLORO-1,4-NAPHTHOQUINONE (I)

Naphthoquinone derivatives have been condensed with heterocyclic methylene bases to yield merocyanines.[73] For instance, condensation of (CXXIII) (Fischer Base), the methylene base from 1,3,3-trimethylindolenine methosulfate with 1,4-naphthoquinone at 40–50° in ethanol

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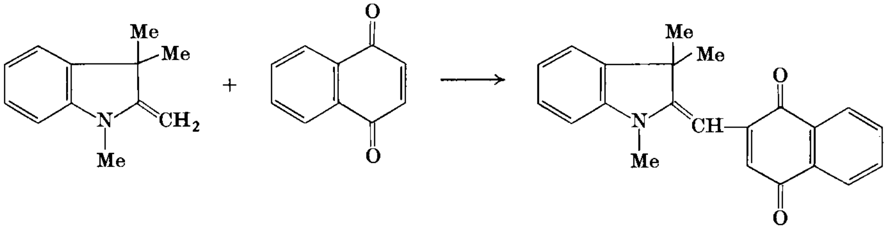
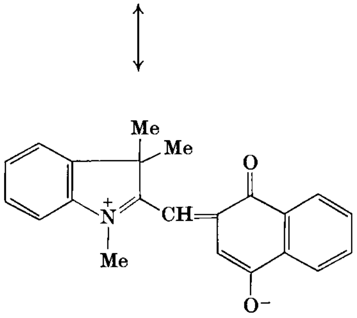
[71] W. A. Boggust, W. Cocker, J. P. Schwarz, and E. R. Stuart, *J. Chem. Soc.* p. 680 (1950).

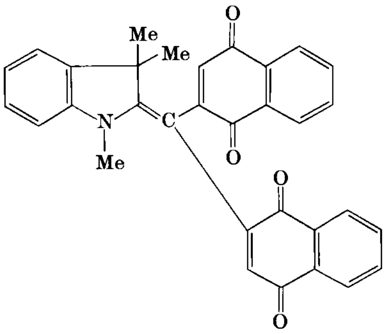
[72] G, *USP* 1,726,265.

[73] S. Petersen, *Ann.* **675**, 101 (1964).

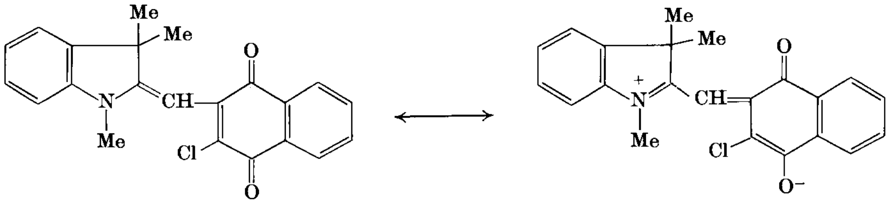


(CXXIII) (CXXIV)

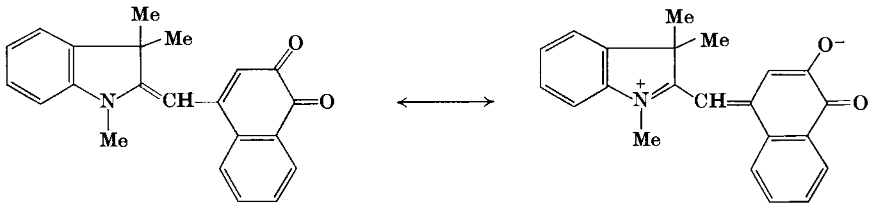




(CXXV)



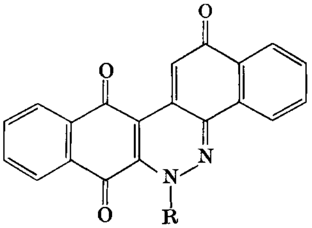
(CXXVI)



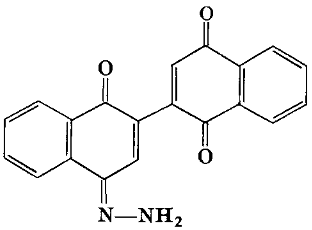
(CXXVII)

yields the dark-colored merocyanine (CXXIV) for a dark blue solution. A yellow product isolated from this reaction was found to be (CXXV). Derivatives of the Fischer base containing substituents such as 5- or 7-Me, Et, OMe, CO_2Me, or Cl also react with 1,4-naphthoquinone to give merocyanines. Whereas the 5-amino derivative of the Fischer base reacts with 1,4-naphthoquinone to yield a merocyanine, the 5-nitro derivative does not. 2,3-Dichloro-1,4-naphthoquinone (I) also reacts with the Fischer base to yield the merocyanine (CXXVI). 1,2-Naphthoquinone-4-sulfonic acid readily loses the sulfonic acid group during its reaction at room temperature with the Fischer base to yield the violetish black merocyanine (CXXVII).

When 1,4-naphthoquinone is treated with hydrazine, a highly insoluble black pentacyclic cinnoline (CXXVIII) is obtained. The structure (CXXIX), suggested previously by Pummerer *et al.*,[74] was discarded on the basis of elemental and spectral analysis, formation of relevant derivatives, and the behavior of the compound on reduction and oxidative degradation.

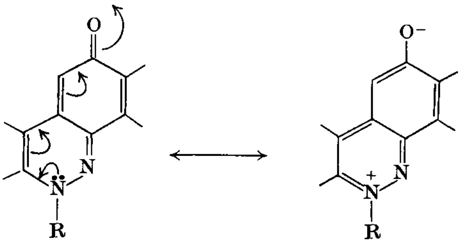


(CXXVIII)
R = H, CH_3



(CXXIX)

(CXXVIII) shows extensive absorption in the visible and UV region of the spectrum. The absorption spectrum may be accounted for on the basis of a merocyanine type of resonance. The compound also exhibits solvatochromism.[75]



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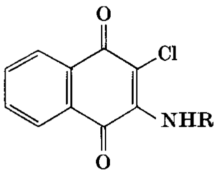
[74] R. Pummerer, A. Pfaff, G. Riegelbauer, and E. Rosenhauer, *Ber. Deut. Chem. Ges.* **72**, 1623 (1939).

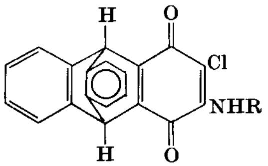
[75] E. S. Hund and T. Cohen, *Tetrahedron* **23**, 2911 (1967).

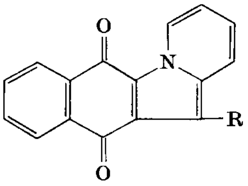
V. Interrelationship between Coplanarity and Substantivity of Naphthoquinonoid Dyes for Cellulosic and Hydrophobic Fibers

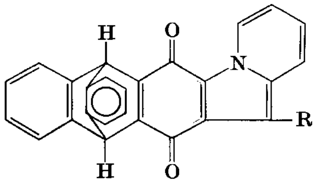
Although the necessity of coplanar configuration of quinonoid dyes in vat dyeing is generally taken for granted, little systematic work has been done to experimentally establish the essentiality or otherwise of coplanarity as a contributory factor regarding substantivity of quinonoid dyes for cellulosic and synthetic fibers.[76]

Tilak, Daruwalla, and Rao [77] have discussed the unsatisfactory character of the evidence cited in the literature regarding these studies. To

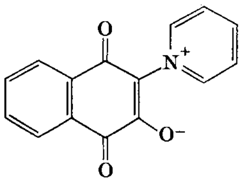


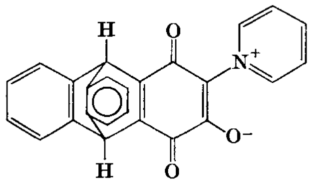


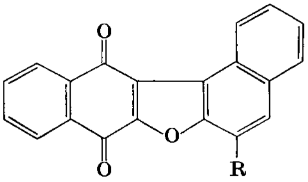


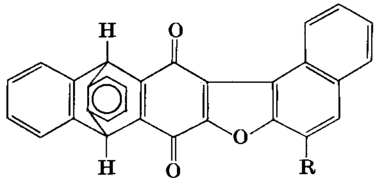


R = CO_2Et, CONHR′, CONHAr









R = H, CO-NHAr

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[76] T. Vickerstaff, "The Physical Chemistry of Dyeing," p. 307. Oliver and Boyd, London (1954).

[77] B. D. Tilak, E. H. Daruwalla, and S. S. Rao, *J. Soc. Dyers Colourists* **76**, 418 (1960).

study the influence of coplanarity in dyeing of cellulosic and hydrophobic fibers by quinonoid dyes (as vat and disperse dyes), two series of dyes were synthesized and quantitative determinations of substantivity and affinity values were made. The first series of dyes comprised a set of coplanar quinonoid dyes derived from (I) and a corresponding noncoplanar analog for each of the coplanar dyes. The noncoplanar dyes were identical with the coplanar dyes as regards the number and location of hydrogen-bonding groups and had nearly the same van der Waals attractive forces.[77, 78] The noncoplanar dyes were synthesized from *endo*-9,10-*o*-phenylene-2,3-dichloro-9,10-dihydro-1,4-anthraquinone.

The results of substantivity studies on this series of dyes made on cellulose,[77] cellulose acetate,[77] and other hydrophobic fibers such as nylon, Terylene, and Orlon[79] showed that whereas the coplanar dyes were highly substantive, the noncoplanar analogs had very little affinity for these fibers. The low substantivitity of these dyes for cellulose acetate and other hydrophobic fibers was not a solubility effect since these dyes had the same (and in some cases more) solubility in amyl acetate as the coplanar analogs.

In the second series of dyes investigated, Tilak and Venkateswaran[6, 60] synthesized dyes of increasing noncoplanarity by positioning substituents in a manner which results in steric crowding, thereby making the molecule noncoplanar to a varying degree, as in Series (A). Noncoplanarity was also brought about by having two heteroatoms in the molecule, as in the case of the *lin*-naphthothiazinequinone Series (B). Removal of either hetero atom results in planar derivatives such as 2,3-benzo-9-thiafluorene-1,4-dione or 2,3-phthaloylindole. The latter is the well-known vat dye Helindone Yellow R. 2,3-Phthaloylpyrrocoline was also studied for its affinity values. The effect of van der Waals forces brought about by extended conjugation to offset the influence of noncoplanarity was studied by the determination of affinity values of dyes of the Series (C), which have an additional benzene ring.

From a determination of affinity and saturation values on cellulose acetate, nylon, and Terylene, it is found that the coplanarity of the molecule influences the affinity and saturation values, the affinity values decreasing progressively with progressive increase in noncoplanarity. Affinity values between different dyes of a series of related chemical constitution vary with the different fiber substances examined. With extended conjugation in the dye molecule, the affinity and saturation values for all fibers increase. This work leads to the conclusion that for

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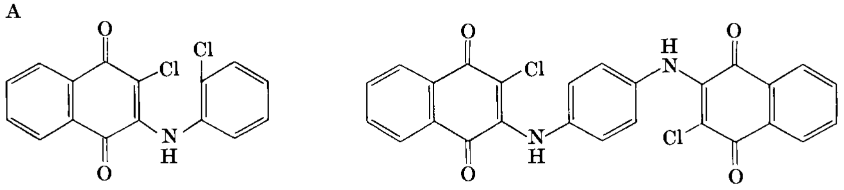
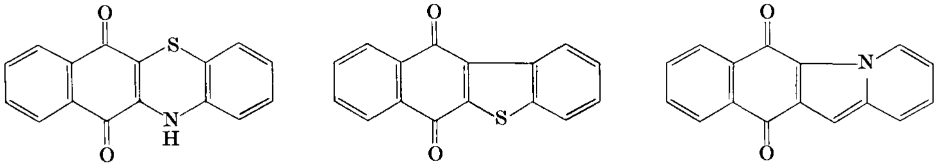
[78] B. D. Tilak and S. S. Rao, *Chem. Ind.* (*London*) 1320 (1957).

[79] E. H. Daruwalla, S. S. Rao, and N. J. Bhatt, *Textil-Rundschau* **20**, 133 (1965).

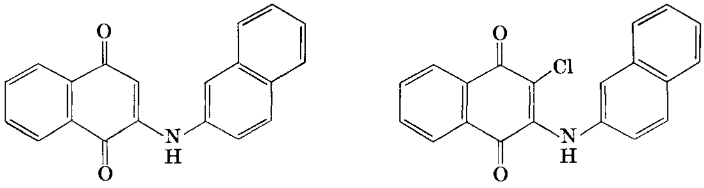
A



B



C



quinonoid dyes of the above type to be substantive to cellulose and hydrophobic fibers, coplanarity appears to be an important structural feature.

VI. Conclusion

The work initiated by the author on exploring the possibility of the use of 2,3-dichloro-1,4-naphthoquinone (I) as a versatile intermediate for the synthesis of a wide variety of new heterocyclic quinonoid chromophoric systems has already led to the establishment of phthaloylpyrrocoline pigments (simultaneously discovered by the author and Pratt *et al.*) which are considered to be fast enough to merit inclusion in a modern commercial range of pigments. These outstandingly fast pigments hold promise. The possibilities of development of naphthoquinone dyes and pigments are still not exhausted, as revealed by the recent synthesis by the author of the highly interesting 3,4-phthaloyl-2-thiaquinolizine chromophoric system, which, like the corresponding phthaloylpyrrocoline chromophoric system, holds promise of commercial exploitation. In any event, for the organic chemist the naphthoquinone dyes and pigments represent a fascinating field of investigation.

CHAPTER II

ACID ANTHRAQUINONE DYES

W. Schoenauer, F. Benguerel, and J. Benz

SANDOZ LTD., SWITZERLAND

The acid anthraquinone dyes are important members of every commercial range of acid dyes, a class which finds its major uses in the dyeing of wool, synthetic polyamides, and silk. Along with the anthraquinone types, the acid ranges consist for the most part of monoazo and disazo dyes. Derivatives of other chromophoric systems such as nitrodiphenylamine, diazine, and triphenylmethane are of minor importance.

The predominant acid anthraquinone dyes are the blues, which range in shade from reddish blue to blue-green. Blue azo dyes are available for the aforenamed fibers, but they do not match anthraquinone blues in brilliance, nor in some cases in lightfastness. The blue 2:1 premetallized dyes also are comparatively dull on these substrates. The green acid anthraquinone dyes are likewise notable for high lightfastness and in part for brilliance, and thus have achieved considerable importance, but they have to compete with combinations of blue and yellow dyes. The volume of production of the very brilliant acid anthraquinone violets varies a great deal with the dictates of fashion. Reds based upon anthraquinone have gained but a modest place compared with the red acid dyes of the azo series. Numerous attempts have been made to build up dyes of other shades based upon the anthraquinone structure, but they have not been successful as acid dyes mainly because of the high cost.

Formerly wool dyeing was the only important area in which acid dyes were used. Silk, the world production of which fluctuated between 59,000 and 34,000 metric tons in the period from 1930 to 1968, has always been of secondary importance. The situation changed with the rapid expansion in the production of synthetic polyamide fibers, which created a second important substrate for acid dyes. Figure 1 shows the relative levels of world consumption of wool and synthetic polyamides[1]:

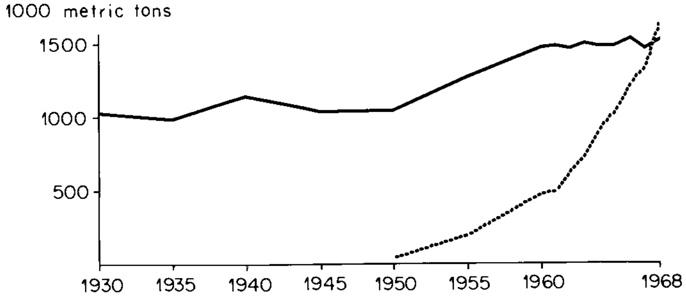


FIG. 1. World consumption of wool and synthetic polyamide fibers. (———), Wool; (------), synthetic polyamide fibers.

The world production of wool has grown slowly in the past 15 years. Although relatively expensive, wool has valuable textile properties, such as soft hand, good perspiration absorption, heat insulation, and a low tendency to build up static electricity. In recent years the industry has attempted to convert the greatest possible proportion of its wool into high-quality goods. This has led to the setting of increasingly stringent requirements for the fastness properties of wool dyes, often accompanied by a demand for high brilliance. Recent developments in the chemistry of acid anthraquinone dyes reflect the attention that has been given to these requirements. In the recent past high-grade milling dyes and

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[1] Textile Organon, June 1958 and July 1967; *Z. ges. Textil.-Ind.* 3/69.

reactive dyes for wool having excellent wet-fastness, even on goods with a shrinkproof finish, have appeared. As a result, many of the older acid dyes of only moderate fastness have become less important for wool. Today acid leveling dyes are used only if difficulties with level dyeing and penetration make them appear favorable alternatives and the modest wet-fastness properties suffice.

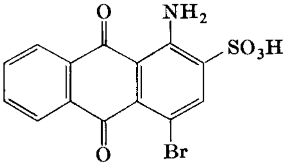
As synthetic polyamide fibers gained in importance, emphasis in the development of the acid class as a whole, and hence the anthraquinone series, shifted more and more to the dyeing of these substrates. The leading synthetic polyamide fibers are those obtained from polymerization of ϵ-caprolactam (perlon, nylon 6) and the polycondensation of hexamethylenediamine with adipic acid (nylon 6.6).

As wool and synthetic polyamides are structurally related, virtually all acid dyes are capable of dyeing both types of fiber. But because of the differences between the synthetic and the natural polyamides, each shows a specific dyeing behavior. Dyes also vary in their fastness properties, being generally more wet-fast on synthetic polyamides than on wool. In contrast to wool, synthetic polyamide fibers may be dyed with simple leveling dyes containing only one sulfo group, resulting in satisfactory wet-fastness. Moreover these properties can be considerably improved by aftertreatment, most markedly with heavy dyeings. There is no comparable method of improving the wet-fastness of wool dyeings. Acid dyes are as a rule also faster to light on synthetic polyamides than on wool. A considerable number of the simpler leveling types which were in use for many years lost some of their importance for wool, but have more than recovered their position by their widespread acceptance for synthetic polyamide fibers.

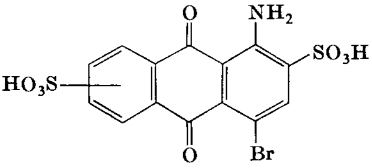
When the first synthetic polyamide fibers were marketed, suitable acid dyes were selected to form commercial ranges. This was followed by the development of specific dyes, with emphasis on brilliance, compatibility with existing dyes for combination dyeing, and coverage of barriness, in addition to the usual requirements. As part of this trend, together with the development of new wool dyes of very high fastness, the chemistry of anthraquinone intermediates was reexplored in order to improve and refine the existing production methods. Also, in the synthesis of new condensation intermediates, numerous advances have been achieved in recent years.

I. Dyes Derived from 1-Aminoanthraquinone-2-sulfonic Acid

The commercial dyes of this series are formed by the condensation of 1-amino-4-bromoanthraquinone-2-sulfonic acid (bromaminic acid) (I), or the analogous disulfonic acids of type (II) with amines. Most of the amines used are derivatives of aniline. The *o,o'*-disubstituted aniline derivatives are especially noteworthy. They form condensation products with bromaminic acid in which coplanarity between the anthraquinone structure and the substituted benzene ring is hindered. Cyclohexylamine and its derivatives are also important. Depending on the structure of the amine, the shade of these dyes ranges from reddish blue to blue-green.



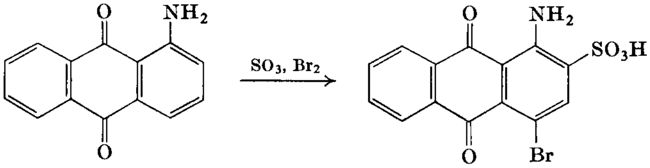
(I)



(II)

The color sensation of a dye is given by the shape of the spectral absorption curve in the visible region. Generally it can be estimated quite well from the positions of the maxima. The spectral properties of the anthraquinone derivatives will be discussed later using the partial chromophore method devised by Morton[2] and by Scott[3] for quinone derivatives. By this method the visible spectrum (electron-transfer bands) of any given anthraquinone derivative can be interpreted as a cross-conjugated benzophenone–quinone system.

Bromaminic acid, a very important precursor, is synthesized by sulfonation with oleum and bromination of 1-aminoanthraquinone[4]:



After isolation, dissolving, and precipitation, the bromaminic acid is obtained in good yield and in high purity.

The routes leading to 1-amino-4-bromoanthraquinone-2,6-disulfonic

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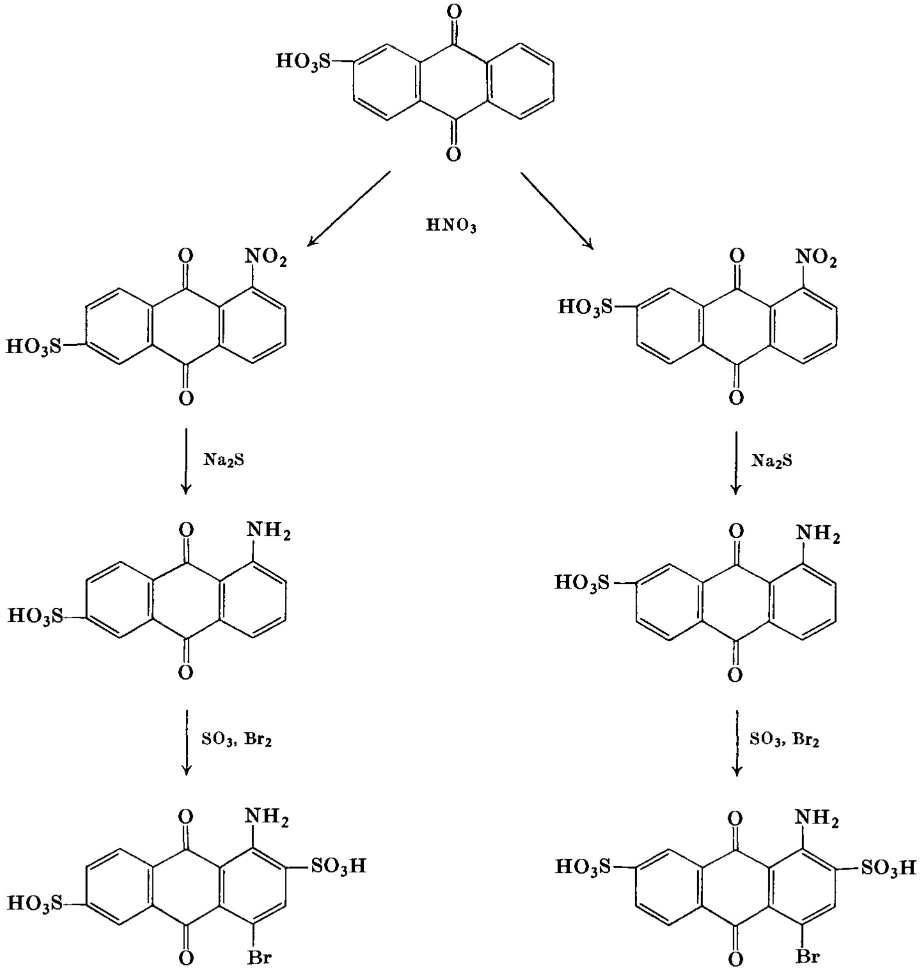
[2] R. A. Morton and W. T. Earlam, *J. Chem. Soc.* p. 159 (1941).

[3] A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products." Pergamon Press, Oxford, 1964.

[4] FIAT, *1313* II 214.

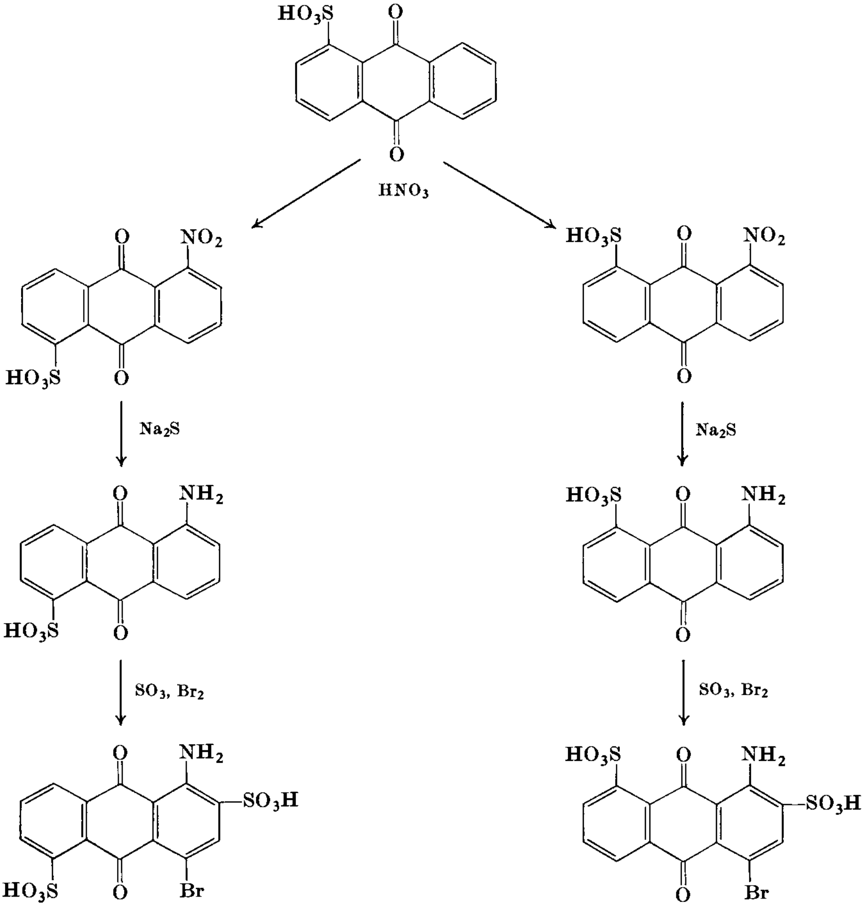
acid and 1-amino-4-bromoanthraquinone-2,7-disulfonic acid from anthraquinone-2-sulfonic acid are shown below.



Separation of the mixture of 1-nitroanthraquinone-6-sulfonic acid and 1-nitroanthraquinone-7-sulfonic acid obtained on nitration is achieved by taking advantage of the different solubilities of their potassium salts. The nitro compounds are then reduced with sodium sulfide in aqueous solution. Sulfonation and bromination of the isomeric 1-aminoanthraquinone-6- and -7-sulfonic acids can again be carried out in a single operation.

The 1-aminoanthraquinone-2,6- and -2,7-disulfonic acids formed as intermediates may also be prepared by first reacting 1-nitroanthraquinone-6- or -7-sulfonic acid with aqueous sodium sulfide to give 1-amino-2-mercaptoanthraquinone-6- or -7-sulfonic acid, and then converting the mercapto group to a sulfonic acid group with an oxidizing agent such as sodium hypochlorite.[5] The route is based on an old method by which 1-aminoanthraquinone-2-sulfonic acid is prepared from 1-aminoanthraquinone via 1-amino-2-mercaptoanthraquinone.[6]

In an analogous manner 1-amino-4-bromoanthraquinone-2,5-disulfonic acid and 1-amino-4-bromoanthraquinone-2,8-disulfonic acid are formed. Often the mixture of isomers produced by nitration of anthraquinone-1-sulfonic acid is not separated into the two components but reacted further to the final dyes.



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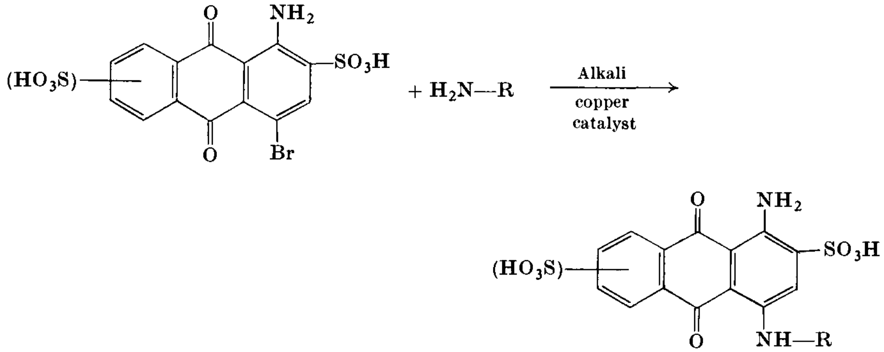
[5] FBy, *DBP* 1,226,598.

[6] Chem. Fabrik Griesheim-Elektron, *DRP* 290,084.

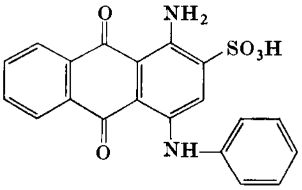
As a rule the condensation of bromaminic acid or the corresponding disulfonic acids with an amine is carried out in aqueous solution.[7]



An alcohol–water mixture is often used as a solvent for amines which are only sparingly water-soluble. The hydrogen bromide liberated during the condensation reaction must be neutralized with alkali, to adjust the reaction solution to a pH value 0.5 to 1 units above the pH of the aqueous solution of the amine. If aromatic amines are used, addition of sodium hydrogen carbonate or sodium carbonate is adequate. With aliphatic amines a stronger alkali such as sodium hydroxide is necessary. Further, a catalyst is required, e.g., metallic copper powder or a copper compound such as copper(II) sulfate, copper(I) or (II) oxide, copper(I) acetate or copper(I) chloride. Condensation normally takes place between 40° and 100°. Milder conditions produce smaller amounts of by-products such as the violet 1-amino-4-hydroxyanthraquinone-2-sulfonic acid due to hydrolysis and the orange 1-aminoanthraquinone-2-sulfonic acid arising from cleavage of bromine.

A. Coplanar Condensation Products of Bromaminic Acid with Aromatic Amines

The oldest dye of this series and the classical example is *Acilan Direct Blue A* (CI Acid Blue 25)[8]:



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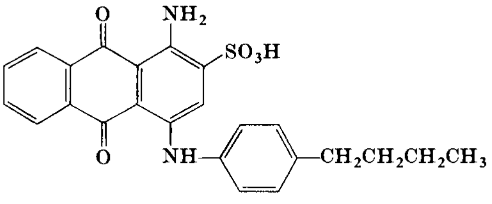
[7] AGFA, *DRP* 280,646; 288,665.

[8] BIOS, *1484*, 41.

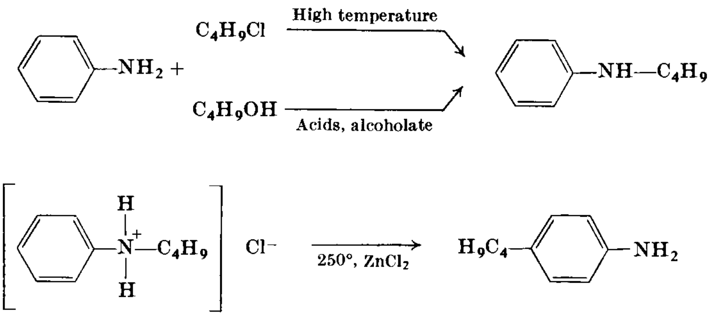
This economical dye builds up on wool and nylon from a neutral medium to give dyeings of moderate wet-fastness. Heavy dyeings on nylon require aftertreatment with tannin/tartar emetic or with a fixing agent, such as Nylofixan P, if good wet-fastness is a prime consideration.[9]

Synthetic agents of the Nylofixan P type are high molecular weight condensation products of formaldehyde, aromatic sulfonic acids, and dihydroxydiphenyl sulfones. The interaction mechanism has not yet been fully elucidated. It is generally assumed that these agents are attached to the molecular fiber chains due to their high phenolic hydroxyl content, which enables them to form hydrogen bonds, and through van der Waals forces. The diffusion of the dye, fixed to the fiber by saltlike bonding, is thereby strongly inhibited. With the tannin aftertreatment the fixation is improved due to the insoluble tannate formed by the tartar emetic addition. The disadvantage of this method compared with the use of synthetic agents is that it has to be carried out in two stages.

Nylosan Blue N-GL (CI Acid Blue 251) is somewhat greener than Acilan Direct Blue A.[10]



The *p*-butylaniline used for its synthesis is obtained by the following route[11]:



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[9] C. Călin, *Textil-Praxis* **20**, 835 (1965).

[10] ICI, *BP* 446,819.

[11] W. J. Hickinbottom and A. C. Waine, *J. Chem. Soc.* p. 1565 (1930).

In the first step aniline is condensed to *N*-butylaniline with butyl chloride at high temperature, or with butyl alcohol in the presence of acids or alcoholates. In the second step the Hofmann-Martius rearrangement to the *C*-alkylated amine is accomplished by heating the corresponding hydrochloride, either at 250–300° under pressure or at 200–250° in the presence of metal chlorides such as $CoCl_2$, $CdCl_2$, or $ZnCl_2$. The alkyl group migrates preferentially to the para position.

Due to the presence of the hydrophobic carbon chain in the aromatic amine, Nylosan Blue N-GL has improved neutral and wet-fastness properties. For satisfactory coverage of barry nylon a leveling agent must be added to the dyebath.[12]

In general, low affinity for the substrate and slow dyeing rates result in optimal levelness; affinity and levelness thus work in opposition. The reason for this lies in the more or less pronounced stability of the fiber–dye bond. Normally, strong attraction results in good wet-fastness but poor level dyeing. The dye, once adsorbed on the surface of the fiber, cannot migrate to other free amino groups unless the dye–fiber bond is easily broken. Highly substantive dyes are likely to remain at their initial sites.

Many acid dyes tend to accentuate the chemical and physical irregularities originating during fiber manufacture, e.g., variations in the amino group content and differences in cold drawing. Synthetic polyamides contain only amino end groups and provide no more than one such group per polyamide chain for salt formation with a sulfonic acid group of the dye, whereas wool has terminal amino groups plus side chains bearing other types of amino groups, belonging, e.g., to arginine and lysine residues. If the amino end groups are unevenly distributed, due, for example, to differences in chain length, varying amounts of dye will be adsorbed, resulting in unlevel dyeings.

The levelness of a dyeing can be influenced to some extent by the choice of dyeing conditions (pH, salt concentration, temperature, and time). A decided improvement can be realized with leveling agents, which may be divided into three groups based upon their chemical structure:

(1) anion-active (with affinity for the fiber)
(2) cation-active (with affinity for the dye)
(3) nonionic (with low affinity for both)

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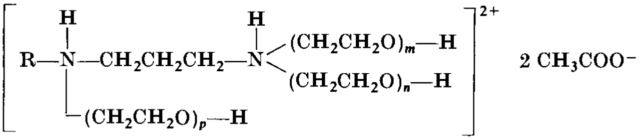
[12] A. Chwala, "Textilhilfsmittel," p. 343. Springer, Vienna, 1939; H. Rath, "Lehrbuch der Textilchemie," 2nd ed., p. 678. Springer, Berlin, 1963; K. Lindner, "Tenside-Textilhilfsmittel-Waschrohstoffe," 2nd ed., Vol. I, p. 561. Wiss. Verlagsges., Stuttgart, 1964; E. P. Frieser, *SVF* (Schweiz. *Ver. Faerbereifachleuten*) *Fachorgan Textilveredlung*, **18**, No. 2, 104 (1963) and *Chemiefasern* **12**, 636 (1962); G. Weckler and N. Kollodzeiski, *ibid.* **6**, 445; **7**, 523; **8**, 590 (1965); S, *USP* 2,967,755.

The anion-active agents include ricinoleic sulfonates, aralkyl sulfonates, and the condensation products of higher fatty acids with aminoalkylsulfonic acids, such as

$$C_{17}H_{33}\text{-}CO\text{-}N(CH_3)\text{-}CH_2CH_2SO_3Na$$

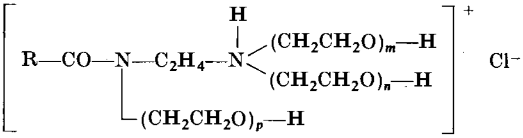
They are adsorbed on the fiber as "colorless dyes" more rapidly than the less mobile dye anions. A fraction of the amino groups are thereby occupied, so that dye anions must penetrate deeper into the fiber, and the leveling agent anions are gradually displaced. Thus the rate of dyeing is retarded, and leveling is improved.

Cation-active leveling agents are obtained by condensation of higher alkylamines or fatty acid amides with ethylene oxide; two examples are



$$\left[R-\underset{\lfloor (CH_2CH_2O)_p-H}{\overset{H}{\overset{|}{N}}}-CH_2CH_2CH_2-\overset{H}{\overset{|}{N}}\!<\!\begin{array}{l}(CH_2CH_2O)_m-H\\(CH_2CH_2O)_n-H\end{array}\right]^{2+}\quad 2\,CH_3COO^-$$

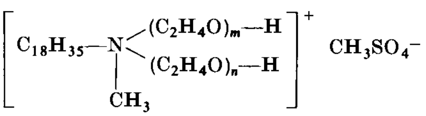
and



$$\left[R-CO-\underset{\lfloor (CH_2CH_2O)_p-H}{N}-C_2H_4-\overset{H}{\overset{|}{N}}\!<\!\begin{array}{l}(CH_2CH_2O)_m-H\\(CH_2CH_2O)_n-H\end{array}\right]^{+}\quad Cl^-$$

Because of their cationic character and the ability of the polyglycol groups to form hydrogen bonds, they form addition complexes with the dye molecules which initially prevent adsorption of the dye. As the temperature of the dyebath is increased, these agglomerates break down and allow the dye to penetrate the fiber. The choice of cation-active leveling agents is limited because those with pronounced cationic activity tend to precipitate the dyes.

Peregal OK is an example of a leveling agent which has both cationic and weakly anionic character. It is a mixture consisting of



$$\left[C_{18}H_{35}-\underset{CH_3}{\underset{|}{N}}\!<\!\begin{array}{l}(C_2H_4O)_m-H\\(C_2H_4O)_n-H\end{array}\right]^{+}\quad CH_3SO_4^-$$

and oleyl sarcosine

$$C_{17}H_{33}CO-N(CH_3)CH_2COONa$$

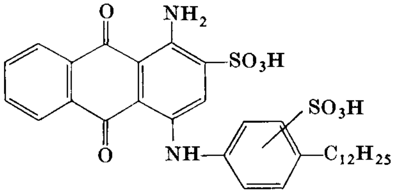
The cationic character allows complex formation with the dye, while its anionic component inhibits precipitation until adsorption of the dye has occurred.

The main representatives of the nonionic leveling agents are higher fatty alcohols and polyethoxylated fatty alcohols, e.g.,

$$C_{18}H_{35}\text{—}(OCH_2CH_2)_n\text{—}OH$$

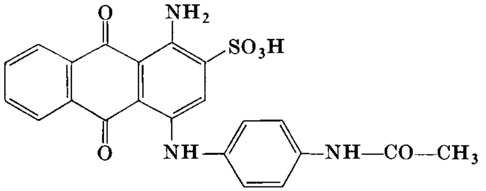
Because of their dipole character, they are capable of attracting water molecules. Accordingly they have a slight degree of affinity for dyes, while at the same time they promote wetting of the fiber.

Carbolan Blue B (CI Acid Blue 138),[13] for which *p*-dodecylaniline is used as a long-chain amine, is of similar shade to Nylosan Blue N-GL.



A second sulfonic acid substituent has to be introduced into the molecule for sufficient solubility of the dye. Because of its relatively high molecular weight and increased hydrophobic character this dye shows good affinity for the fiber and the dyeings have very good wet-fastness properties. However, its leveling qualities are only moderate even in the presence of a leveling agent, and the dye is not able to cover barry nylon satisfactorily. The *p*-dodecylaniline is prepared similarly to *p*-butylaniline.[11]

Anthralan Blue G (CI Acid Blue 40)[14] is distinctly more greenish than the dyes so far named. It is formed by condensing bromaminic acid with *p*-aminoacetanilide. The hydrophilic CH_3CONH group gives the dye good leveling properties but only moderate wet-fastness.



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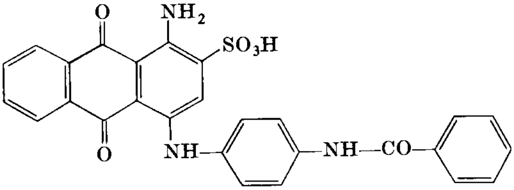
[13] ICI, *BP* 443,776.

[14] BIOS, *987*, 133, 135.

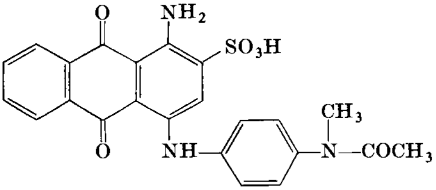
The dye obtained by condensation of bromaminic acid with *p*-aminobenzanilide also has a greenish blue shade[15]:



It builds up better from a neutral bath than Anthralan Blue G and also has better wet-fastness. Moreover, like Acilan Direct Blue A and Nylosan Blue N-GL, it is suitable for the Nylosol dyeing process.

In the Nylosol process nylon chips are exhaust-dyed from a concentrated aqueous solution. After drying, the chips are melt-spun at 275–290°. However, many acid dyes and especially unmetallized azo dyes undergo partial reductive decomposition in the nylon melt. Certain 2:1 premetallized and some acid anthraquinone dyes are the most suitable types for the Nylosol process.

A hypsochromic shift of the absorption maxima relative to those of Anthralan Blue G is observed when the acetylamino group is replaced by an acetyl-*N*-methylamino group, as in *Anthralan Blue B* (Acid Blue 41)[16]:



As previously stated, the visible spectra of anthraquinone compounds can be treated in a first approximation as overlapping electron-transfer bands of substituted benzophenone and quinone derivatives.[1,2]

In the bromaminic acid dyes the bands responsible for the color are located at approximately 600 and 400 mμ. The usually poorly resolved bands of longer wavelength are mostly of quinoid origin (electron-transfer bands overlapping with the n–π^* carbonyl absorption). The

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[15] S, *USP* 2,541,623.

[16] IG, *DRP* 469,565; G, *USP* 1,750,228.

weaker bands at 400 mμ are attributed primarily to the second electron-transfer band of the substituted benzophenone chromophores, frequently superimposed by the n–π^* carbonyl and benzenoid bands of other substituents.

The visible absorption spectra of two bromaminic acid dyes such as examples I and II, together with those of selected members of the dye classes discussed later, are shown in Fig. 2.

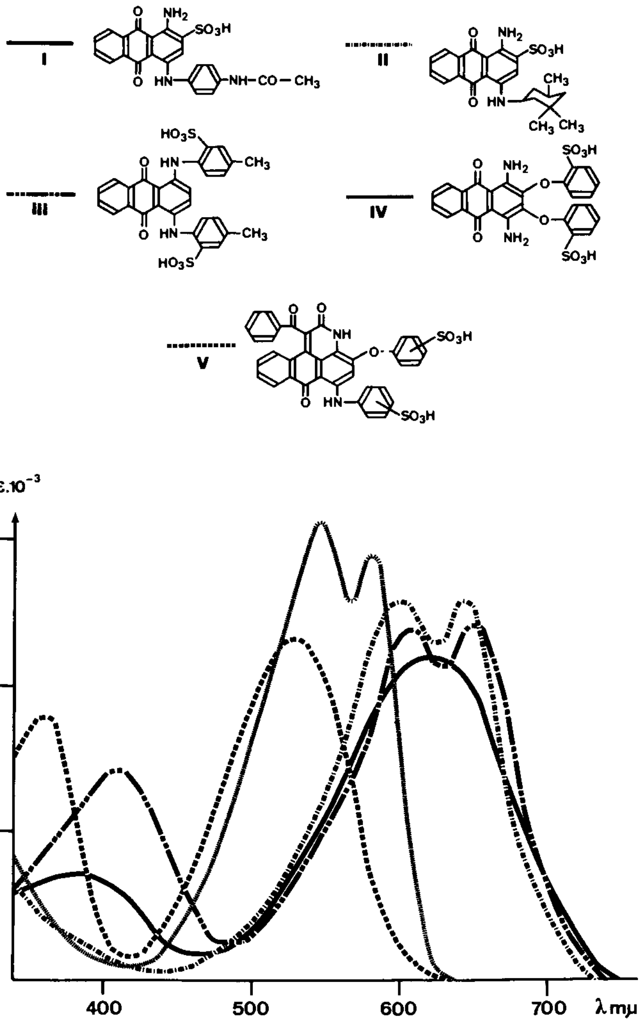
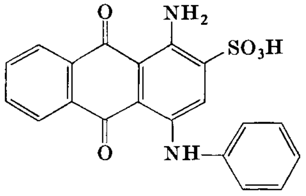
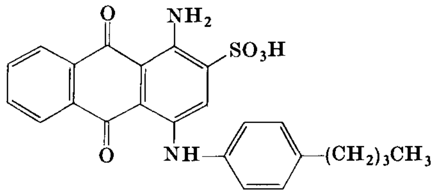


FIG. 2. Visible absorption spectra of selected anthraquinone derivatives (H_2O, 25°).

In the qualitative interpretation of the spectra of



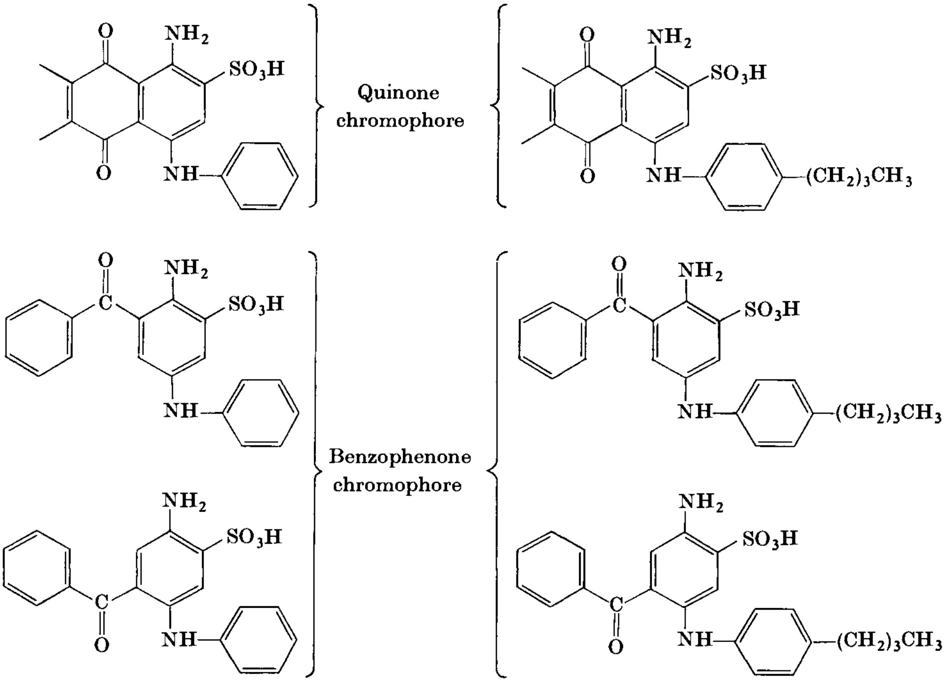
and



Acilan Direct Blue A

Nylosan Blue N-GL

the partial chromophores are defined as



If it is true that for most molecules the electron distribution in the excited state cannot be described in a simple manner, the excitation of nonbonding electrons in ketones, quinones, azo, and nitro compounds is fairly well understood and can be rationalized in terms of simple resonance structures.[17] Showing only one valence structure, one of the

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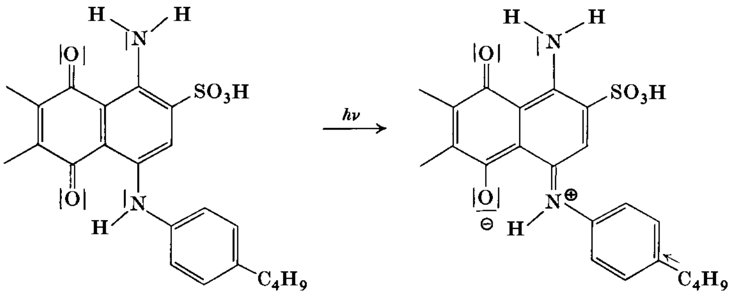
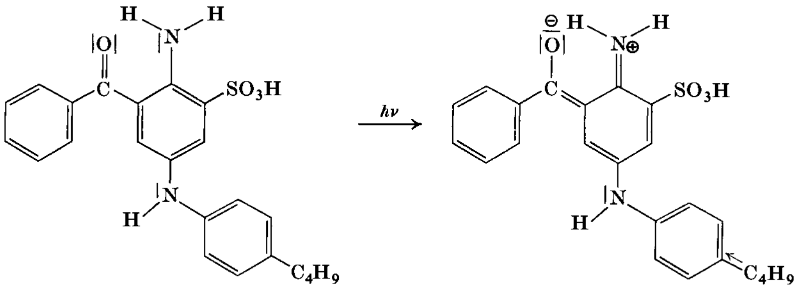
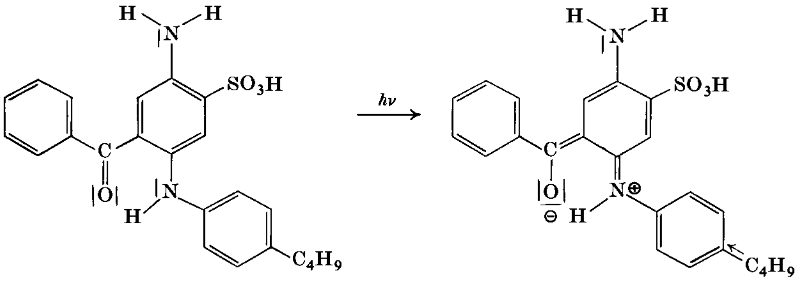
[17] N. J. Turro, "Molecular Photochemistry." Chapters 2 and 7. Benjamin, New York, 1965; F. Dörr, *Z. Elektrochem.* **64**, 581 (1960); H. E. Zimmermann *et al.*, *J. Am. Chem. Soc.* **83**, 4486 (1961).

possible excitation mechanisms for each chromophore is illustrated. The multiplicity of the excited species, formulated here in the classical way, is not specified, despite the fact that available photochemical data[18] indicate that intersystem crossing to the triplet occurs with high efficiency for most anthraquinone derivatives. The weak electron-donating effect of the butyl group increases polarizability and thus causes a minor bathochromic shift of the quinone and benzophenone bands. As a result Nylosan Blue N-GL is more greenish than Acilan Direct Blue A.







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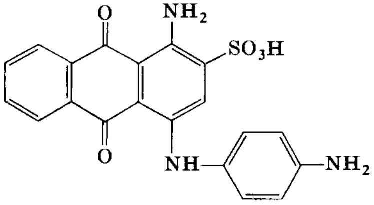
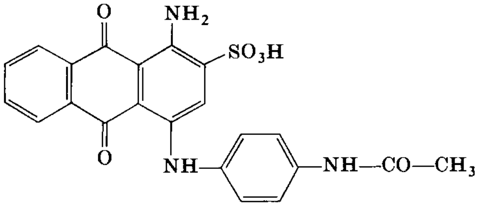
[18] F. Wilkinson, *J. Chem. Phys.* **66**, 2569 (1962); N. K. Bridge, *J. Soc. Dyers Colourists* **76**, 484 (1960); H. C. A. van Beek *et al.*, *J. Soc. Dyers Colourists* **81**, 400 (1965).

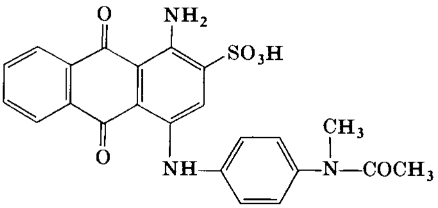
Since an amino group has a stronger electron-donating effect than the butyl group, the compound



is greener than Acilan Direct Blue A. On the other hand, acetylation of this amino group diminishes polarizability. The shade of Anthralan Blue G is slightly redder (hypsochromic shift) than the nonacetylated compound, but still greener than Acilan Direct Blue A. In Anthralan Blue B the electron-acceptor character of the carbonyl function is weakened by the methyl group. Because of the compensating electron-withdrawing and -donating effects, the shade of Anthralan Blue B is comparable to that of Acilan Direct Blue A.



Anthralan Blue G



Anthralan Blue B

Similar observations are made with the following dye, which is obtained by condensation of bromaminic acid with *p*-aminophenol, followed by esterification of the hydroxyl group using *p*-toluenesulfonyl chloride.[19]

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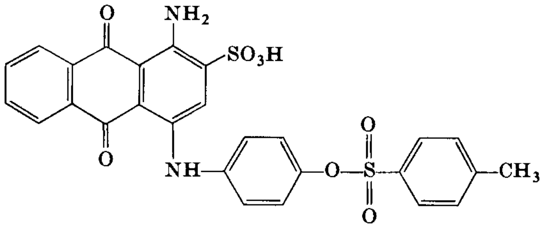
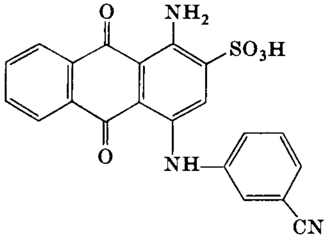
[19] IG, *DRP* 748,554.

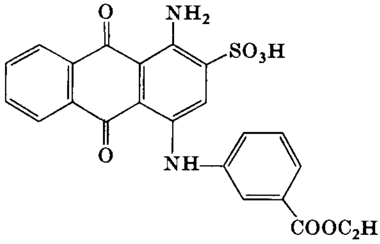


Here again the electron-donating effect of the oxygen in the para position is largely compensated by the sulfone group, and the resulting shade is very similar to that of Acilan Direct Blue A.

This economical neutral blue shows good affinity and levelness when used under neutral dyeing conditions, but its light- and wet-fastness properties are only moderate. It is suitable for combination dyeings together with selected azo yellows and reds. For the dyes obtained by condensation of bromaminic acid with *m*-aminobenzonitrile or ethyl *m*-aminobenzoate, a minor hypsochromic shift of the benzophenone and quinone bands relative to Acilan Direct Blue A is expected due to the nitrile and carboxylate groups acting as electron acceptors. Thus *Supracen Blue R* (CI Acid Blue 53)[20] and *Alizarine Sky Blue FFB* (CI Acid Blue 51)[21] are both more reddish than Acilan Direct Blue A. This effect is pronounced with electron-withdrawing substituents in the para position.

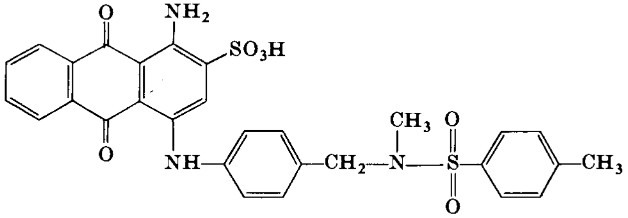


Supracen Blue R



Alizarine Sky Blue FFB

A hypsochromic shift is also observed with the following blue.[22]



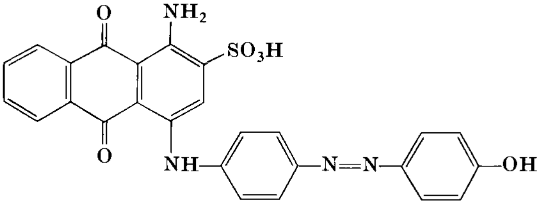
[20] IG, *DRP* 511,043.

[21] BIOS, *987*, 139; G, *USP* 1,902,084.

[22] FBy, *BP* 1,099,756.

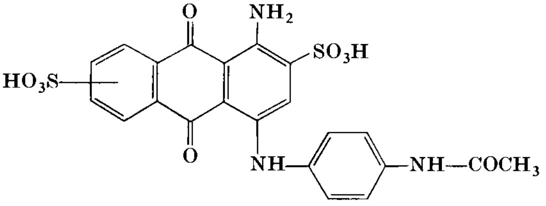
The sulfone group completely inhibits the electron-releasing effect of the *N*-methyl substituent, and the dye is a reddish blue in comparison with Acilan Direct Blue A. It has good lightfastness and good wet-fastness properties, as well as high solubility.

On the other hand, the shade of the following dye[23] is a bluish green.



The blue-shifted quinone and benzophenone bands are superimposed in the yellow region by the benzenoid bands of the azo grouping and are thus similar in intensity to the long-wavelength (blue) absorption bands. The dye exhausts well from a neutral dyebath and has good wet-fastness properties on nylon. It covers barry nylon well, but has only moderate lightfastness.

Condensation of 1-amino-4-bromoanthraquinone-2,5(8)-disulfonic acid or 1-amino-4-bromoanthraquinone-2,6(7)-disulfonic acid with *p*-aminoacetanilide yields *Alizarine Light Blue 4GL* (CI Acid Blue 23)[24] or *Alizarine Light Blue 5GL* (CI Acid Blue 52), respectively.[25] They are



slightly greener than Anthralan Blue G, which has only one sulfonic acid group. The second sulfonic acid group in the anthraquinone nucleus causes a bathochromic shift of the quinone bands. Since polarizability is diminished, a marked weakening of the benzophenone bands can be expected. Not surprisingly, this effect is greatest with a sulfonic acid group in the para position of the benzophenone structure (Alizarine Light Blue 5GL).

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[23] ICI, *BP* 478,665.

[24] S, *USP* 1,885,065.

[25] S, *BP* 580,351.

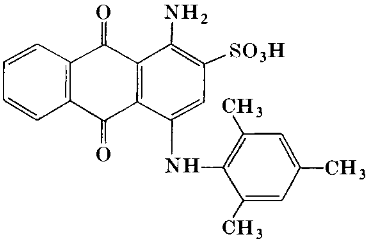
These two dyes exhaust more slowly than the corresponding monosulfonic acids. On wool they are somewhat more wet-fast than those dyes with only one sulfonic acid group.

Special care is needed for combination dyeing of disulfonated and monosulfonated types, especially in heavy shades, since blocking effects are not uncommon. For dyes of similar structure and molecular weight, polysulfonated types normally are inferior in buildup to monosulfonated dyes, as disulfonic acids require a lower pH for dyeing than monosulfonic acids. The limited number of reactive sites in the polyamide fiber is then occupied preferentially by the monosulfonated dye, and consequently exhaustion of the polysulfonated type is largely obstructed, or even blocked.[26]

B. CONDENSATION PRODUCTS OF BROMAMINIC ACID WITH *o,o'*-DISUBSTITUTED ANILINE DERIVATIVES

The condensation of bromaminic acid with *o,o'*-disubstituted aromatic amines leads to brilliant reddish blue dyes. Because of the *o,o'*-disubstitution, coplanarity between the anilino group and the anthraquinone nucleus is hindered and as a result full resonance is restricted. The shortening of the benzophenone and quinone chromophoric systems is responsible for the reddish blue shade of these dyes.

The first dye of this nature to be marketed was *Brilliant Alizarine Sky Blue BS* (CI Acid Blue 129),[27] which is synthesized by condensation of bromaminic acid with mesidine. It has remained an important dye, having good lightfastness on wool and nylon. For good wet-fastness on polyamide fibers an aftertreatment is necessary. It covers barry nylon well. Mesidine used for its synthesis is prepared by condensing a mixture of *m*-xylidine hydrochloride and *m*-xylidine with methyl alcohol under pressure at 270°. Fractional distillation is used to separate



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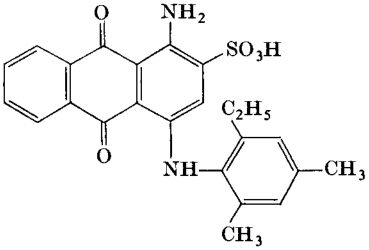
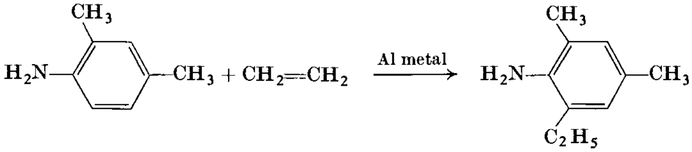
[26] H. Rath, "Lehrbuch der Textilchemie," 2nd ed., p. 563. Springer, Berlin, 1963; E. Frieser, *Textil-Rundschau* **17**, 8 (1962).

[27] S, *USP* 2,121,928.

the mesidine from by-products, which consist mainly of homologs of mesidine and secondary amines. In an alternative route mesitylene is nitrated and subsequently reduced.[28]

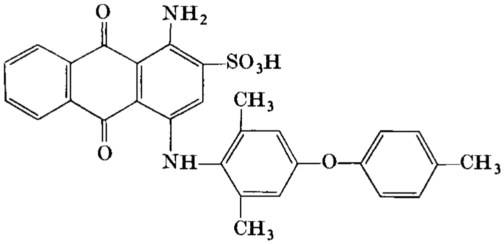
The following blue dye obtained from bromaminic acid and 2,4-dimethyl-6-ethyl-aniline[27] is closely related to Brilliant Alizarine Sky Blue BS. The amine is obtained in good yield by condensation of *m*-xylidine with ethylene.[29]





A very similar dye, noted for its good solubility, is obtained by condensation of bromaminic acid with 1-amino-2-methyl-4,6-diethylbenzene.[30] The amine used is prepared from 1-methyl-3,5-diethylbenzene via nitration, which is not an entirely homogenous reaction, and subsequent reduction.

The following dye, which likewise gives reddish blue dyeings, is formed by condensation of bromaminic acid with a two-ring derivative of *m*-xylidine.[31]



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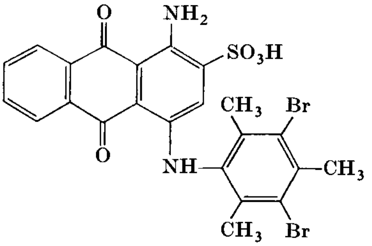
[28] E. Nölting and S. Forel, *Chem. Ber.* **15**, 1012 (1882); *Org. Syn.* Coll. Vol. II, 449 (1955); R. Fittig and J. Störer, *Ann. Chem.* **147**, 3 (1887).

[29] R. Strok, J. Ebersberger, H. Haberland, and W. Hahn, *Angew. Chem.* **69**, 126 (1957).

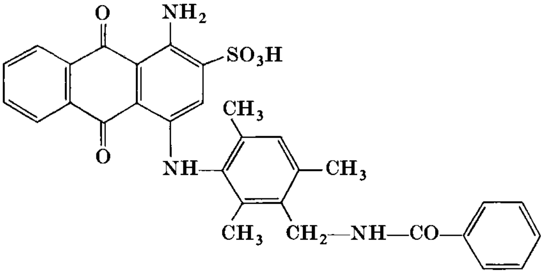
[30] S, *FP* 1,509,724.

[31] Gy, *FP* 1,197,064.

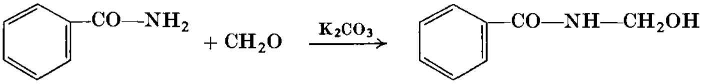
A still redder dye than the preceding two results from bromination of Brilliant Alizarine Sky Blue BS.[32] The steric effect of the methyl groups is increased by the electronic effects of the two bromine atoms. This dye has milling character and accordingly good wet-fastness.



The dye obtained by condensation of 1-amino-4-mesidinoanthraquinone-2-sulfonic acid (Brilliant Alizarine Sky Blue BS) with *N*-hydroxymethylbenzamide in sulfuric acid[33] is similar in shade to the



parent dye. The hydrophilic $-CH_2-NH-CO-$ grouping imparts good solubility and the dye retains good fastness properties. The methylolamide intermediate is obtained, according to Einhorn,[34] from benzamide by condensation with aqueous formaldehyde in the presence of catalytic amounts of potassium carbonate.



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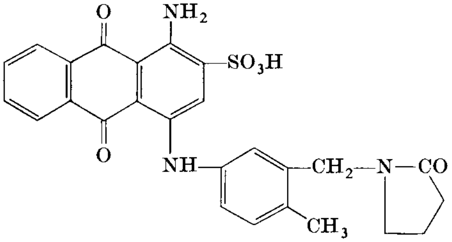
[32] S, *USP* 2,427,527.

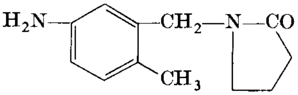
[33] Gy, *BP* 945,806.

[34] A. Einhorn, E. Bischkopff, and B. Szelinski, *Ann. Chem.* **343**, 223 (1905); A. Einhorn, *DRP* 156,398; 157,355; 158,088.

The following dye, which likewise contains an amide group bound to an aryl ring via a methylene bridge, is prepared by another method.[35]



For this synthesis, the amine shown below is first prepared using the

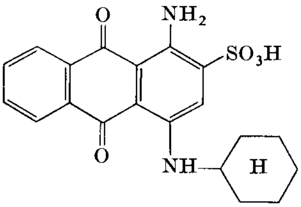


Einhorn method by condensation of 4-nitrotoluene with paraformaldehyde and 2-pyrrolidone in concentrated sulfuric acid and subsequent reduction of the nitro group.[36] Finally, the amine is condensed with bromaminic acid.

C. Condensation Products of Bromaminic Acid with Aliphatic Amines

The dyes of this group are more brilliant than the corresponding condensation products with aromatic amines. As in the case of dyes with *o,o′*-disubstituted aromatic amines, the resonance system is shorter than with Acilan Direct Blue A and consequently the dyes are reddish blues. It is notable that the long-wavelength quinone band, as in the *o,o′*-disubstituted aniline derivatives, is split (see Fig. 2, example II). Because of the interrupted conjugation, the benzophenone bands appear as very weak shoulders.

The oldest dye of this type is *Alizarine Brilliant Sky Blue R* (CI Acid Blue 62),[37] which is formed by condensation of bromaminic acid with



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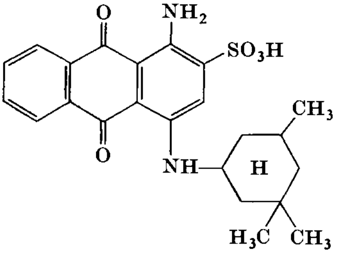
[35] G, *USP* 2,615,021.

[36] *Org. Reactions* **14**, Chapter 2, 125 (1965).

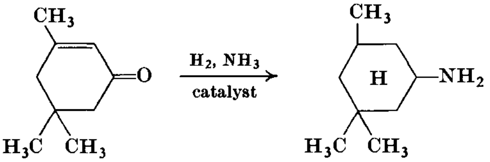
[37] BIOS, *1484*, 30; IG, *BP* 276,408; *DRP* 485,521.

cyclohexylamine. It has excellent leveling properties but is only moderately wet-fast.

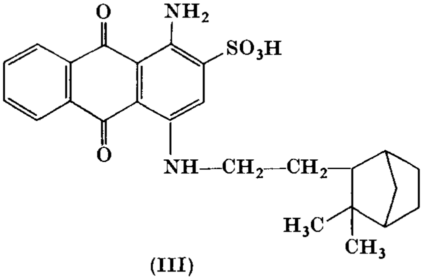
The blue of the following structure[38] has a similar shade. The dye is



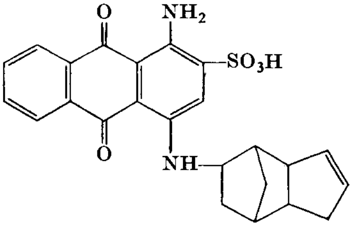
obtained by condensation of bromaminic acid with 3,3,5-trimethylcyclohexylamine. It exhausts better from a neutral medium than Alizarine Brilliant Sky Blue R and is more wet-fast. The amine is prepared by reductive amination of isophorone.[39]



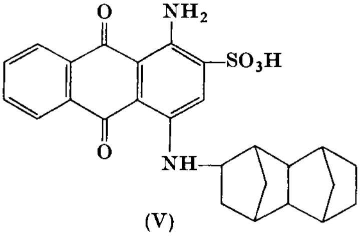
The following dyes possess similar structures.



(III)



(IV)



(V)

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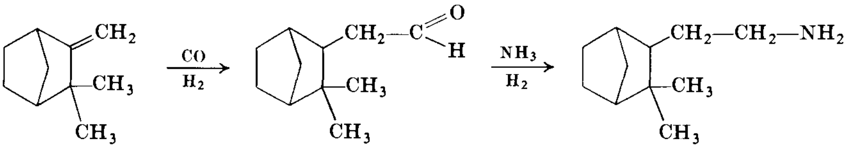
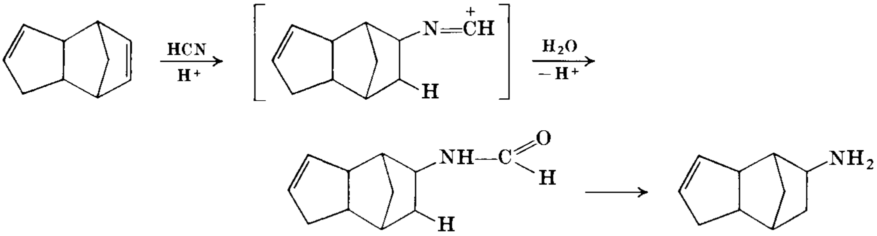
[38] S *BeP* 731,013.

[39] P. Mastagli, M. Métayer, and A. Bricard, *Bull. Soc. Chim. France* [5] **17**, 1046 (1950); M. Métayer, P. Mastagli, and H. Larramona, *ibid.* p. 1053; D. G. Norton, V. E. Haury, F. C. Davis, L. J. Mitchell, and S. A. Ballard, *J. Org. Chem.* **19**, 1055 (1954).

The amine required for dye (III)[40] is prepared from camphene. This is converted to isocamphanaldehyde with carbon monoxide and hydrogen under pressure in the presence of cobalt. Isocamphanylmethylamine is then obtained by reductive amination.[41]



The amine employed in the preparation of dye (IV)[42] for condensation with bromaminic acid is formed by means of the Ritter reaction from dicyclopentadiene.[43]



Starting material for the amine used for dye (V)[44] is cyclopentadiene, which is condensed with ethylene to give octahydrodimethanonaphthalene. This is converted with nitrosyl chloride to the nitrosochloro compound, which is reduced to decahydrodimethanonaphthylamine through the opening of the N=N double bond and splitting off of the chlorine atoms.[45]

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[40] BASF, *DBP* 1,117,244.

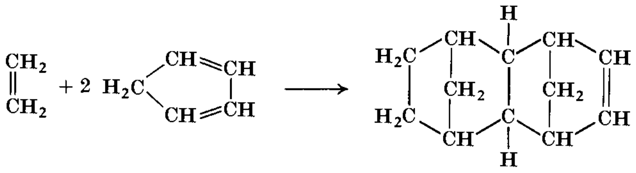
[41] Houben-Weyl, Methoden der org. Chemie, 4. Auflage, Bd. VII/1, 55 (1954).

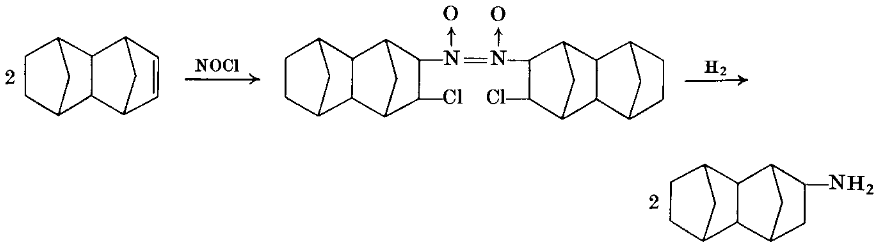
[42] BASF, *DBP* 1,272,476; BASF, *SP* 467,834.

[43] Houben-Weyl, Methoden der org. Chemie, 4. Auflage, Bd. XI/1, 994 (1957); BASF, *DBP* 1,215,145; BASF, *DBP* 1,239,302; BASF, *FP* 1,482,396.

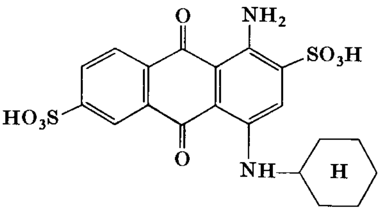
[44] BASF, *FP* 1,554,370.

[45] Hercules Powder Company, *FP* 1,366,458.





Condensation of 1-amino-4-bromoanthraquinone-2,6-disulfonic acid with cyclohexylamine[46] results in a dye slightly greener than Alizarine Brilliant Sky Blue R. As in the case of Alizarine Light Blue 5GL, the



introduction of a sulfo group in the anthraquinone nucleus is associated with a distinct weakening of the benzophenone bands.

D. Dyes Containing Two Anthraquinone Moieties

Dyes with very good wet-fastness and milling properties are obtained when two bromaminic acid groups are attached to a diamine. A dye of this type, *Supranol Fast Blue GG* (CI Acid Blue 127),[47] is obtained from 2 moles of bromaminic acid and 1 mole of 4,4′-diaminodiphenyl-2,2-propane. It dyes wool from a neutral or weakly acid bath in bright blue shades of very good all-round fastness.

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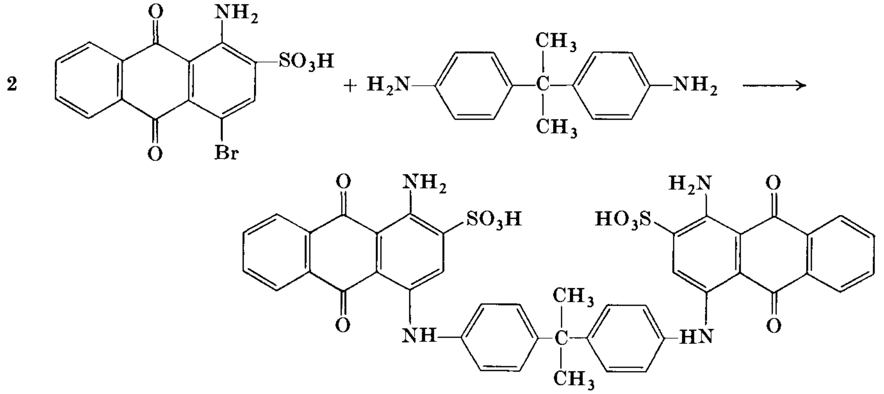
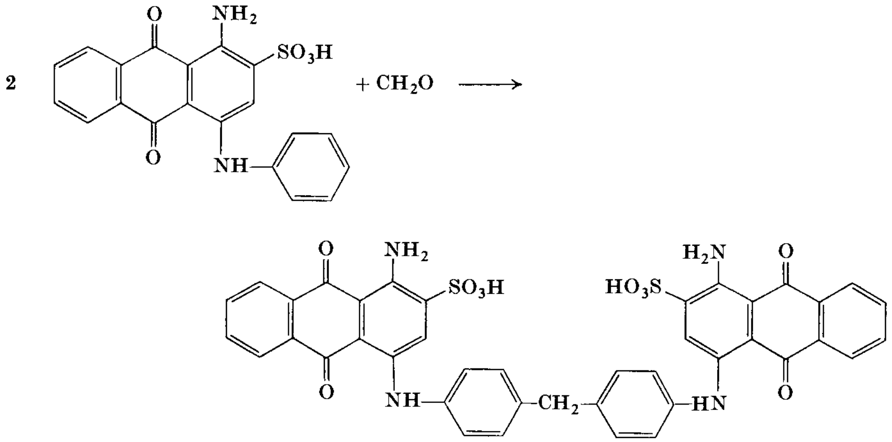
[46] S, *USP* 2,453,285.

[47] FIAT, *1313*, II 230; G, *USP* 2,156,887.



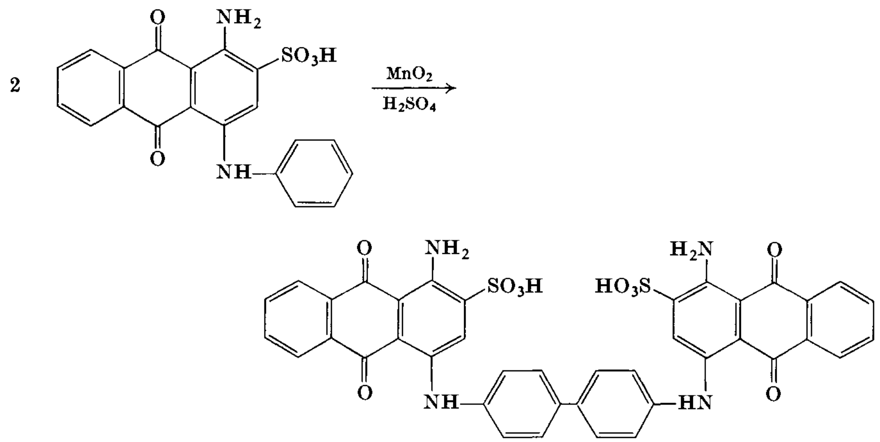
A comparable dye, *Brilliant Alizarine Milling Blue G*,[48] is formed by condensation of 2 moles of 1-amino-4-phenylaminoanthraquinone-2-sulfonic acid (Acilan Direct Blue A) with formaldehyde in sulfuric acid. When applied to wool from neutral or weakly acid medium, it gives greenish blue dyeings which are very wet-fast and fast to milling. However, it does not cover barry nylon.



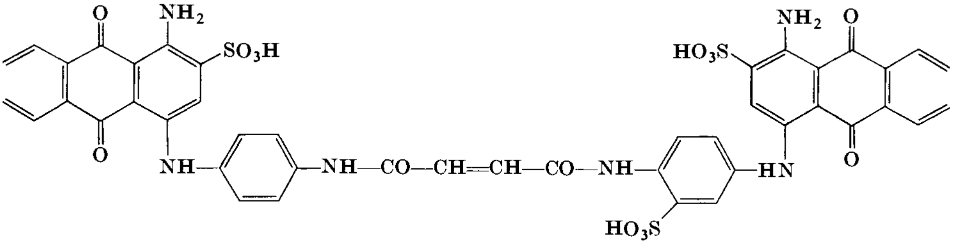
Oxidative coupling of two molecules of Acilan Direct Blue A through the phenyl rings in the para position is carried out with manganese dioxide as a mild oxidizing agent in sulfuric acid.[49] The product, *Alizarine Milling Blue SL* (CI Acid Blue 150) is a greenish blue giving rather dull dyeings. It has similar dyeing properties to the two aforenamed dyes.

[48] S, *USP* 2,008,796.

[49] S, *DRP* 621,369.



The dye formed by condensation of 1-amino-4-(4′-aminophenylamino)-anthraquinone-2-sulfonic acid and 1-amino-4-(4′-aminophenylamino)-anthraquinone-2,3′-disulfonic acid with fumaric acid dichloride[50] illustrates another type of linkage between two anthraquinone moieties.



The dye is a mixture of the two corresponding symmetrical and the unsymmetrical compounds. It dyes cellulosic fibers bluish green with outstanding lightfastness. The benzenoid bands of the bridging component are superimposed with the benzophenone bands. As the intensity ratio of the bands at about 630 and 400 mμ is 1.6, the dye is almost a green.

If the dichloride of muconic acid is used instead of fumaric acid dichloride, a dye mixture with similar properties is obtained.[51] Definitely bluish products with outstanding lightfastness properties, but somewhat poorer affinity on cellulosic fibers, are obtained by the use of terephthalic acid dichloride and isophthalic acid dichloride.[52]

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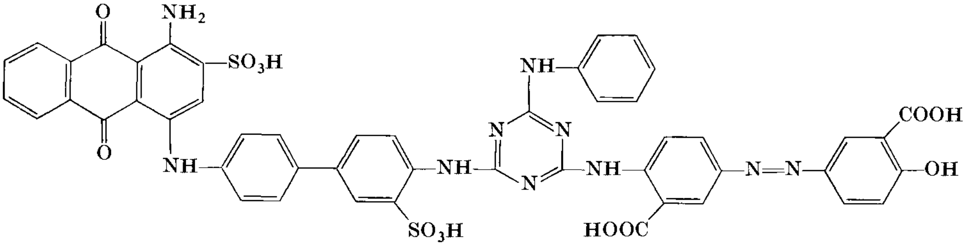
[50] S, *USP* 2,779,772.

[51] S, *USP* 2,278,839.

[52] S, *BP* 808,603.

Homogeneous brilliant green cotton dyes may be prepared by stepwise condensation of cyanuric chloride with a greenish blue aminoanthraquinone component and a greenish yellow aminoazo dye. An example of this type of dye is shown by the compound below, in which the third chlorine atom of cyanuric chloride is replaced by aniline.[53] Dyeings of this product on cellulosic fibers have good light- and wet-fastness properties.



E. Reactive Dyes Derived from Bromaminic Acid

Since reactive dyes will be reviewed in a separate chapter, only a few representative examples which are derived from the condensation products of bromaminic acid with amines will be discussed here.

The reactive groups enable these dyes to form stable chemical bonds with the hydroxyl groups of cellulose[54] and with the amino and thiol groups of wool.[55] As a result, the dyeings have excellent wet-fastness properties.

The reactive hook in the following blue[56] consists of a β-hydroxyethylsulfone–sulfuric acid ester group. The dye is prepared by condensing bromaminic acid with *m*-aminophenyl-β-hydroxyethyl sulfone, followed by esterification with sulfuric acid. On wool and especially on cotton it gives reddish blue dyeings of high brilliance.

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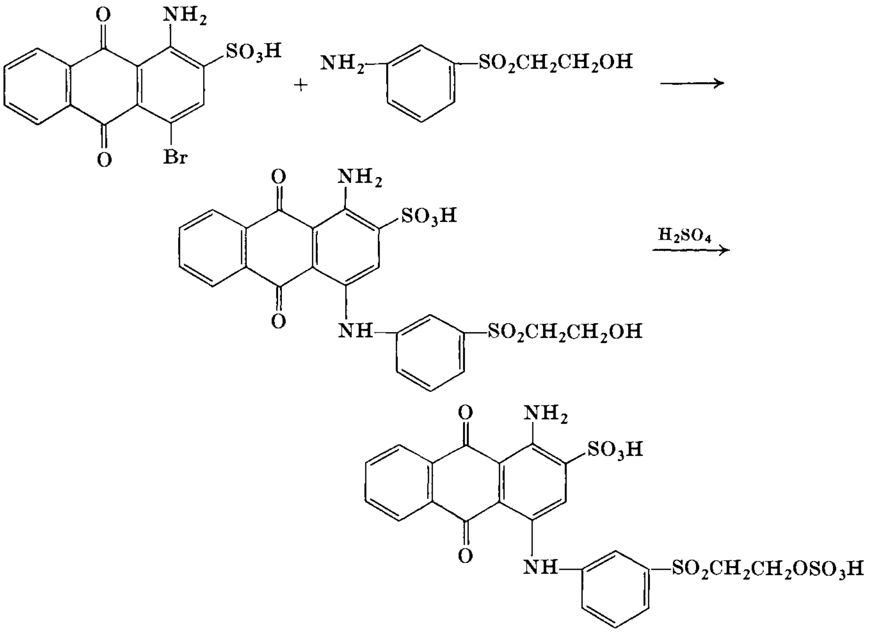
[53] S, *USP* 2,963,473.

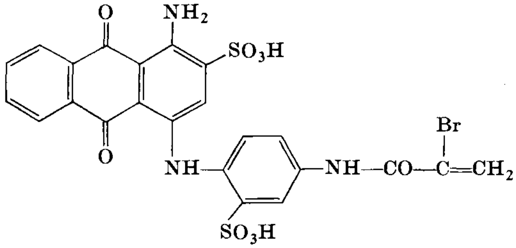
[54] H. Zollinger, *Angew. Chem.* **73**, 125 (1961); D. A. Stamm, H. Zollinger, H. Zähner, and E. Gäumann, *Helv. Chim. Acta* **44**, 1123 (1961).

[55] G. Reinert, K. Mella, P. F. Rouette, and H. Zahn, *Melliand Textilber.* **11**, 1313 (1968); H. Zahn and P. F. Rouette, *Textilveredlung* **3**, 241 (1968).

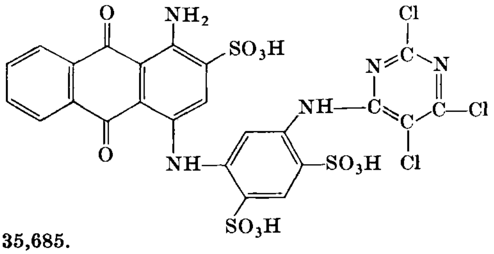
[56] FH, *USP* 2,657,205.



In another dye type[57] a 2-bromoacryl group is present to form the bond with the reactive groupings of wool. A blue of this type derived from bromaminic acid is



In the following blue, which has a trichloropyrimidyl group, the mobile chlorine atoms react with the hydroxyl groups of cellulose[58]:



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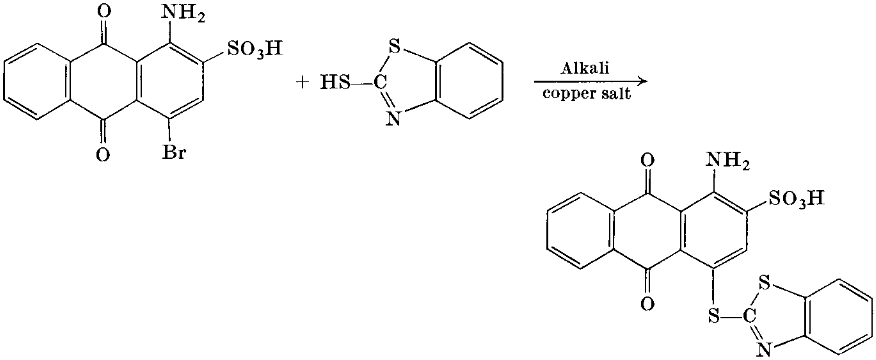
[57] CIBA, *BP* 1,135,685.

[58] S, *DBP* 1,228,023.

This dye is produced by condensation of 1-amino-4-(3′-aminophenylamino)anthraquinone-2-sulfonic acid and tetrachloropyrimidine, followed by sulfonation.

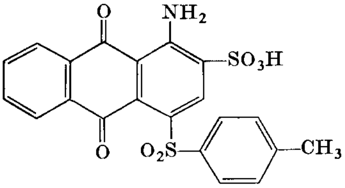
F. Condensation Products of Bromaminic Acid with Other Nucleophiles

Bromaminic acid can be condensed with other nucleophilic compounds, for example 2-mercaptobenzothiazole, in a similar manner to amines.



Replacement of the imino group in the 4-position by a thioether bridge causes a marked hypsochromic shift of the quinone and benzophenone bands.[2] The resulting dye produces brilliant red dyeings on wool and nylon, which are not sufficiently fast to light. However, desulfonation in hot dilute sulfuric acid yields a disperse dye which gives lightfast dyeings on polyester fibers.[59]

Derivatives of bromaminic acid containing sulfo groups, for example, the dye



are obtained if the corresponding thioether compound, which is easily prepared by condensation of bromaminic acid with *p*-thiocresol, is treated with an oxidizing agent such as hydrogen peroxide or chlorine.[60]

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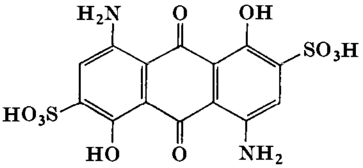
[59] S, *BP* 1,078,675.

[60] BASF, *DBP* 1,029,964.

The dye gives orange-red dyeings on wool and nylon, which, however, exhibit only moderate wet-fastness and poor lightfastness properties.

II. Diaminodihydroxyanthraquinonesulfonic Acids

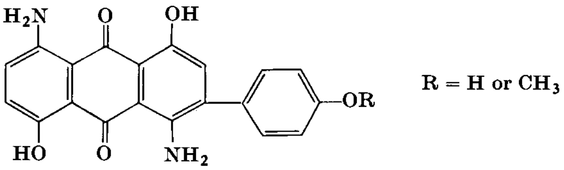
One of the classical anthraquinone dyes which is still of some importance today is *Acilan Sapphirol B* (CI Acid Blue 45),[61] an attractive blue with good leveling, light-, and wet-fastness properties on wool. It is



synthesized from 1,5-dihydroxyanthraquinone (anthrarufin), which is sulfonated to the 2,6-disulfonic acid, dinitrated in the 4- and 8-positions, and finally reduced to the diamino compound.

With aluminum salts the dye forms a lake which is used for the pigmentation of soaps and plastics. Another interesting application is the dyeing of anodized aluminum, in which a fine film of aluminum oxide is produced on the surface of the metal. The oxide is capable of forming aluminum cations at the metal–water interface. It is assumed that the dye anions or their aggregates form saltlike bonds with the aluminum cations.[62]

Acilan Sapphirol B is an important intermediate for blue disperse dyes, such as



By elimination of one of the sulfonic acid groups with sulfuric acid in the presence of small amounts of boric acid, Acilan Sapphirol B is converted into *Acilan Sapphirol SE* (CI Acid Blue 43).[63] This dye is

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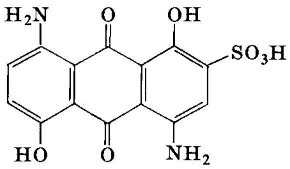
[61] BIOS, *1484*, 41.

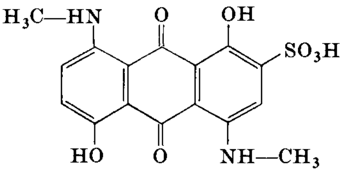
[62] C. H. Giles and K. V. Datye, *Trans. Inst. Metal Finishing* **40**, 113 (1963).

[63] BIOS, *1484*, 42.

somewhat more reddish than Acilan Sapphirol B. The leveling properties on wool are good, but it is only moderately wet-fast. This dye is also employed for dyeing anodized aluminum.



Supracen Blue SES (CI Acid Blue 55)[64] has similar properties to the two dyes mentioned above, although its shade is slightly greener than that of Acilan Sapphirol B. This blue is derived from Acilan Sapphirol B by methylation of the two amino groups with formaldehyde in sulfuric acid, followed by splitting off one of the two sulfonic acid groups. Its leveling and wet-fastness properties are comparable to those of Acilan Sapphirol SE.



III. Dyes Formed by Sulfonation of a Dye Base

A. SYMMETRICALLY SUBSTITUTED 1,4-DIAMINOANTHRAQUINONES

1. *1,4-Diarylaminoanthraquinones*

The dyes of this type range in shade from blue to green depending on the structure of the amine. The most common method for their synthesis is condensation of 1,4-dihydroxyanthraquinone (quinizarin) (VI) with aromatic amines. Sulfonation of the dye base (VII) produces the dye (VIII). Since quinizarin (VI) reacts sluggishly with amines, it must be at least partially converted into the more reactive leuco form (IX) prior to condensation. Apparently it is the tautomeric form (X) which reacts

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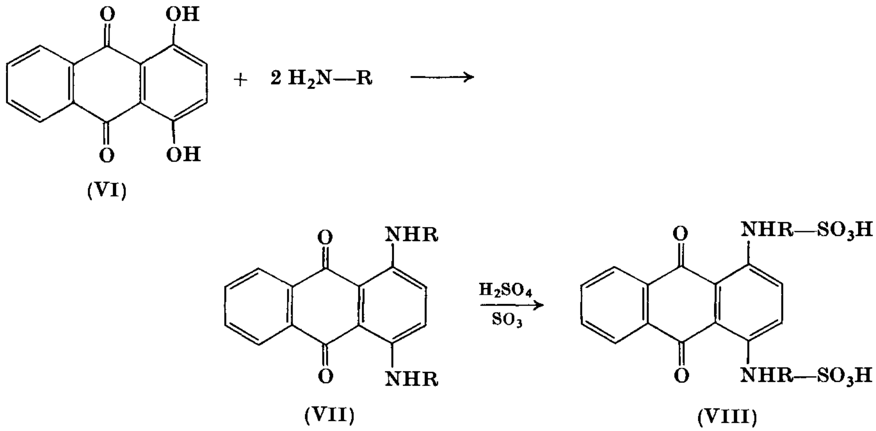
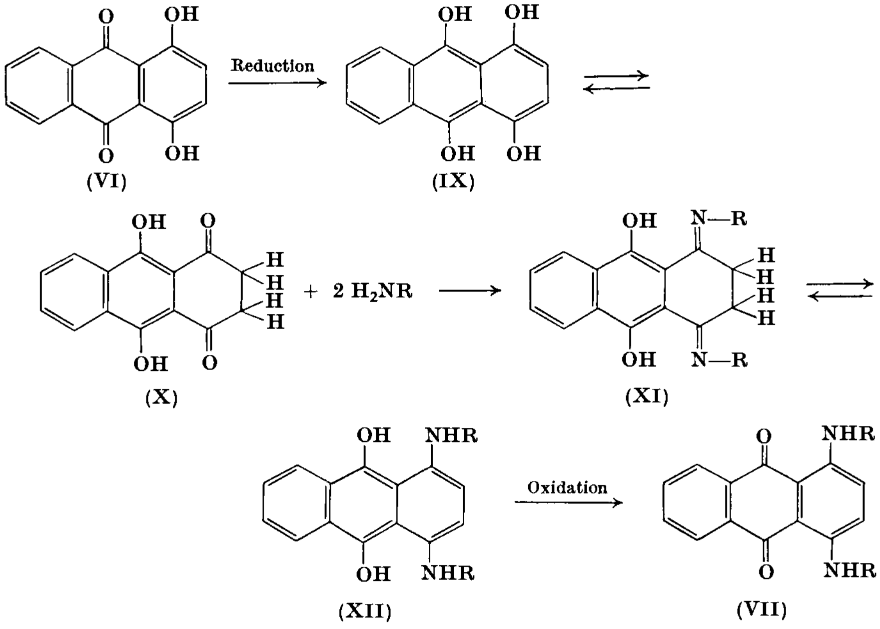
[64] IG, *BP* 250,968.



(VI) (VII) (VIII)

with the amine to give the leuco compound of diaminoanthraquinone; the latter may likewise be present in two tautomeric forms [(XI) and (XII)]. The leuco compound is then oxidized to the dye base (VII), either with air or oxygen or by heating in nitrobenzene in the presence of a little piperidine.[65] The condensation reaction is greatly facilitated



(VI) (IX) (X) (XI) (XII) (VII)

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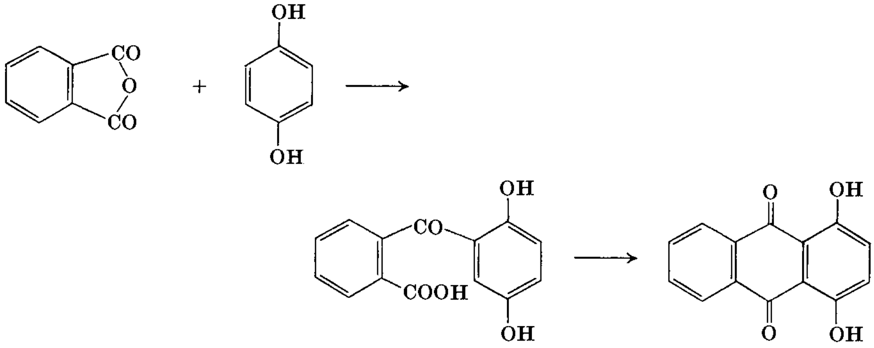
[65] K. Zahn and P. Ochwat, *Ann. Chem.* **462**, 78 (1928); S. C. Flett, *J. Chem. Soc.* p. 1447 (1948); E. Grandmougin, *J. Prakt. Chem.* [2] **76**, 139 (1907); FBy, *DRP* 91,149; 91,152.

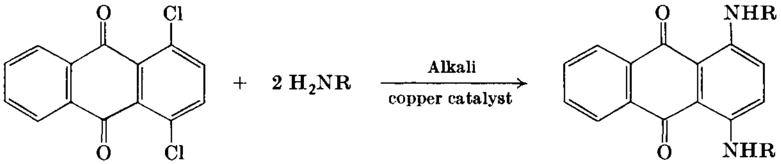
by the presence of boric acid. Its catalytic effect is due to the intermediate formation of boric acid complexes.[66] For this reason these condensation reactions are carried out with a mixture of quinizarin and leucoquinizarin in the presence of boric acid at 90–120°. The leucoquinizarin can be formed in the course of the reaction by the addition of a reducing agent such as zinc dust and hydrochloric acid, or hydrosulfite. In most cases the amine also acts as a solvent; alternatively higher boiling alcohols can be used.

If aqueous alcohol is used as the solvent, the reaction generally stops at the monocondensation stage to give 1-hydroxy-4-arylaminoanthraquinones.[67]

Friedel-Crafts type condensation of phthalic anhydride with hydroquinone in an aluminum chloride–sodium chloride melt at 200–220° gives a purer product as well as a higher yield of quinizarin than the older *p*-chlorophenol process.[68] The quinizarin is isolated by dropping the melt into dilute hydrochloric acid and decomposing the aluminum complex by heating. The quinizarin is then filtered, washed, and dried.



1,4-Diarylaminoanthraquinones may also be prepared from 1,4-dichloroanthraquinone by condensation with amines in the presence of alkali and, if necessary, a copper catalyst.[69] The reaction requires temperatures greater than 130°.



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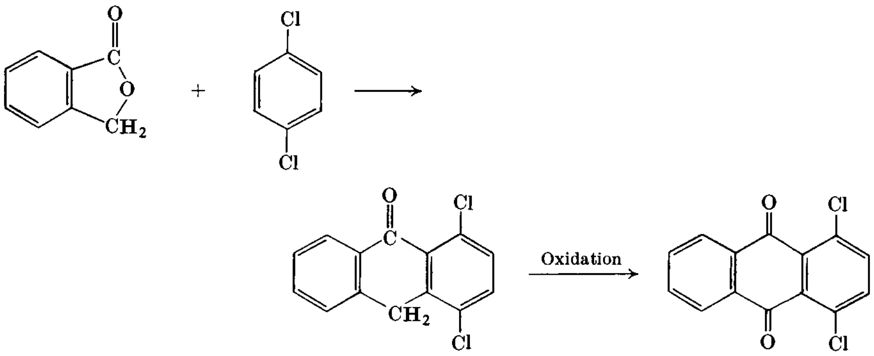
[66] FBy, *DRP* 86,150; V. I. Shal'kova and S. M. Barkov, *J. Org. Chem. USSR* (English *Transl.*) **5**, 1244 (1969).

[67] BIOS, *1484*, 48.

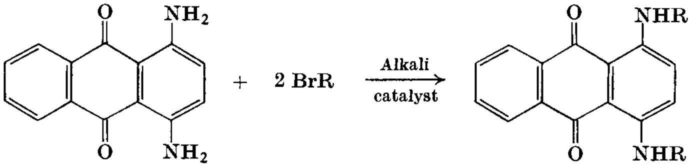
[68] PB 74,885.

[69] FBy, *DRP* 125,698.

1,4-Dichloroanthraquinone itself can be obtained by Friedel-Crafts condensation of 3,6-dichlorophthalic anhydride with benzene.[70] Another method involves condensation of *p*-dichlorobenzene with phthalide followed by oxidation of the resulting 1,4-dichloroanthrone.[71]



In yet another method 1,4-diaminoanthraquinone is condensed with a halogenated benzene derivative in the presence of alkali and a copper catalyst. The medium may be an excess of the halogenated derivative or another high-boiling solvent, e.g., nitrobenzene.[72]



The 1,4-diaminoanthraquinone is obtained by reacting leucoquinizarin with ammonia to give the leucodiaminoanthraquinone, which is then oxidized in nitrobenzene in the presence of piperidine.[73]

For the sake of completeness it may be mentioned that 1,4-diarylaminoanthraquinones can also be obtained from 1-chloro-4-nitro-, 1-hydroxy-4-chloro-, 1-hydroxy-4-nitro-, and 1-hydroxy-4-aminoanthraquinone. However, these methods have not achieved practical significance.

Whereas the dyes derived from 1-amino-4-bromoanthraquinone-2-sulfonic acid (bromaminic acid) contain the water-solubilizing group in

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[70] F. Ullmann and G. Billig, *Ann. Chem.* **381**, 14 (1911).

[71] IG, *DRP* 677,327; BASF, *DBP* 1,263,737.

[72] DuP, *BP* 579,519.

[73] FIAT, *1313*, II 51.

the anthraquinone nucleus, the 1,4-diarylaminoanthraquinone dye bases require further treatment with concentrated sulfuric acid or oleum for conversion into soluble dyes.[74] Since sulfonation occurs primarily on the aryl groups, the reaction conditions vary according to the structure of these groups. Thus, while 1,4-dianilinoanthraquinone can be sulfonated in 90% sulfuric acid at room temperature, other dye bases require sulfuric acid of greater strength, or oleum, and possibly higher temperatures, if the particular anilino group is deactivated. The effect of substituents on sulfonation depends on their number, their nature, and their positions in the phenyl ring. If an electron-accepting substituent, such as a carboxyl group, is present, or if there is severe steric hindrance, it may be found that sulfonation does not occur or that the dye molecule is degraded prior to sulfonation. In certain cases chlorosulfonic acid is used in place of sulfuric acid or oleum.[75] The sulfonated dye is precipitated in water or salt solution, filtered, washed until neutral, and dried. Normally it is isolated in the form of the sodium salt. If difficulties arise with the sodium salt, the dye may be isolated as the potassium, lithium, or ammonium salt.

If the aniline nucleus is unsubstituted the sulfo group enters para to the imino group. When this position is occupied ortho substitution occurs.[76] The unsubstituted anilino group or a phenyl ring bearing an electron-donating substituent, e.g., a methoxy group in ortho or meta position, can be readily disulfonated. Thus the conditions used for such easily sulfonated dye bases must be carefully chosen in order to avoid over-sulfonation. In certain cases the sulfonation of 1,4-diarylaminoanthraquinones can be carried out in such a manner that at the end of the reaction a mixture is obtained consisting mainly of monosulfonated dye with a small amount of disulfonated material; this may have a beneficial effect on the dyeing properties.

a. Coplanar Condensation Products with Aromatic Amines. It can be seen from Fig. 2, example III, that 1,4-diaryl substitution results in distinct splitting of the quinone bands. The primary feature here compared with the bromaminic acid derivatives is the greater intensity of the benzophenone bands, which imparts to the dyes of this group a bluish green to green shade.

The first commercial dye of this type was *Alizarine Cyanine Green G* (CI Acid Green 25),[77] which is still important today. It is produced by

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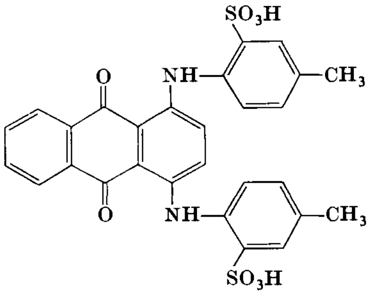
[74] FBy, *DRP* 84,509; H. E. Fierz-David and L. Blangey, "Grundlegende Operationen der Farbenchemie," 5th ed., p. 301. Springer, Vienna, 1943.

[75] Gy, *BP* 736,187.

[76] C. F. H. Allen, G. F. France, and C. V. Wilson, *J. Org. Chem.* **6**, 736 (1941).

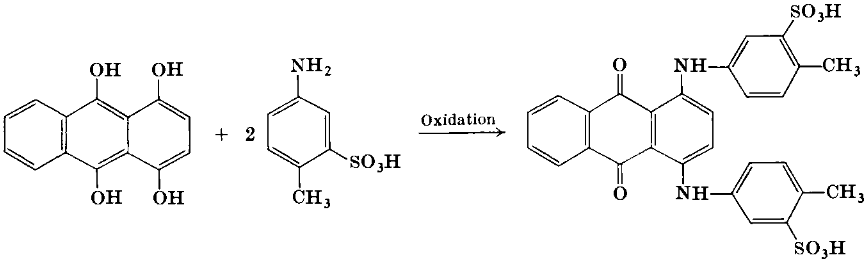
[77] FIAT *1313*, II 215.

condensation of quinizarin with *p*-toluidine in the presence of hydrochloric acid, zinc dust, and boric acid. After completion of the reaction the dye base is precipitated with alcohol, filtered, washed, dried, and sulfonated with 5% oleum. On wool this dye gives bluish green dyeings showing good lightfastness but only moderate wet-fastness. The wet-fastness properties on nylon are good; it does not, however, cover barry nylon.



If the sulfonation conditions are such that the bulk of the product is monosulfonated, a green dye is obtained which has distinctly better affinity than Alizarine Cyanine Green G under neutral dyeing conditions.

Alizarine Direct Green G (CI 61575),[78] shows dyeing properties similar to Alizarine Cyanine Green G, which differs from the former solely in the positions of the two sulfo groups. It is formed by condensation of leucoquinizarin with 1-amino-4-methylbenzene-3-sulfonic acid in the presence of boric acid. High wet-fastness and notably good milling fastness are very often critical factors for wool dyes. The purpose of milling is to felt the woven wool fabric and so convert it into cloth of greater density. To accomplish this the fabric is squeezed in a warm,



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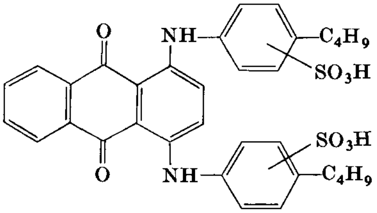
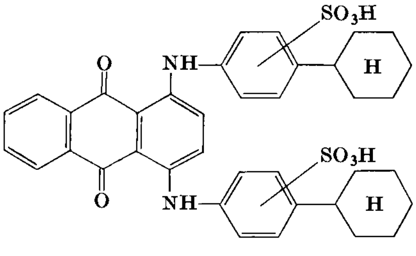
[78] MLB, *FP* 339,192.

weakly alkaline soap solution or in moderately warm dilute sulfuric acid. If dyed piece goods are to withstand this treatment the dye–fiber bond must be stable, i.e., the dye must have high affinity for the fiber. This can be achieved if the dye molecule has few hydrophilic groups and is suitably substituted, for example, by the introduction of alkyl, cycloalkyl or aryl groups, or halogen into the anilino group.

Although Alizarine Cyanine Green G itself has poor milling fastness, this property can be improved by lengthening the alkyl chain para to the imino group. For perfect milling fastness the chain must have at least four carbon atoms, such as in *Carbolan Green G* (CI Acid Green 27),[79] which is formed by condensation of quinizarin with *p*-*n*-butylaniline and sulfonation of the dye base. Its shade is similar to that of Alizarine Cyanine Green G but is a little brighter.



Alizarine Cyanine Green GWA (CI Acid Green 44)[80] is a trace yellower than Alizarine Cyanine Green G. It is the sulfonated condensation product of quinizarin with *p*-cyclohexylaniline:



The amine is prepared by alkylation of benzene with cyclohexyl chloride, nitration of the product, and reduction of the 4-nitro isomer.[81]

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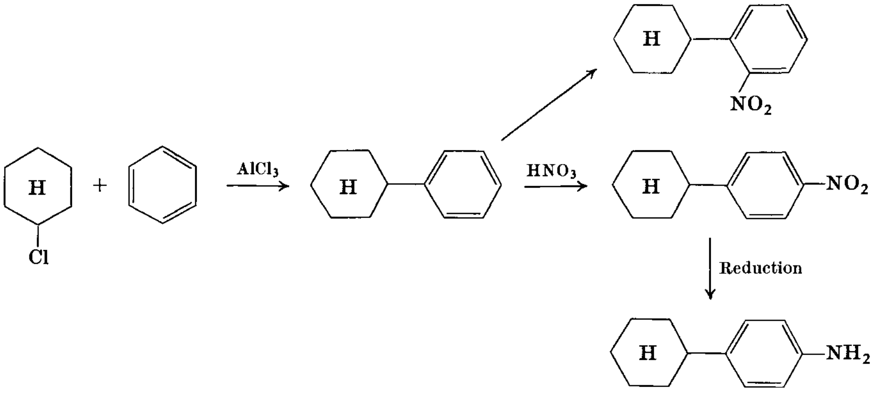
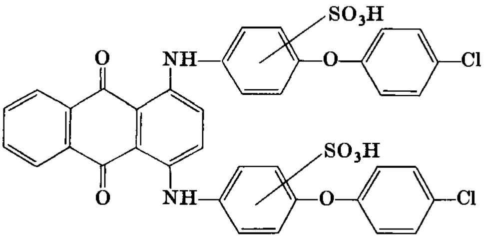
[79] ICI, *BP* 449,010.

[80] IG, *BP* 434,429.

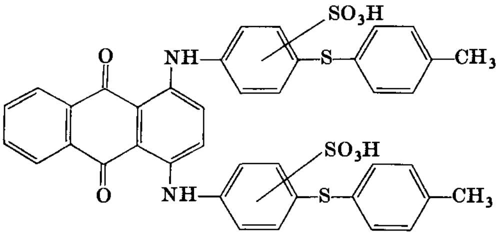
[81] H. A. Mayer and E. E. Turner, *J. Chem. Soc.* p. 504 (1929).



Dyes of comparably good milling fastness are the two greens (XIII)[82] and (XIV)[75] for which quinizarin is condensed, respectively, with 4-amino-4′-chlorodiphenyl ether or with 4-amino-4′-methyldiphenyl thioether and the product sulfonated. In both dyes the presence of the additional aryl group dulls the shade to some extent. Dyeings of (XIII) are slightly bluish green, while the thioether bridge in (XIV) is responsible for a yet more pronounced bathochromic shift. The two amines are



(XIII)



(XIV)

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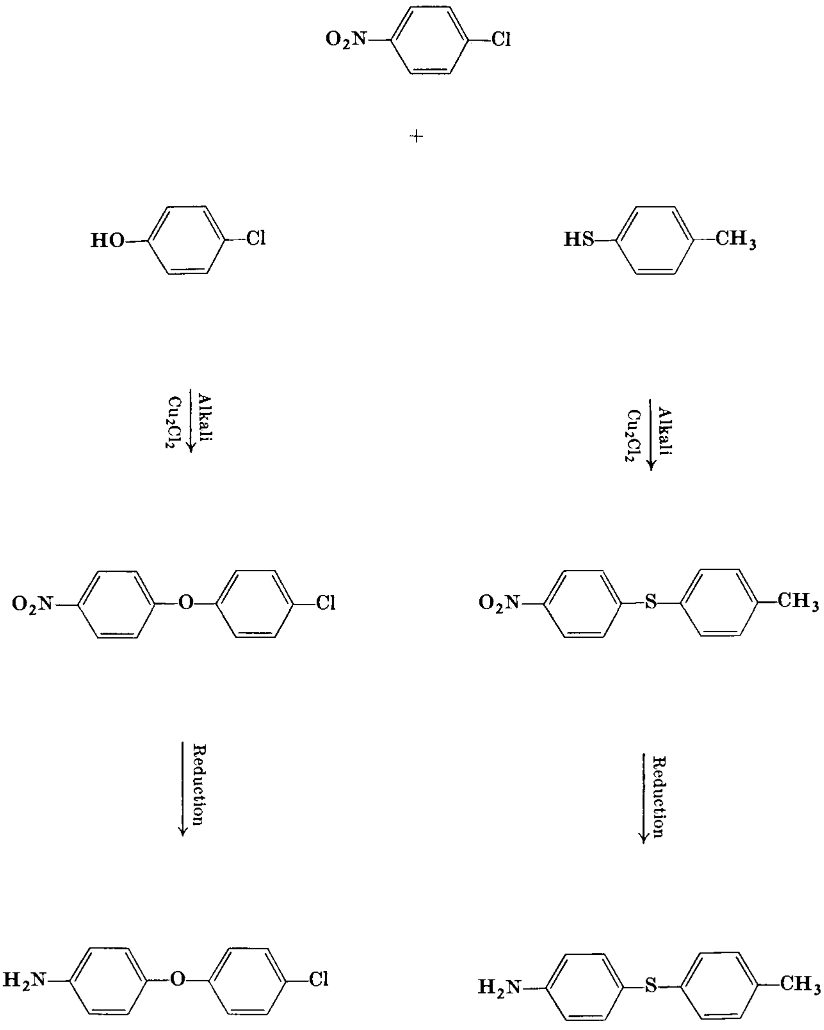
[82] S, *USP* 2,559,330.

obtainable by condensation of *p*-nitrochlorobenzene with *p*-chlorophenol[83] or *p*-thiocresol,[84] respectively, in the presence of alkali and a catalyst, followed by reduction of the intermediate nitro compound.



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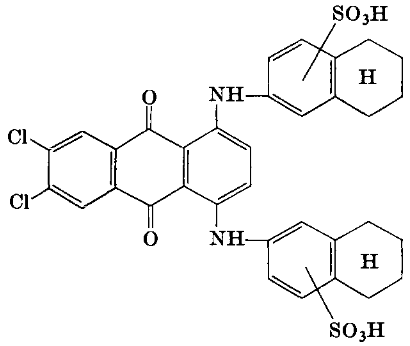
[83] C. Haeussermann and H. Teichmann, *Chem. Ber.* **29**, 1447 (1896).

[84] M. E. Bourgeois and P. Huber, *Rec. Trav. Chim.* **31**, 30 (1912).

In the dyes thus far considered the changes in shade and wet-fastness result from modification of the substituents in the anilino groups; similar effects can be obtained by introducing suitable substituents such as halogen or hydroxyl groups into the previously unsubstituted ring of the anthraquinone skeleton.

Condensation of 6,7-dichloroquinizarin with 6-aminotetralin in a manner analogous to that used with quinizarin, followed by sulfonation, yields a dye of this type.[85] The introduction of two chlorine atoms in the anthraquinone nucleus leads to a bathochromic shift of the quinone bands. In addition the chlorine substituents in para positions facilitate the polarizability of the benzophenone chromophores. Since the two chlorine atoms increase the hydrophobicity and molecular weight of the dye, the wet-fastness properties are substantially improved.



The 6,7-dichloroquinizarin is obtained by a Friedel-Crafts condensation of hydroquinone with 4,5-dichlorophthalic acid.[86] The acid is obtained by chlorination of phthalic acid in weakly alkaline aqueous solution, which yields a mixture of dichlorophthalic acid isomers from which the 4,5-dichlorophthalic acid is isolated.[87] Chlorination in oleum also produces an isomeric mixture, which, however, contains only a small amount of 4,5-dichlorophthalic acid and which is difficult to separate.[88] In another method phthalic anhydride is chlorinated in the

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[85] S, *USP* 2,494,240.

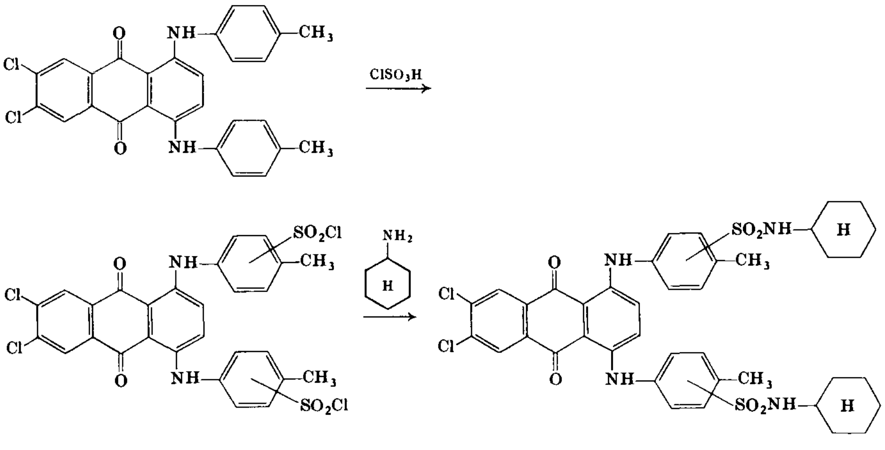
[86] H. Waldmann, *J. Prakt. Chem.* [2] **126**, 253 (1930).

[87] E. E. Ayling, *J. Chem. Soc.* p. 254 (1929).

[88] V. Villiger, *Chem. Ber.* **42**, 3529 (1909).

vapor phase at 400° in the presence of manganese chloride on activated alumina.[89] The 6-aminotetralin is prepared by nitration of tetralin, separation of the isomers, and subsequent reduction.[90]

In this context it may be mentioned that certain acid anthraquinone dye bases can be converted into solvent-soluble dyes. For example, 1,4-di-*p*-toluidino-6,7-dichloroanthraquinone can be treated with chlorosulfonic acid and the resulting sulfonyl chloride reacted with cyclohexylamine to give (XV).[91] Being readily soluble in alcohols, ketones, and glycol ethers, this product is used for the coloration of clear lacquers and cellulose acetate.



(XV)

If substituents such as hydroxyl groups, which are stronger electron donors than the chlorine atoms discussed above, are introduced into the anthraquinone nucleus, increased polarizability of all the partial chromophores results. Significant bathochromic shifts of the quinone and benzophenone bands are observed, and therefore the greens are slightly yellower.

Thus *Alizarine Cyanine Green 3G* (CI Acid Green 38)[92] is a little yellower than the dye obtained from 6,7-dichloroquinizarin and decidedly more yellow than Alizarine Cyanine Green G. The dye base is produced by

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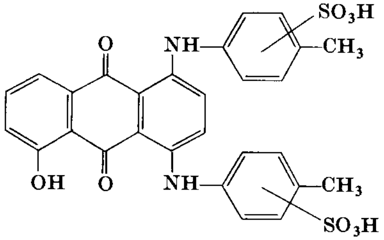
[89] H. Brintzinger and H. Orth, *Monatsh. Chem.* **85**, 1017 (1954).

[90] G Schroeter, *Ann. Chem.* **426**, 19 (1922).

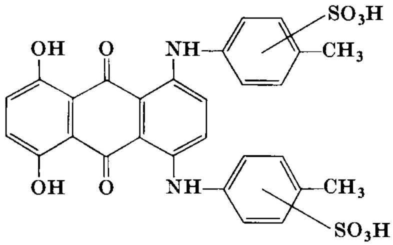
[91] S, *USP* 2,852,535.

[92] BIOS, *1484*, 33.

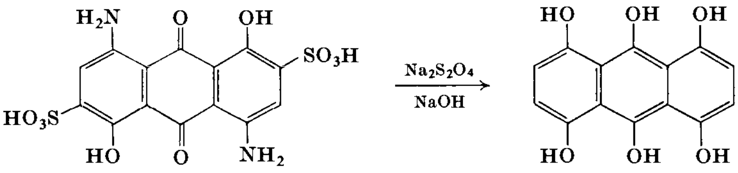


condensing 1,4,5-trihydroxyanthraquinone with *p*-toluidine in the presence of boric acid, hydrochloric acid, and zinc dust. 1,4,5-Trihydroxyanthraquinone is obtained by oxidation of 1,8-dihydroxyanthraquinone (chrysazin) with strong oleum in the presence of boric acid.[93]

The introduction of a second hydroxyl group leads to the yellowish green *Alizarine Cyanine Green 5G* (CI Acid Green 41).[94] The synthesis proceeds via condensation of *p*-toluidine with leuco-1,4,5,8-tetrahydroxyanthraquinone and oxidation of the resulting leuco compound followed by sulfonation:



The leucotetrahydroxyanthraquinone is formed by reduction of Acilan Sapphirol B with hydrosulfite in strongly alkaline aqueous solution under nitrogen.[95]



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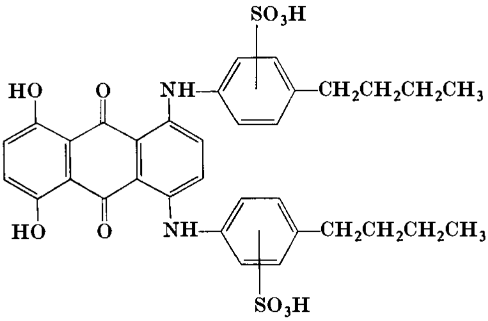
[93] BIOS, *1484*, 22; FBy, *DRP* 161,026.

[94] IG, *USP* 1,713,576; BIOS, *1484*, 35.

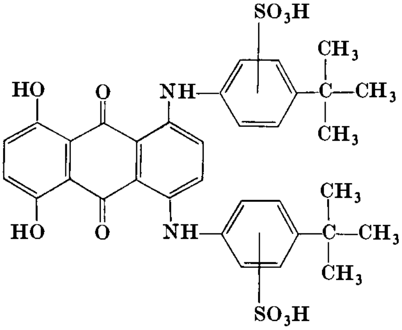
[95] BIOS, *1484*, 18.

Both Alizarine Cyanine Green 3G and Alizarine Cyanine Green 5G show only moderate fastness to milling.

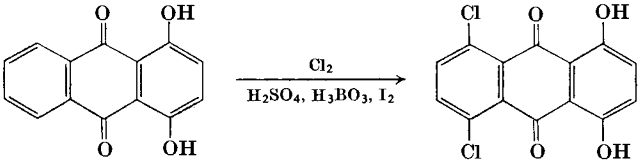
If leucotetrahydroxyanthraquinone is condensed with *p*-*n*-butylaniline in place of *p*-toluidine, a dye with excellent wet-fastness results.[94]



In dyeing properties it closely resembles the green of the following structure[96]:



Another route is employed for this latter dye. It was found that quinizarin is converted into 5,8-dichloroquinizarin by chlorination in sulfuric acid or chlorosulfonic acid in the presence of boric acid and iodine.[97] This



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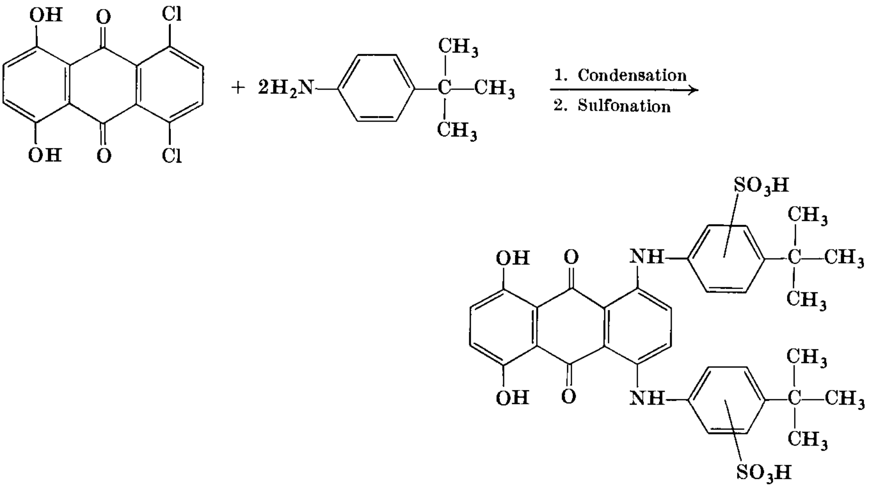
[96] FBy, *USP* 3,436,410.

[97] FBy, *DBP* 1,199,279.

substituted quinizarin derivative can be condensed with *p*-tert-butylaniline[98] in the presence of sodium carbonate at high temperature to the dye base, which is sulfonated to the final dye.



Further, a patent describes the stepwise replacement of the two chlorine atoms in 5,8-dichloroquinizarin.[99] Using different amines it is possible to produce in this way asymmetrically substituted 1,4-diamino-5,8-dihydroxyanthraquinones.

It should be emphasized that most dyes bearing hydroxyl groups in the anthraquinone nucleus are sensitive to strong alkalis and chromium ions.

b. Condensation Products with o,o′-Disubstituted Anilines. An important discovery was made when condensation of quinizarin with *o,o′*-disubstituted aromatic amines was successfully utilized to prepare blue 1,4-diarylaminoanthraquinones and the corresponding sulfonated dyes. Coplanarity of the two phenyl rings with the anthraquinone skeleton is hindered by the two ortho substituents. This greatly weakens the benzophenone bands and a hypsochromic shift of the quinone bands occurs.

The oldest dye of this type is *Brilliant Alizarine Milling Blue BL* (CI Acid Blue 80).[100] It is produced by condensing a mixture of quinizarin and leucoquinizarin with mesidine in the presence of boric acid, and

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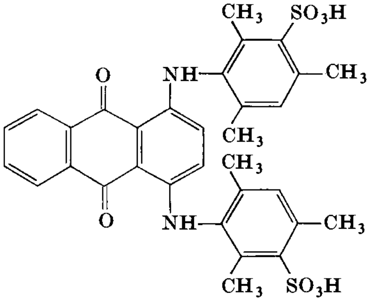
[98] D. Craig, *J. Am. Chem. Soc.* **57**, 195 (1955); W. J. Hickinbottom and G. H. Preston *J. Chem. Soc.* p. 1566 (1930); Phillips Petroleum Company, *USP* 2,507,755.

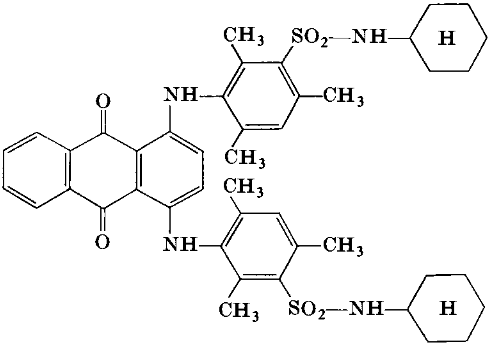
[99] FBy, *DBP* 1,285,646.

[100] S, *DRP* 631,518.

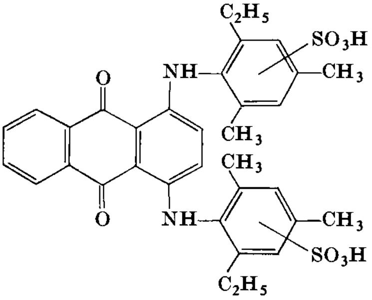
sulfonating the dye base with weak oleum. This dye has very good light-fastness and fairly good wet-fastness on wool.



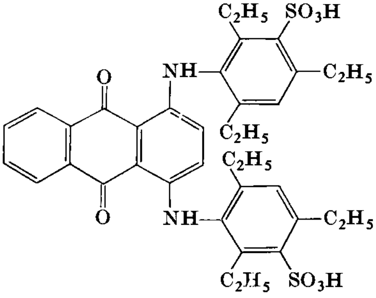
The dye base itself is used to form a blue solvent-soluble dye as described for the green type referred to in Section III,A,1,a.[101]



If the hydrophobicity of the dye is increased by the introduction of ethyl instead of methyl groups, the wet-fastness is improved. Thus dye (XVI)[100] has good and (XVII)[72] excellent milling fastness. The larger



(XVI)



(XVII)

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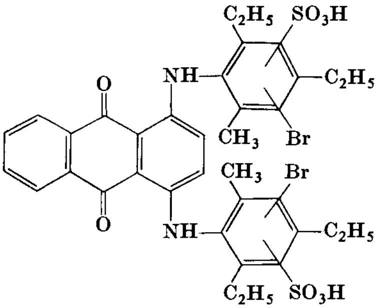
[101] S, *USP* 2,731,476.

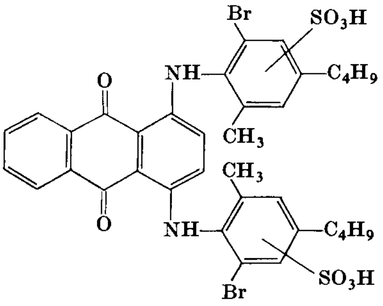
the substituents in the positions ortho to the imino group of the phenyl ring, the more the ring is twisted out of the plane of the anthraquinone nucleus. This results in an increased hypsochromic shift and therefore both dyes are slightly redder than Brilliant Alizarine Milling Blue BL.

While dye (XVI) can be obtained by the classical method from quinizarin and 2,4-dimethyl-6-ethylaniline,[29] the synthesis of (XVII) starts with 1,4-diaminoanthraquinone. This is condensed with 2,4,6-triethylbromobenzene in the presence of alkali and a copper catalyst and the resulting dye base sulfonated.

The 2,4,6-triethylbromobenzene is obtained by ethylation of benzene with ethyl chloride[102] or ethylene[103] in the presence of aluminum chloride using the Friedel-Crafts method, followed by bromination of the triethylbenzene.[104] Rearrangement of the unsymmetrical triethylbenzenes occurs under the conditions of the Friedel-Crafts alkylation. Dyes of more reddish shade result when the phenyl ring is halogenated, as in the case of the following two blues:



(XVIII)



(XIX)

(XVIII) is obtained by condensation of 1,4-diaminoanthraquinone and 2,4-diethyl-6-methylbromobenzene in the presence of alkali and a copper catalyst, followed by bromination and sulfonation of the dye base in oleum.[105]

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[102] J. F. Norris and D. Rubinstein, *J. Am. Chem. Soc.* **61**, 1166 (1939); L. I. Smith and C. O. Guss, *ibid.* **62**, 2627 (1940).

[103] W. B. Dillingham and E. E. Reid, *J. Am. Chem. Soc.* **60**, 2606 (1938); E. M. Marks, J. M. Almand, and E. E. Reid, *J. Org. Chem.* **9**, 13 (1944).

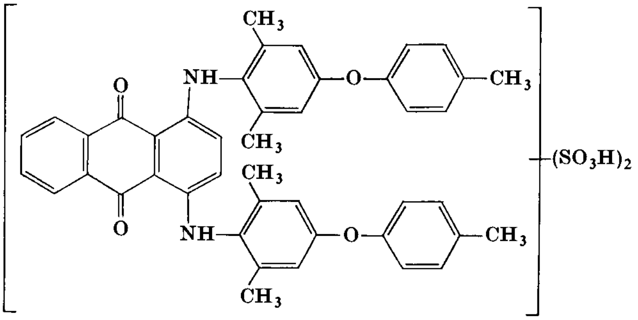
[104] R. C. Fuson and J. Corse, *J. Am. Chem. Soc.* **60**, 2065 (1938); W. T. Nauta and D. Mulder, *Rec. Trav. Chim.* **58**, 516 (1939).

[105] S, *USP* 2,736,731.

The 2,4-diethyl-6-methylbromobenzene is prepared by a Friedel-Crafts reaction of toluene with ethyl chloride in the presence of aluminum chloride to produce diethyltoluene, which is then brominated.[102, 104]

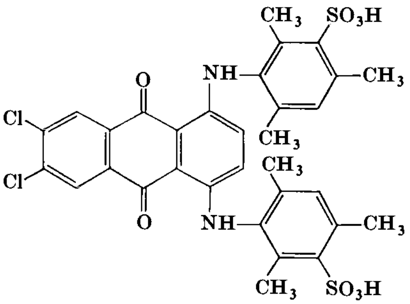
The synthesis of (XIX) involves condensation of quinizarin with 2-methyl-4-*n*-butylaniline followed by bromination and sulfonation of the dye base.[106] The amine can be prepared by condensing *o*-toluidine with *n*-butyl alcohol in the presence of zinc chloride at 220–250°.[107]

If *o,o′*-disubstituted arylamines bearing an aryloxy group in the para position are used in the quinizarin condensation reaction, a slight bathochromic shift in the dyes is observed. This effect is illustrated by the dye (XX) which gives slightly greener dyeings than Brilliant Alizarine Milling Blue BL. Like dyes (XVIII) and (XIX) above, it has good wet-fastness.[108]



(XX)

A minor bathochromic shift of the quinone bands and an increased intensity of the benzophenone bands occur when the anthraquinone nucleus is substituted in one or more of the 5-, 6-, 7-, and 8-positions. Hence the sulfonated condensation product of 6,7-dichloroquinizarin



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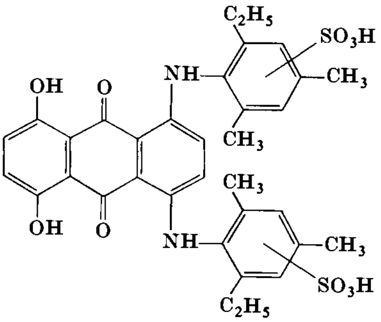
[106] ICI, *BP* 514,770.

[107] J. Reilly and W. J. Hickinbottom, *J. Chem. Soc.* **117**, 133 (1920).

[108] Gy, *USP* 2,859,221.

with mesidine is a greenish blue. This dye is faster to milling but somewhat duller than the unchlorinated analog.[109]

If the 5- and 8-positions of the anthraquinone nucleus bear hydroxyl groups which increase the polarizability, the shade is more of a green-blue. An example is the greenish blue of the following structure,[94] which has very good fastness properties.



2. *1,4-Diaralkylamino- and Diaralkylcycloalkylaminoanthraquinones*

Dyes formed by condensation of quinizarin with aliphatic or cycloaliphatic amines are bright greenish to reddish blues and are similar to the dyes containing *o,o′*-disubstituted anilino groups. Because of their brilliance their preparation has received much attention in the past two decades. These dyes are obtained by the usual method involving condensation of leucoquinizarin with the amine, oxidation of the leuco compound, and conversion into the dye. For this purpose amines are selected which can react with sulfuric acid to form an aryl sulfonic acid or sulfate ester. Further, it is desirable for the nitrogen to be attached to a secondary carbon atom, as dyes formed from straight-chain aliphatic amines have inferior lightfastness on wool.

The oldest dye of this type is *Alizarine Brilliant Sky Blue SE* (CI Acid Blue 35), which is produced by condensing a mixture of quinizarin and leucoquinizarin with 2-aminotetralin in a higher alcohol, followed by sulfonation of the dye base.[110] This dye gives bright blue dyeings of good lightfastness, but only moderate wet-fastness on wool. The amine is obtained by partial reduction of β-naphthylamine with sodium in amyl alcohol.[111]

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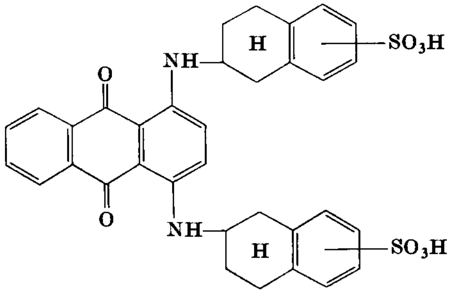
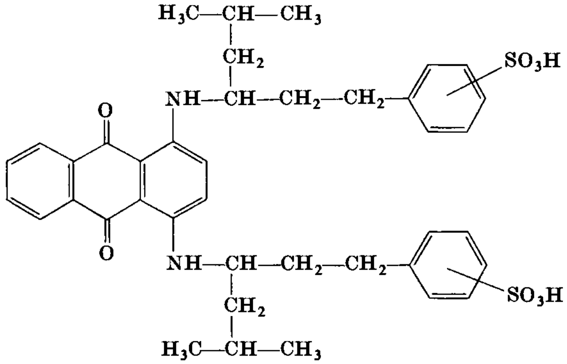
[109] S, *USP* 2,315,788.

[110] BIOS, *1484*, 43.

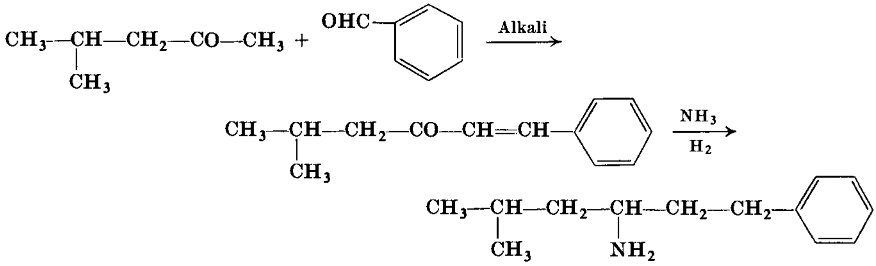
[111] E. Bamberger and R. Müller, *Chem. Ber.* **21**, 850 (1888); E. Bamberger and M. Kitschelt, *ibid.* **23**, 876 (1890).



Very bright blue dyes such as



are prepared by condensation of leucoquinizarin with aralkyl amines in a solvent such as alcohol, oxidation with air, and sulfonation of the dye base with concentrated sulfuric acid.[112] This dye has very good wetfastness and good lightfastness properties. Like the majority of milling type dyes, it also shows poor coverage of barry nylon. The amine can be obtained by a Claisen-Schmitt condensation of isobutyl methyl ketone with benzaldehyde in alkaline medium[113] followed by reductive amination of the resulting ketone for conversion into the amine.[39]



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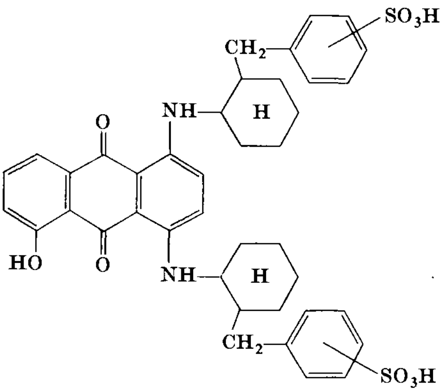
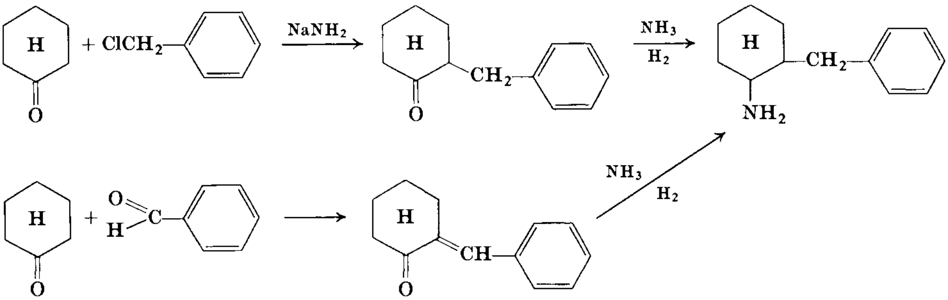
[112] FBy, *DBP* 1,099,669.

[113] C. V. Gheorghiu and B. Arwentiew, *J. Prakt. Chem.* [2] **118**, 297 (1928).

An equally bright but more greenish blue is obtained when leuco-1,4,5-trihydroxyanthraquinone is condensed with 2-benzylcyclohexylamine and the dye base sulfonated.[114]



The amine can be prepared either by condensation of benzyl chloride and cyclohexanone in the presence of sodium amide[115] and reductive amination of the resulting ketone[39] or by reaction of benzaldehyde with cyclohexanone[116] and hydrogenation of the 2-benzylidene cyclohexanone in liquid ammonia.[114] Alternatively, the desired amine may be prepared from the oxime of the 2-substituted cyclohexanone, followed by reduction.[117]



Condensation of leuco-1,4,5,8-tetrahydroxyanthraquinone with 2-hydroxyethylamine and oxidation of the leuco compound yields a

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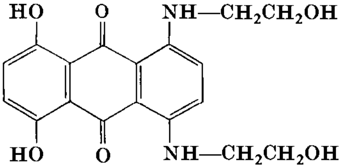
[114] ICI, *BP* 564,859.

[115] M. Tiffeneau and M. Porcher, *Bull. Soc. Chim. France* [4] **31**, 331 (1922).

[116] J. D. Billimoria, *J. Chem. Soc.* p. 1126 (1955); R. Cornubert, G. Barraud, M. Cormier, M. Descharmes, and H. G. Egger, *Bull. Soc. Chim. France* p. 404 (1955).

[117] C. Schöpf and E. Boettcher, *Ann. Chem.* **448**, 7 (1926).

dye base which is of no importance as an intermediate for acid dyes but is marketed as a blue-green disperse dye under the name *Celliton Fast Blue Green B* (CI Disperse Blue 7).[118]



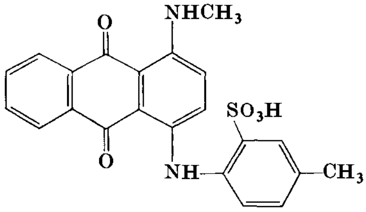
B. UNSYMMETRICALLY SUBSTITUTED 1,4-DIAMINOANTHRAQUINONES

1. *1-Alkylamino- and 1-Cycloalkylamino-4-arylaminoanthraquinones*

As previously stated, dyes with two sulfonic acid groups usually do not cover barry nylon sufficiently and show poor behavior in combination with monosulfonated dyes (blocking effect). Any attempt to introduce a single sulfonic acid group into 1,4-diarylamino- or diaralkylamino-anthraquinones results in a mixture of monosulfonated and disulfonated species, often containing some unsulfonated dye base. The latter is likely to have an adverse effect on the fastness properties, such as the rubbing fastness.

If level-dyeing nylon dyes are desired, it is preferable to use unsymmetrically substituted 1,4-diaminoanthraquinones bearing only one aromatic ring for sulfonation.

A member of this class which has been used for a great many years in wool dyeing is *Acilan Astrol B* (CI Acid Blue 27).[119] This dye is obtained



by condensation of 1-methylamino-4-bromoanthraquinone with *p*-toluidine in the presence of alkali and a copper catalyst and subsequent sulfonation of the dye base. It dyes wool greenish blue, with moderate wet-fastness and relatively poor lightfastness.

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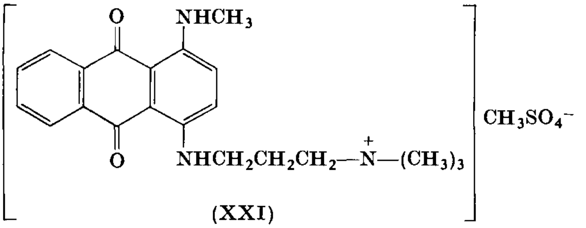
[118] BIOS, *1484*, 59.

[119] BIOS, *1484*, 24.

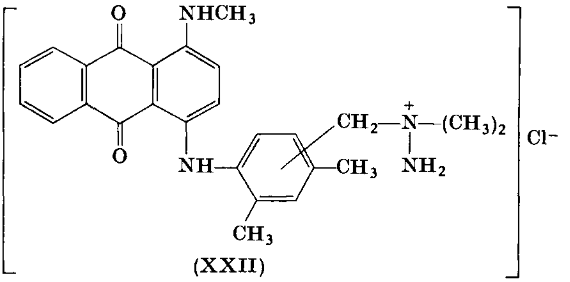
The dye base is also used for the mass coloration of polystyrene.

1-Methylamino-4-bromoanthraquinone can be prepared either by reaction of anthraquinone-1-sulfonic acid (potassium salt) with methylamine in the presence of nitrobenzene–sulfonic acid as oxidizing agent, or by condensation of 1-chloro- or 1-nitroanthraquinone with methylamine. This is followed by bromination of the 1-methylaminoanthraquinone in concentrated hydrochloric acid.[120]

1-Methylamino-4-bromoanthraquinone is also used as an intermediate in the synthesis of cationic dyes for acrylic fibers. Two examples of these dyes are (XXI) and (XXII).[121]

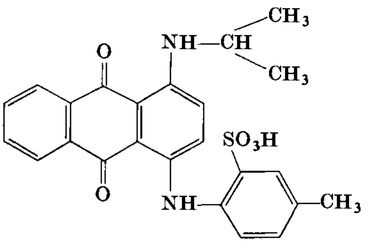


(XXI)



(XXII)

The moderate lightfastness of Acilan Astrol B on wool can be improved by the introduction of an alkylamino group having a secondary carbon atom alpha to the imino group. An example is the following blue dye:



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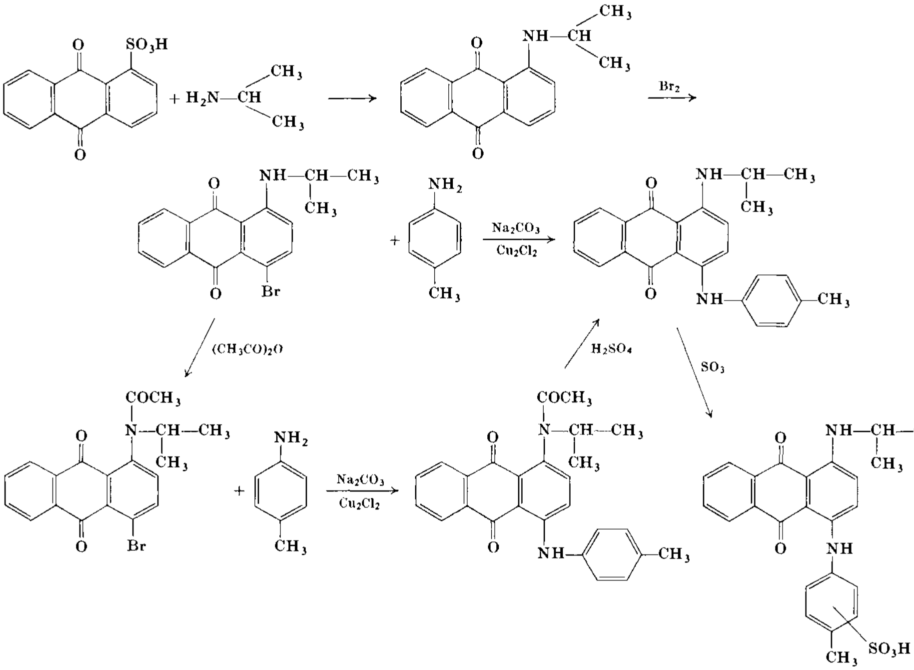
[120] BIOS, *1484*, 19.

[121] FBy, *DBP* 1,150,652; S, *FP* [86,220/1,325,176].

Its synthesis[122] starts with the nucleophilic displacement of the sulfonic acid group of anthraquinone-1-sulfonic acid by isopropylamine. The 1-isopropylaminoanthraquinone is brominated in the 4-position, then condensed with *p*-toluidine, and finally sulfonated in weak oleum. A higher yield is achieved when the alkylamino group is acetylated prior to substitution of the bromine atom. The acetyl group is removed by hydrolysis before or after sulfonation.



Similar dyes are obtained by condensation of 1-isopropylamino-4-bromoanthraquinone with 1-amino-4′-methyldiphenyl ether[123] or 1-amino-4-acetylaminobenzene.[124]

A more greenish dye is formed when 1-amino-4-cyclohexylamino-anthraquinone-2-sulfonic acid is desulfonated and the amino group condensed with *p*-bromophenetol in the presence of sodium carbonate and cuprous chloride. The condensation product is finally sulfonated.[125]

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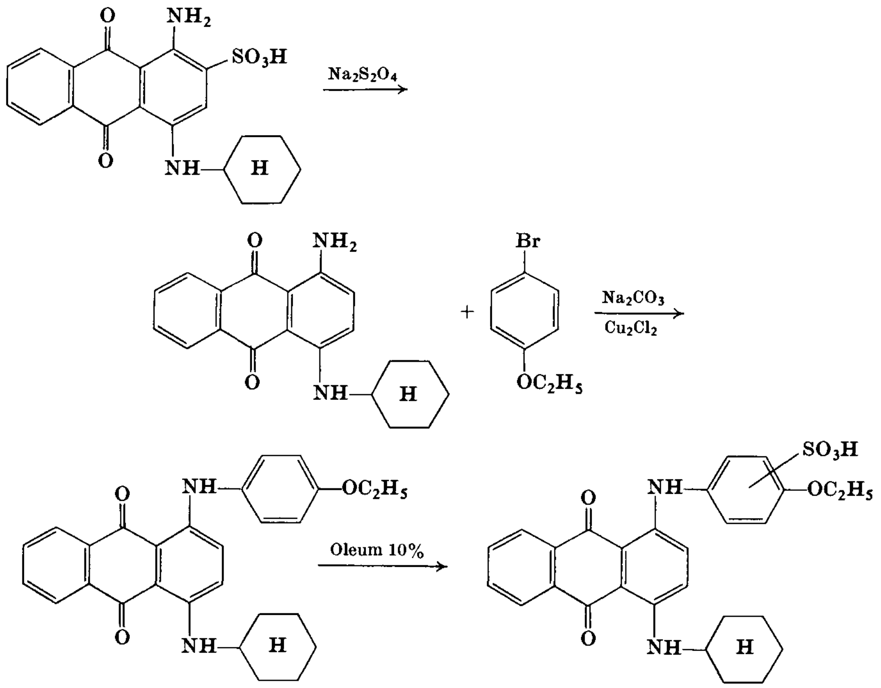
[122] Gy, *FP* 1,461,074.

[123] Gy, *FP* 1,470,511.

[124] Gy, *SP* 467,835.

[125] S, *USP* 3,320,021.



The dyeings on nylon from neutral medium have good light- and wet-fastness.

If 1-amino-4-cyclohexylaminoanthraquinone is condensed with bromomesitylene instead of bromophenetol, a dye is obtained whose shade shows a hypsochromic shift due to the *o,o'*-disubstitution on the arylamino residue.[126] This dye gives blue dyeings on nylon with good fastness properties.

2. *1-Alkylamino- and 1-Cycloalkylamino-4-aralkylaminoanthraquinones*

The dyes of this type are very bright blues. They are comparable in brilliance with those from 1,4-diaralkylamino- and cycloalkylamino-anthraquinones and are well suitable for nylon dyeing.

The synthesis of a typical representative of this series is shown below. 1-Amino-4-cyclohexylaminoanthraquinone is reacted with acrylic acid and the resulting carboxylic acid condensed with aniline in the presence of phosphorus trichloride to give the dye base, which is then sulfonated.[127]

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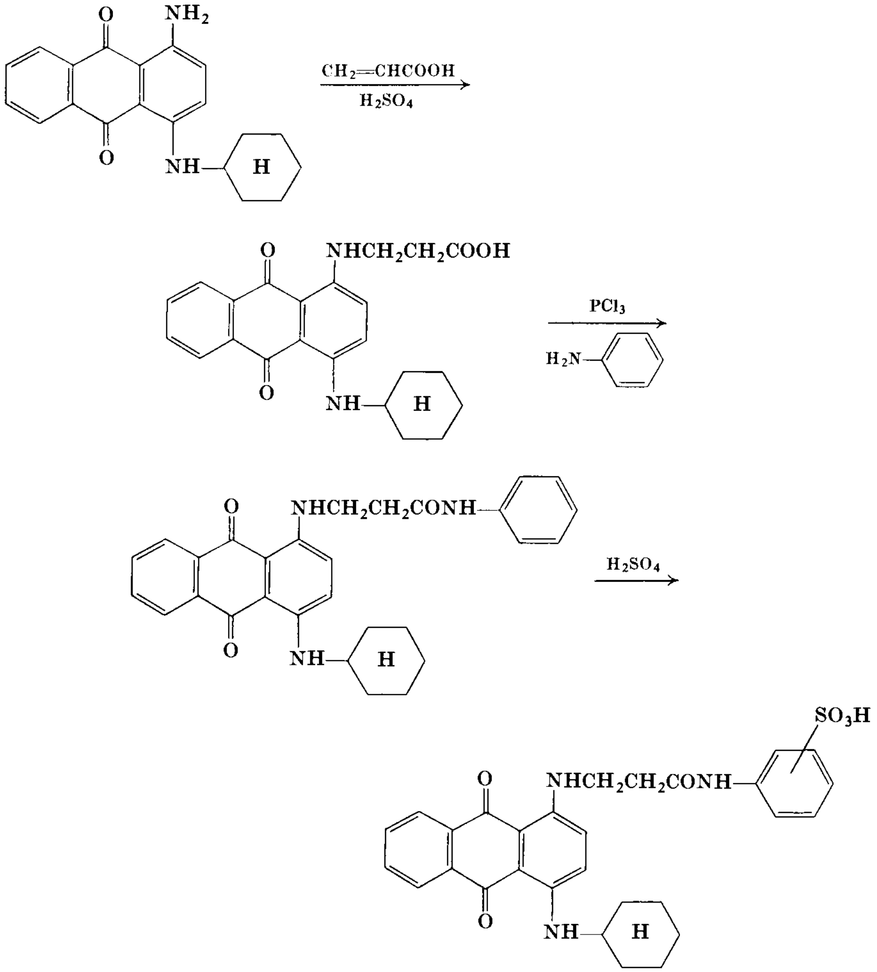
[126] S, *USP* 3,420,856.

[127] S, *FP* 1,536,591; 1,470,597; 1,392,211.



It dyes nylon a brilliant blue shade with good fastness properties. Its lightfastness on wool is moderate due to the primary carbon atom on the imino group.

Dyes of similar shade with good leveling properties are obtained when, e.g., 1-isopropylamino-4-bromoanthraquinone is acetylated and the acetyl derivative condensed with 1-methyl-3-phenylpropylamine in the presence of alkali and a copper catalyst. After removal of the acetyl group the resulting dye base is sulfonated.[128] The dye base can also be

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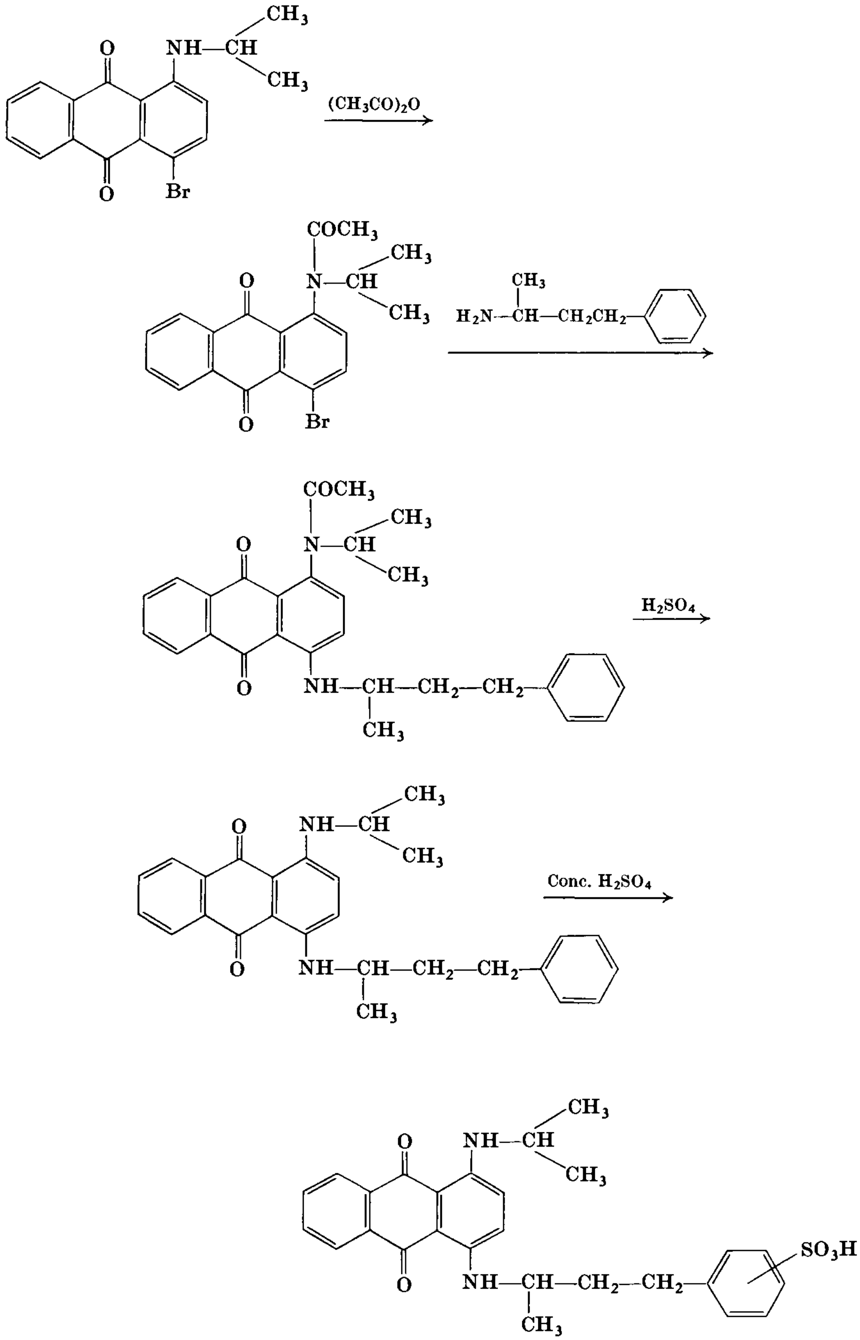
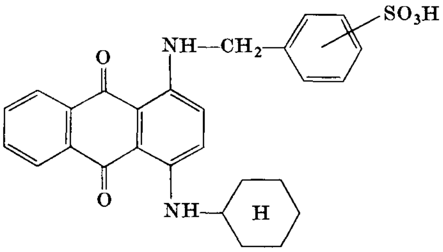
[128] Gy, *USP* 3,431,285.


(CH3CO)2O
CH3
H2N—CH—CH2CH2—
H2SO4
Conc. H2SO4
NH—CH
CH3
CH3
COCH3
N—CH
Br
O
NH—CH—CH2—CH2—
SO3H

prepared by a one-step condensation of 1-isopropylamino-4-bromoanthraquinone with an aralkylamine in the presence of acetate and cuprous chloride. However, this reaction is less homogeneous. Since both carbon atoms alpha to the imino groups are secondary, the dye has good lightfastness on wool.

The 1-methyl-3-phenylpropylamine is prepared by a Claisen-Schmitt reaction between acetone and benzaldehyde[129] followed by reductive amination.[39]

The following dye is based on an interesting preparatory method:



It is obtained if 1-amino-4-cyclohexylaminoanthraquinone is condensed with benzyl alcohol in the presence of iodine, and the dye base sulfonated.[130] This dye gives brilliant reddish blue dyeings on nylon with good wet- and lightfastness properties.

C. 1,4-DIAMINOANTHRAQUINONES SUBSTITUTED IN THE 2- AND IN THE 2- AND 3-POSITIONS

Only a limited number of commercial dyes of this type have achieved any importance. *Supracen Violet 3R* (CI Acid Violet 42) is obtained by condensation of 1,4-diamino-2,3-dichloroanthraquinone with phenol in the presence of alkali and subsequent sulfonation.[131] If the reaction is carried out in the presence of sodium sulfite and manganese dioxide, the product is *Supracen Violet 4BF* (CI Acid Violet 41).[132] Supracen Violet 3R gives reddish violet dyeings, while Supracen Violet 4BF dyes a bluish violet.

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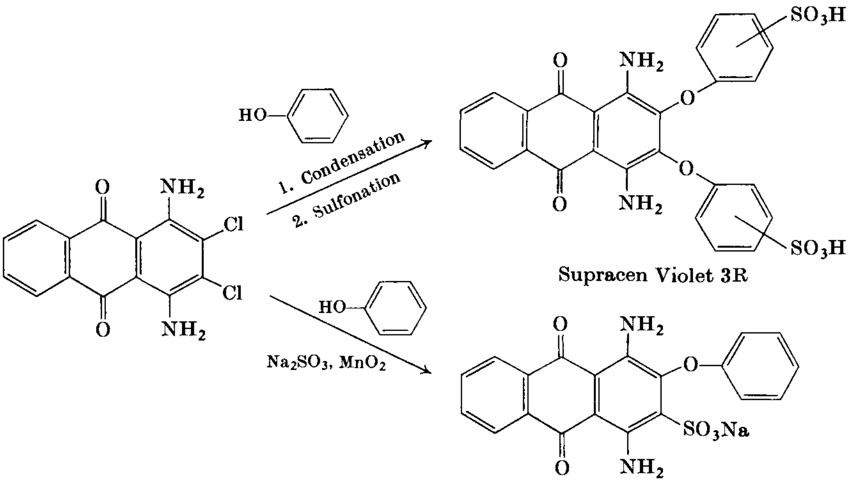
[129] N. L. Drake and P. Allen, *Org. Syn.* **3**, 17 (1923).

[130] S, *DBP* 1,807,746.

[131] BIOS, *1484*, 48.

[132] BIOS, *1484*, 49.



Supracen Violet 3R

Supracen Violet 4BF

The intermediate 1,4-diamino-2,3-dichloroanthraquinone is prepared by chlorination of 1,4-diaminoanthraquinone with sulfuryl chloride in chlorobenzene.[133]

The 1,4-diaminoanthraquinones and 1-amino-4-arylaminoanthraquinones substituted either in the 2- or in the 2- and 3-positions display a considerable hypsochromic shift, which can be explained in terms of the partial chromophore method. If the electron-accepting sulfonic acid group in the 2-position of the previously discussed bromaminic acid derivatives is replaced by an electron-donating group such as an alkyl, alkoxy, or aryloxy group, an excited structure with this donor as a pole will result. Thus the introduction of electron-donating substituents in the 2- or in the 2,3-positions of 1,4-diaminoanthraquinones and 1-amino-4-arylaminoanthraquinones induces a very marked hypsochromic shift of the quinone and benzophenone bands. A sulfonic acid group, however, and likewise halogen, prevents polarization in this direction. In most instances the benzophenone bands are located in the ultraviolet region. If electron-donating substituents are present in both positions, the hypsochromic effect is intensified (see Fig. 2, example IV). Compounds containing a sulfonic acid group or halogen in the 2-position are distinctly blue, while the dyes substituted by an alkyl, alkoxy, or aryloxy group are bluish to reddish violet.

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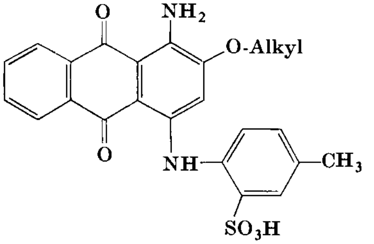
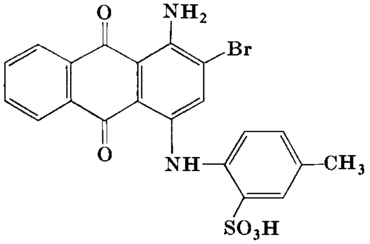
[133] BIOS, *1493*, 18.

The following two compounds illustrate the above discussion:

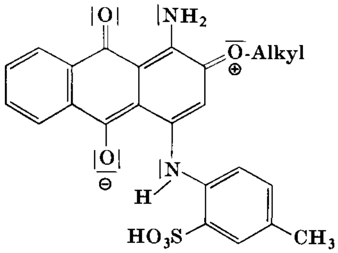


(XXIII)

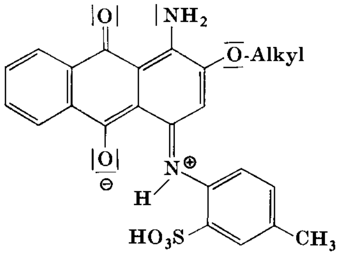


(XXIV)

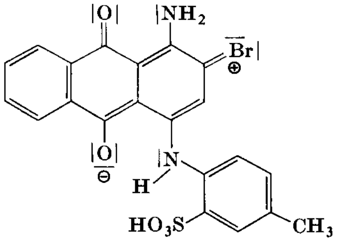
To the excited quinone resonance forms corresponding to compound (XXIII), structure (XXIIIA) contributes substantially and therefore a hypsochromic shift occurs. In compound (XXIV), however, structure (XXIVB) is the preferred form. The same can be said for the benzophenone resonance structures. In compound (XXIII) structure (XXIIIA′) makes an important contribution. Whereas in compound



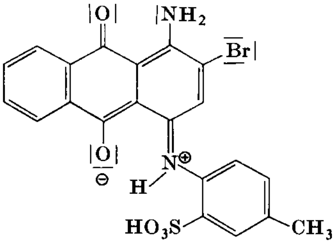
(XXIIIA)



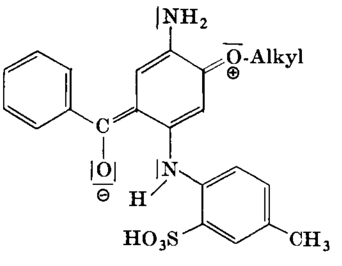
(XXIIIB)



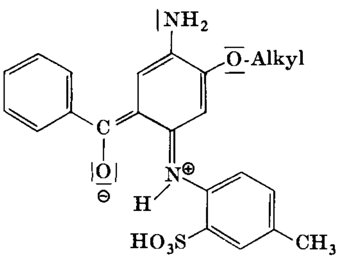
(XXIVA)



(XXIVB)

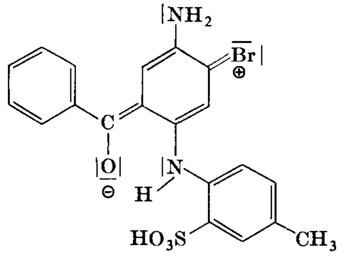


(XXIIIA′)

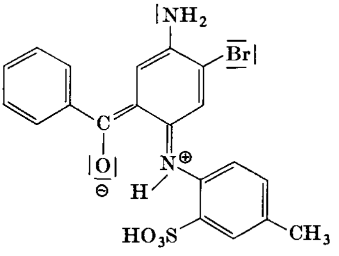


(XXIIIB′)

(XXIV), structure (XXIVB′) again is the favored form. The pronounced



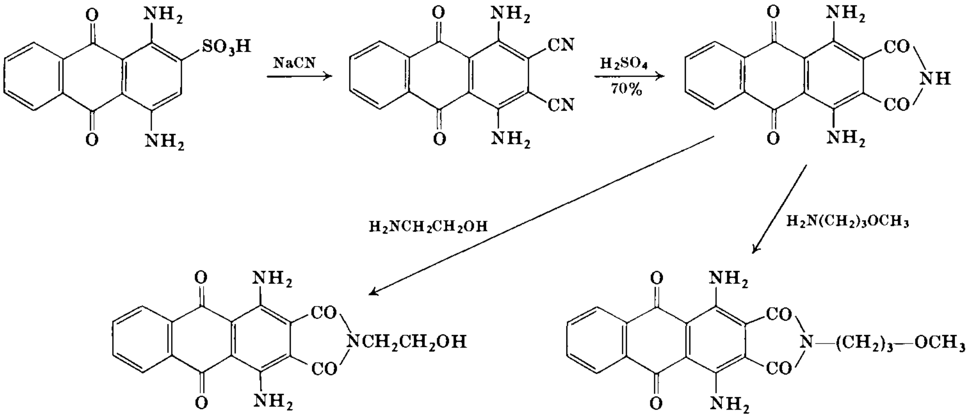
(XXIVA′)



(XXIVB′)

hypsochromic shifts of the quinone and benzophenone bands which are observed in (XXIII) compared to those of (XXIV) may be understood on this basis. Compound (XXIII) is violet, whereas (XXIV) is a blue.

In this context it may be noted that 1,4-diaminoanthraquinone-2-sulfonic acid[134] gives violet dyeings of only low wet-fastness. Although of no importance as an acid anthraquinone dye, it is used as a starting material for the preparation of turquoise disperse dyes such as the following two[135]:



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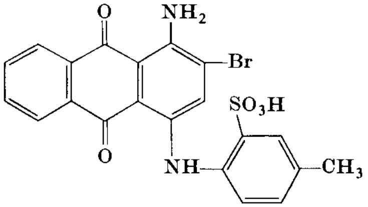
[134] BASF, *FP* 1,273,712; AGFA, *DRP* 293,100.

[135] DuP, *USP* 2,628,963; 2,753,356.

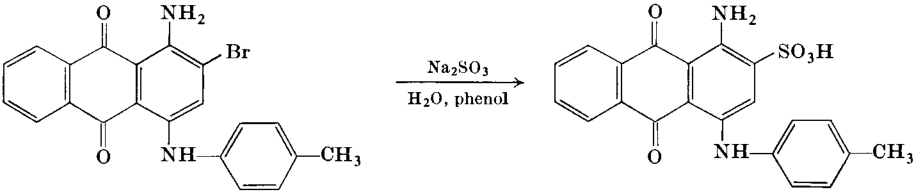
D. 1-AMINO-4-ARYLAMINOANTHRAQUINONES WITH A SUBSTITUENT OTHER THAN A SULFONIC ACID GROUP IN THE 2-POSITION

This class comprises reddish blue to violet dyes. Although some of them are among the oldest acid anthraquinone dyes known, they have retained a certain commercial importance.

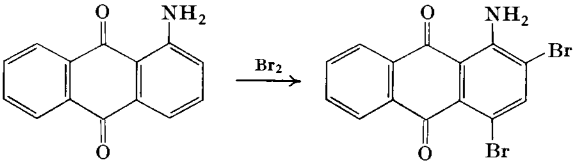
One of the classical members is *Alizarine Sky Blue B* (CI Acid Blue 78),[136] a rather dull blue with moderate wet-fastness but good leveling properties. To obtain the dye base, 1-amino-2,4-dibromoanthraquinone is condensed with *p*-toluidine in the presence of alkali and a copper catalyst. Only the bromine atom in the 4-position is displaced, being much more mobile than the other.



If the monobromo derivative is treated with sodium sulfite in aqueous phenol solution under pressure, the bromine atom in the 2-position reacts as well and the same dye is obtained as from *p*-toluidine and bromaminic acid.[137]



The 1-amino-2,4-dibromoanthraquinone can be prepared by bromination of 1-aminoanthraquinone in nitrobenzene solution or in aqueous acid suspension.[138]



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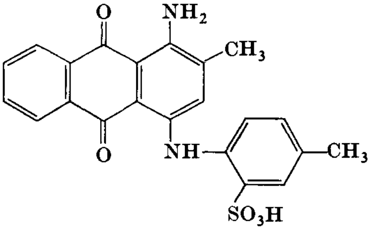
[136] BIOS, *1484*, 38.

[137] FBy, *DRP* 288,878.

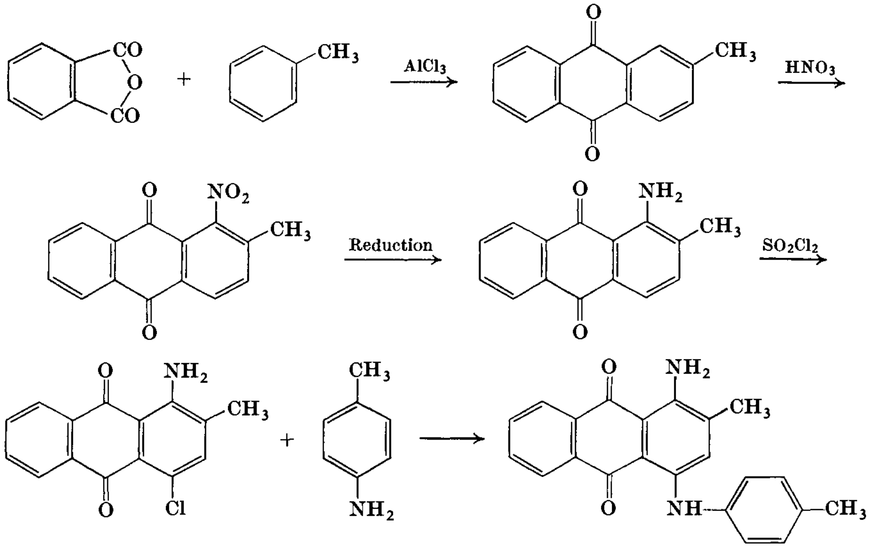
[138] BIOS, *1484*, 6; F. Ullmann and O. Eiser, *Chem. Ber.* **49**, 2165 (1916).

Although Alizarine Sky Blue B is an economical dye, it cannot be used for combination dyeings, in particular for green shades with certain yellow azo dyes, because of catalytic fading. The term refers to the rapid fading shown by combination dyeings of dye which in themselves have good lightfastness. It is believed that by photolysis one of the components sensitizes the photooxidative degradation of the other, thus changing the shade in favor of the more stable dye.

If the 2-position of the anthraquinone nucleus is occupied by an alkyl group instead of bromine, a hypsochromic shift is observed. *Acilan Fast Blue RX* (CI Acid Blue 47) is a reddish leveling blue with unsatisfactory wet-fastness properties.[139]



The dye base can be obtained by the following route:



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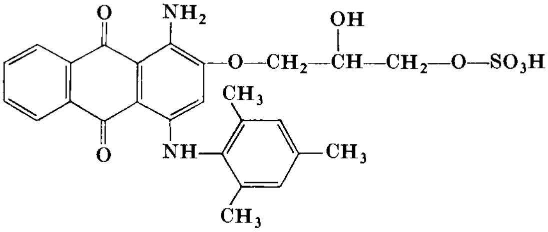
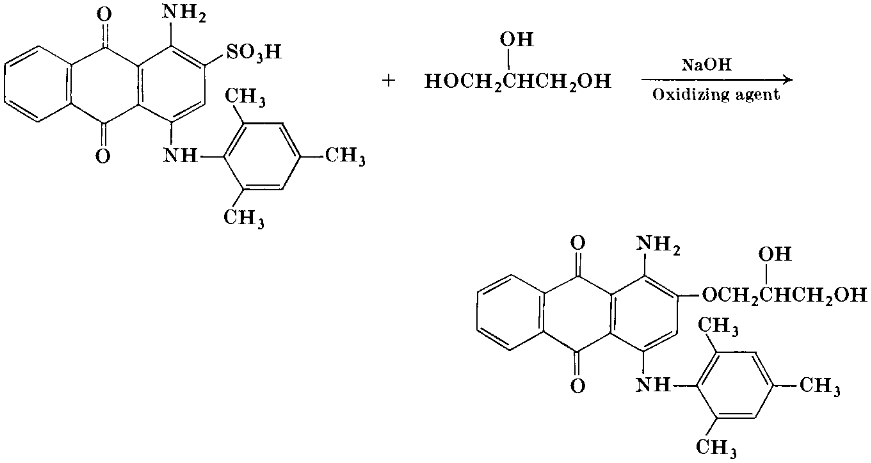
[139] BIOS, *1484*, 31.

The 2-methylanthraquinone is obtained from phthalic anhydride and toluene by a Friedel-Crafts reaction. It is then nitrated and reduced to give 1-amino-2-methylanthraquinone. Upon chlorination with sulfuryl chloride, 1-amino-2-methyl-4-chloroanthraquinone is obtained, which is condensed with *p*-toluidine. Sulfonation yields the dye.

An alkoxy or aryloxy group in the 2-position invariably results in violet dyes (cf. Supracen Violet 3R and 4BF). Thus the dye of the following structure



produces brilliant reddish violet dyeings of good light- but moderate wet-fastness.[140] Water solubility is imparted by a sulfato group, obtained upon esterification of the glycerin side chain with sulfuric acid. Preparation of the intermediate starts with 1-amino-4-mesidinoanthraquinone-2-sulfonic acid (Brilliant Alizarine Sky Blue BS), which is condensed with glycerin in the presence of an oxidizing agent such as *m*-nitrobenzenesulfonic acid:



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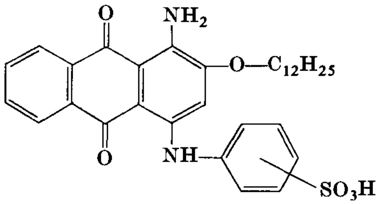
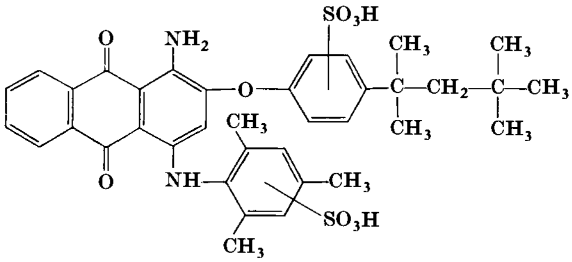
[140] S, *USP* 2,117,569.

For dyes with better wet-fastness properties, aliphatic alcohols having long carbon chains or substituted phenols are used. Dyes of this type are *Carbolan Violet 2R* (CI Acid Violet 51),[141] the sulfonated condensation product of 1-amino-4-anilinoanthraquinone-2-sulfonic acid with dodecyl alcohol

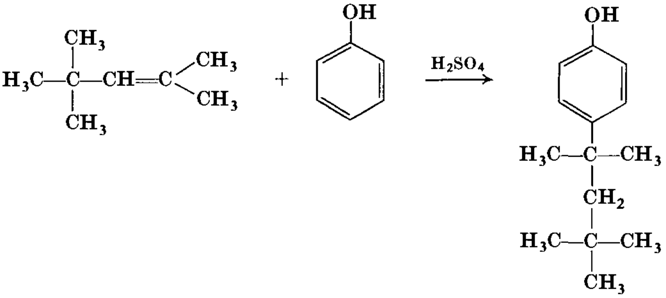


and the milling violet obtained by condensation of 1-amino-4-mesidinoanthraquinone-2-sulfonic acid with *p-tert*-octylphenol and subsequent sulfonation of the resulting dye base.[142]



Both are reddish violet dyes with very good wet-fastness properties.

The *p-tert*-octylphenol is prepared by condensing diisobutylene with phenol in sulfuric acid.[143]



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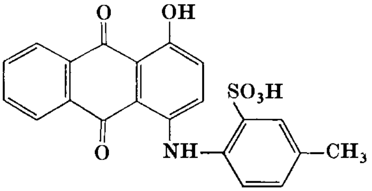
[141] ICI, *BP* 430,160.

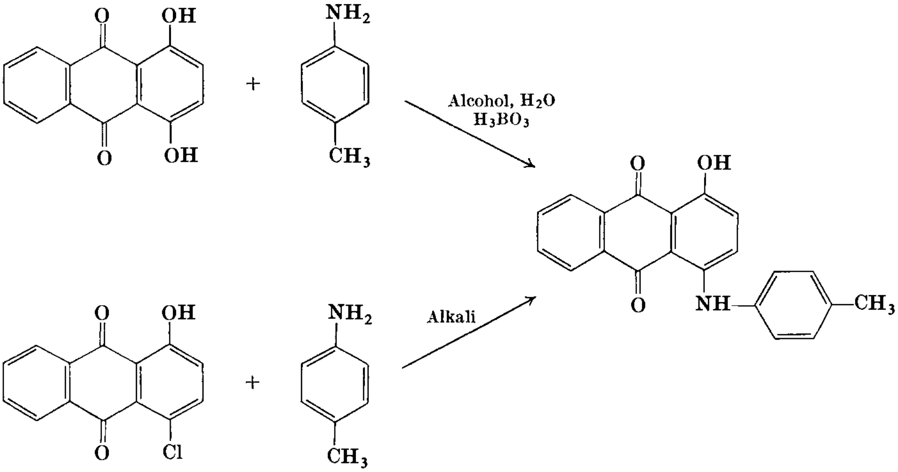
[142] S, *USP* 2,580,190.

[143] J. B. Niederl, *Ind. Eng. Chem.* **30**, 1269 (1938); J. H. Simons and S. Archer, *J. Am. Chem. Soc.* **62**, 451 (1940).

E. 1-HYDROXY-4-AMINOANTHRAQUINONES

A well-known dye of this type is *Supracen Violet 3B* (CI Acid Violet 43).[67] It is moderately wet-fast but due to the hydroxyl group it is sensitive to chromium ions and alkali. The starting materials are the same as for the synthesis of Alizarine Cyanine Green G, namely quinizarin, leucoquinizarin, and *p*-toluidine. Since the reaction is carried out in aqueous alcohol, predominantly monocondensation takes place. In an alternative method, 1-hydroxy-4-chloroanthraquinone is condensed with *p*-toluidine.[144]





Only a few representatives of the 1-amino-2-aryloxy-4-hydroxyanthraquinone type are commercially important, such as those produced by condensation of 1-amino-4-hydroxy-2-bromoanthraquinone with phenols in the presence of alkali, followed by sulfonation of the dye base, as for example[145]:

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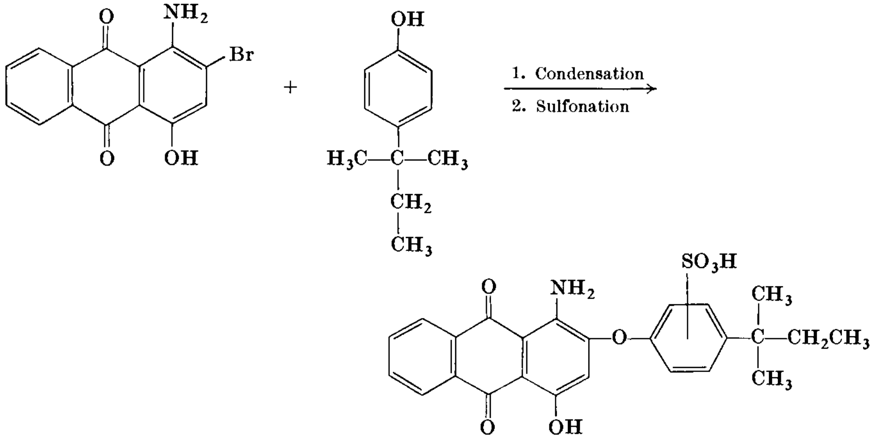
[144] F. Ullmann and A. Conzetti, *Chem. Ber.* **53**, 835 (1920).

[145] Crompton and Knowles Corp., *FP* 1,478,768; 1,478,769.



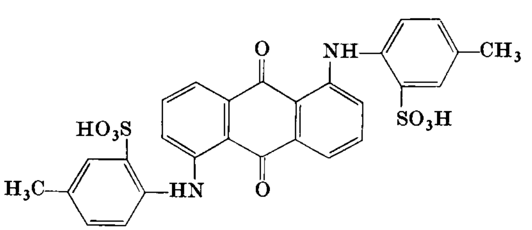
This dye gives a brilliant bluish red on nylon, which has good light- and wet-fastness properties, but is sensitive to alkali.

Some of the unsulfonated dyes obtained by condensation of 1-amino-2-bromo-4-hydroxyanthraquinone with alcohols or phenols are used as red disperse dyes.[146]

The 1-amino-2-bromo-4-hydroxyanthraquinone is prepared by hydrolysis of 1-amino-2,4-dibromoanthraquinone in concentrated sulfuric acid in the presence of boric acid.[147]

F. 1,5-DIAMINOANTHRAQUINONES

A dye of this type seldom used today is *Anthraquinone Violet* (CI Acid Violet 34), which contains the following compound[148]:



The dye base is obtained by condensing 1,5-dichloro- or 1,5-dinitroanthraquinone with *p*-toluidine. In the synthesis of the starting material

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[146] CIBA, *USP* 3,174,983.

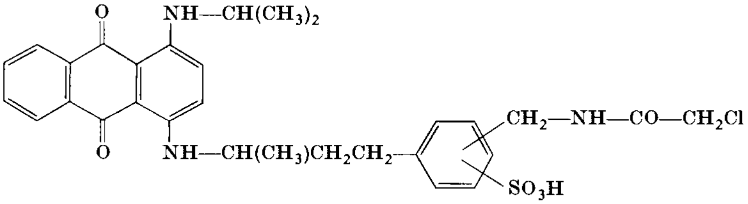
[147] BIOS, *1484*, 5.

[148] BIOS, *1484*, 51.

the 1,8-isomer is invariably formed in considerable quantity. As separation of the isomers is laborious, the commercial dye consists of a mixture of the sulfonated 1,5- and 1,8-di-*p*-toluidinoanthraquinones.

G. REACTIVE 1,4-DISUBSTITUTED ANTHRAQUINONE DYES

Since reactive dyes are reviewed in another chapter, only one example will be cited, namely, the blue of the following structure:



It is synthesized by condensation of 1-isopropylamino-4-(1′-methyl-3′-phenylpropylamino)anthraquinone with *N*-hydroxymethyl chloroacetamide in concentrated sulfuric acid; sulfonation simultaneously occurs.[149] On wool it has very good all-round fastness.

The *N*-hydroxymethyl compound is prepared by the Einhorn method, reacting chloroacetamide with formaldehyde in the presence of a basic catalyst such as potassium carbonate.[34]

H. HETEROCYCLIC ANTHRAQUINONE DERIVATIVES

The dyes discussed in the previous sections have shown that by suitable substitution of the anthraquinone nucleus, shades from reddish violet through blue to yellowish green can be produced. In another approach the structure of the anthraquinone skeleton itself may be modified by forming five- or six-membered heterocyclic rings on the meso position. Pronounced hypsochromic shifts result, permitting the range of shades to be extended to the red and even the yellow regions.

Although 1-methylamino-4-*p*-toluidinoanthraquinone is greenish blue, the formation of a pyridone ring gives rise to a bluish red. This is due to the fact that the long-wave absorption bands assignable to the diene–dione chromophore have undergone a considerable hypsochromic shift compared with those of the original quinone chromophore (see Fig. 2, example V). *Supracen Red 3B* (CI Acid Red 80) is formed by acetylation of 1-methylamino-4-bromoanthraquinone and ring closure

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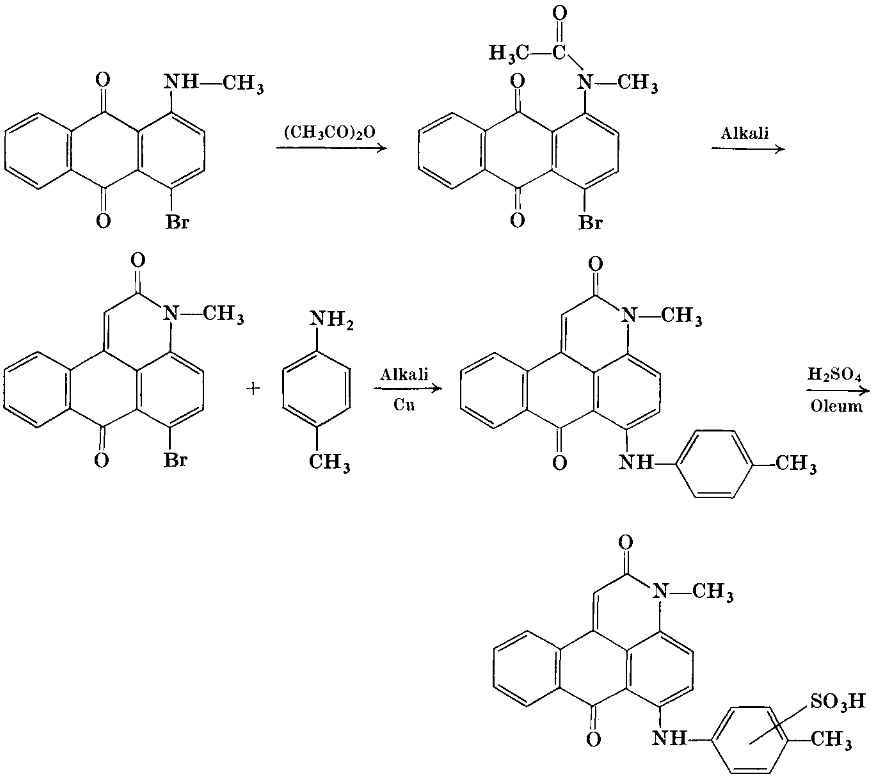
[149] Gy, *USP* 3,431,285.

to anthrapyridone in the presence of alkali, condensation of the anthrapyridone with *p*-toluidine, and sulfonation of the resulting dye base.[150]



Acetylation and cyclization of 1-methylamino-4-toluidinoanthraquinone lead to the same dye. It gives bright bluish red shades on wool and nylon, but has only moderate light- and wet-fastness properties.

The reaction of 1-amino-2-methyl-4-bromoanthraquinone with malonic acid diethyl ester in nitrobenzene in the presence of potassium acetate yields the bromoanthrapyridone. Upon condensation with *p*-toluidine[151] and subsequent sulfonation, the brilliant bluish red dye ***Brilliant Alizarine Light Red 4B*** (CI Acid Violet 26) is obtained, which has fairly good lightfastness and moderately good wet-fastness properties.[152]

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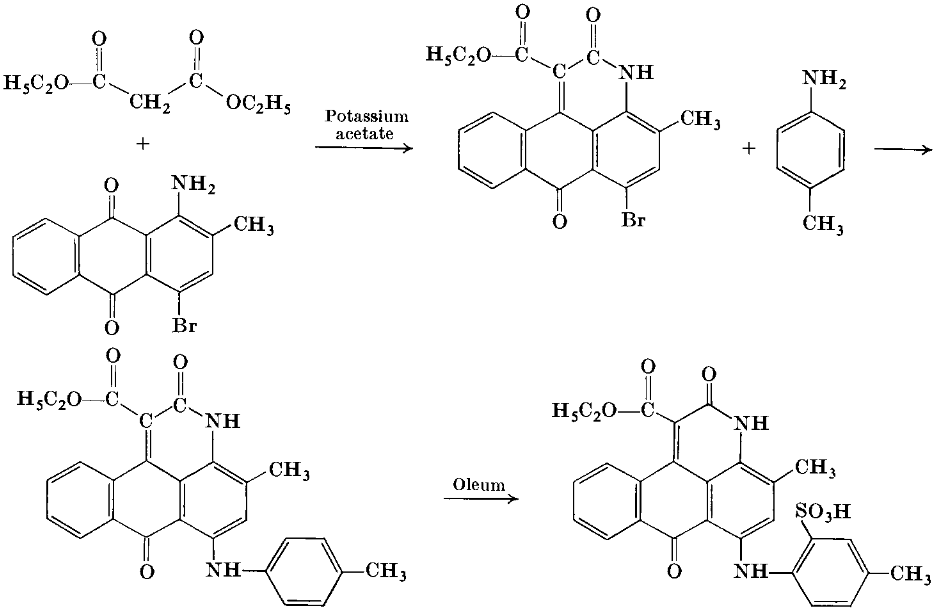
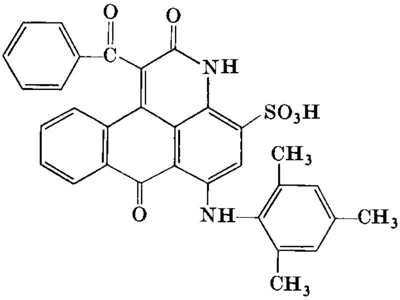
[150] BIOS, *1484*, 46.

[151] S, *USP* 1,891,317.

[152] S, *USP* 1,912,301.



A similar bluish red dye with good fastness on wool and nylon is the following:



It is prepared by reacting 1-amino-4-mesidinoanthraquinone-2-sulfonic acid with benzoylacetic acid ethyl ester in the presence of sodium acetate in phenol solvent.[153]

A red with excellent wet-fastness is obtained by condensation of Acilan Direct Blue A with *p-tert*-amylphenol, ring closure of the inter-

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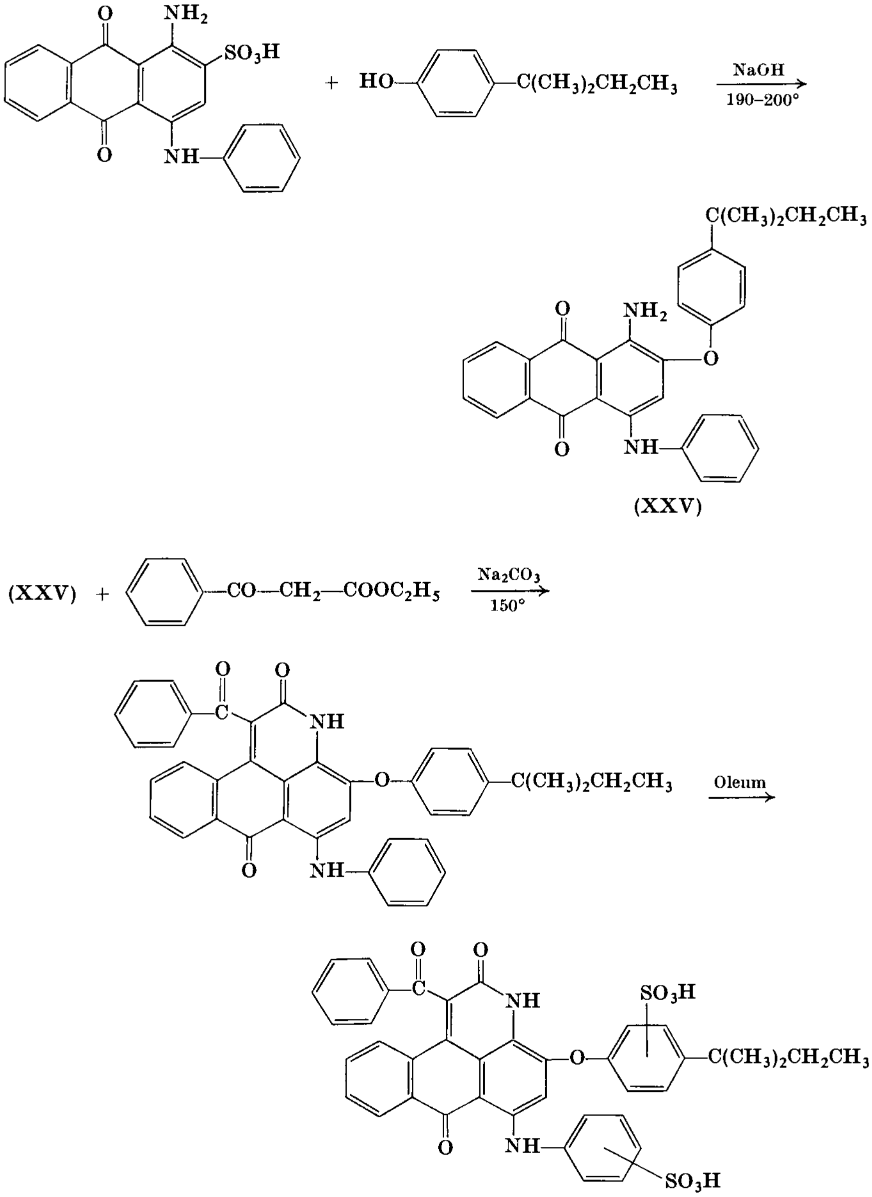
[153] S, *FP* 1,046,856.

mediate with benzoylacetic ester to the anthrapyridone, and subsequent sulfonation.[154]

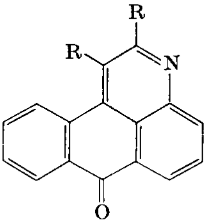


(XXV)

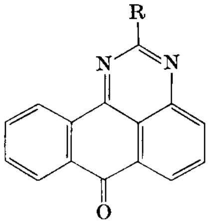
[154] S, *USP* 2,644,821.

Since the red acid dyes of the azo series are generally much more economic than these anthraquinone types, the latter have gained only a modest commercial position in spite of their great brilliance.

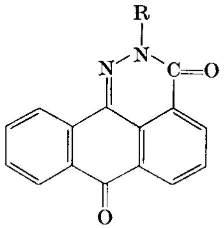
Yellow to red acid anthraquinone dyes are derived from anthrapyridine,[155] anthrapyrimidine,[156] anthrapyridazone,[157] anthrapyrazole,[158] and isothiazolanthrone.[159]



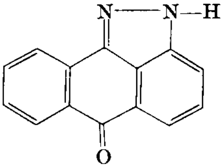
Anthrapyridine



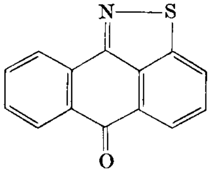
Anthrapyrimidine



Anthrapyridazone

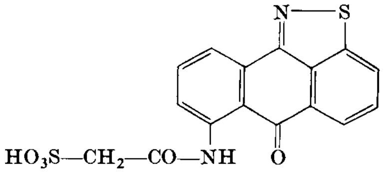


Anthrapyrazole



Isothiazolanthrone

For example, the following yellow, with an isothiazolanthrone structure



is obtained when 5-amino-1,9-isothiazolanthrone is acylated with chloroacetyl chloride and the chlorine atom subsequently replaced with a sulfo group by reaction with sodium sulfite.[159] 5-Amino-1,9-

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[155] S, *USP* 2,759, 939; 2,759,940.

[156] ICI, *USP* 2,778,831; FBy, *USP* 1,004,107; IG, *DRP* 633,599.

[157] F. Ullmann, *DRP* 248,998; F. Ullmann and W. Minajeff, *Ann. Chem.* **388**, 217 (1912); A. Schaarschmidt, *Chem. Ber.* **48**, 834 (1915).

[158] FBy, *DBP* 1,257,149; F. Mayer and R. Heil, *Chem. Ber.* **55**, 2155 (1922).

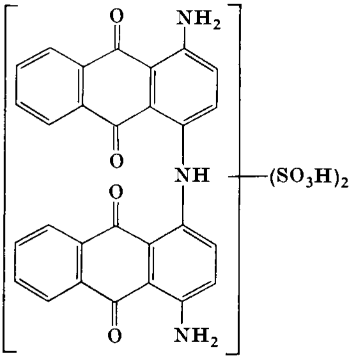
[159] S, *USP* 2,733,976.

isothiazolanthrone is prepared by reacting 5-nitroanthraquinone-1-sulfonic acid with sodium polysulfide and ammonia at elevated temperature and pressure. The nitro group is thereby reduced to an amino group and a 5-amino-1-mercaptoanthraquinone intermediate is formed, which then undergoes ring closure with ammonia under the influence of polysulfide.

These chromophoric systems have not gained acceptance in acid dyes, since they are generally of low tinctorial strength compared with azo dyes of similar shade.

J. DIANTHRIMIDES AND CARBAZOLES

The dyes of the dianthrimide and carbazole types have little importance today. The unsulfonated intermediate of *Alizarine Light Grey BBLW* (CI Acid Black 48)[160] is obtained either by condensation of 1,4-diaminoanthraquinone with 1-amino-4-bromoanthraquinone or by nitration of 1,1-dianthrimide, and reduction of the nitro compound. Sulfonation with strong oleum yields a gray of very good lightfastness but only moderate wet-fastness.



Ring closure of 1-benzoylamino-2-methyl-4(2′-naphthylamino)-anthraquinone with concentrated sulfuric acid produces a carbazole and effects simultaneous sulfonation. The resulting dye is *Alizarine Light Brown BL* (CI Acid Brown 27)[161] which gives reddish brown dyeings with good fastness properties on wool.

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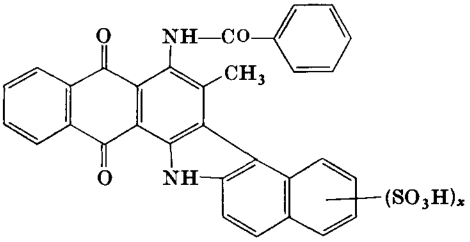
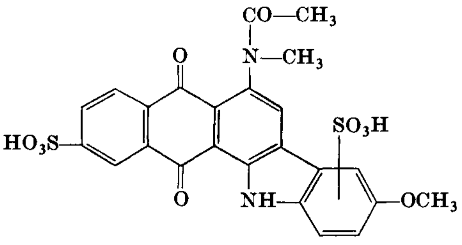
[160] FIAT, *1313*, II 216.

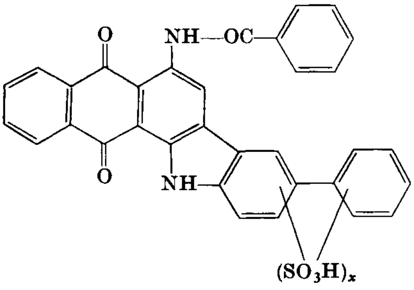
[161] S, *USP* 2,093,355.



Likewise the following dyes give brown dyeings:



(XXVI)



(XXVII)

Dye (XXVI) is prepared by sulfonation of 1-acetylmethylamino-4-(*p*-anisidino)anthraquinone-6-sulfonic acid in sulfuric acid with oleum. Subsequent ring closure to the carbazole compound is carried out in aqueous acid suspension by the addition of sodium bichromate.[162] The starting material for dye (XXVII) is 1-benzoylamino-4-aminodiphenylanthraquinone. This is first sulfonated and then converted to the carbazole compound with nitrosylsulfuric acid in sulfuric acid solution.[163]

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[162] FBy, *DBP* 889,341.

[163] FBy, *DBP* 868,325.

CHAPTER III

ANTHRAQUINONOID VAT DYES

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I. Introduction

Cotton continues to be pre-eminent among the fibers, natural and synthetic, and the anthraquinonoid vat dyes remain the most important class of all dyes for cotton and other cellulosic fibers because of their outstanding all-round fastness. Reactive dyes have the advantages of brightness and ease of application; but the increasing use of the reactive dyes has not worked so far to the prejudice of the vat dyes for cotton. The sale value of vat dyes (nearly all of which were anthraquinonoid) in the United States in 1966 was $57,875,000, in comparison with the total value of $331,453,000 for all dyes.[1] Halogenated indanthrone, violanthrone and its derivatives, acridines of the type of CI Vat Green 3 (CI 69500) obtained by cyclization of the condensation product of 3-bromobenzanthrone and 1-aminoanthraquinone, the anthraquinone–carbazoles, and dibenzopyrenequinones are the major groups as indicated by production figures and patent coverage. Notwithstanding their high cost, indanthrone, brominated violanthrone and isoviolanthrone, and a few other anthraquinonoid vat dyes are used as pigments to a limited extent (see J. Lenoir in this volume). A new area in which anthraquinonoid vat dyes are finding use, although quantitatively a very minor outlet, is in the formulation of greases stable at temperatures of 350° or more.

The present review is a survey of progress from 1950 and is written against the background of the three chapters on anthraquinonoid vat dyes and the chapter on solubilized vat dyes in *CSD II*. Familiarity with the material contained in these chapters is therefore assumed, and the same chemical classification of the dyes has been followed, except for a few minor rearrangements. For each group of dyes the treatment includes in the given order (a) new or modified structures in *Colour Index*, (b) review of scientific literature, and (c) review of patents.

II. Intermediates

Improvements in the known methods of production of intermediates for anthraquinonoid vat dyes are outside the scope of this chapter, but a few examples are cited of new intermediates and of new routes to known intermediates. The relatively simple anthraquinone derivatives are

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[1] "Synthetic Organic Chemicals," U. S. Production and Sales, 1966. U. S. Govt. Printing Press, Washington, D.C., 1968.

considered in this section and the more complex intermediates in connection with the relevant group of dyes.[2]

A review of acylation with di- and polycarboxylic acid derivatives includes many references to condensations with phthalic and chlorinated phthalic anhydrides, which are of interest for the synthesis of anthraquinone and other polycyclic quinone derivatives.[3] Several applications of the Diels-Alder reaction were mentioned in *CSD I* and *II*, and they continue to be explored. From the 1,4-naphthoquinone–butadiene adduct, 2-aminoanthraquinone can be prepared through a series of reactions.[4] 2,3,4-Trichloroanthraquinone-1-carboxylic acid, obtained in good yield from the Diels-Alder adducts of 5,5-dialkoxy-1,2,3,4-tetrachlorocyclopentadiene and 1,4-naphthoquinone by chlorination in organic solvents at high temperature, is useful for vat dyes derived from 1-aminoanthraquinone.[5] The claim[6] that pure 1-nitroanthraquinone can be obtained in very good yield by nitration of anthraquinone with 90% nitric acid at room temperature and subsequent treatment with sodium sulfite cannot be confirmed. The direct chlorination of anthraquinone and some of its derivatives deserves to be studied in detail. 1,4,5,8-Tetrachloroanthraquinone can be prepared by chlorination of anthraquinone in oleum,[7] and a useful development will be to control the reaction to yield α-chloroanthraquinone or 1,5- or 1,8-dichloroanthraquinone. Of interest in this connection are the chlorination of α-aminoanthraquinone in 97% yield to 1-amino-5,8-dichloroanthraquinone,[8] and the conversion of 1,4-diaminoanthraquinone to the 5,8-dichloro derivative by treatment with oleum to form 1,4-*bis*-sulfimidoanthraquinone (I), which is chlorinated and hydrolyzed.[9] The cyclic sulfonyl derivative (I) is also useful for the preparation of other intermediates.[10] Methods have been described for the preparation of fluoroanthraquinones, α-amino-β-

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[2] See also J. M. Straley, "Disperse Dyes," in *CSD III*, because many disperse dyes (or closely related compounds) derived from anthraquinone are intermediates for vat dyes.

[3] A. G. Peto, *in* "Friedel-Crafts and Related Reactions" (G. A. Olah, ed.), Vol. II, pp. 535–910. Wiley (Interscience), New York, 1964.

[4] V. I. Gudzenko, *J. Gen. Chem. USSR* (*English Transl.*) **32**, 609 (1962); see also CCC, *BP* 896,911; CIBA, *SP* 362,066; *BP* 884,881.

[5] P. Kniel, *Helv. Chim. Acta* **46**, 492 (1963); **48**, 837 (1965); CIBA, *BeP* 627,899–900; *BP* 931,316; 960,799; 964,482.

[6] G, *USP* 2,874,168.

[7] E. E. Beard and DuP, *USP* 2,378,745.

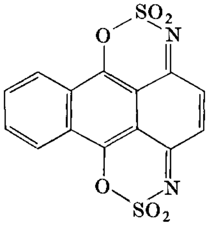
[8] FBy, *DBP* 1,151,517; 1,154,490; and see *DBP* 1,161,252 for the chlorination of α-nitroanthraquinone; see also *BP* 1,033,773.

[9] FBy, *DBP* 1,173,907.

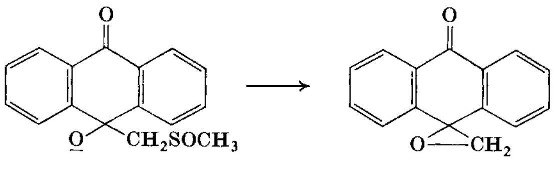
[10] FBy, *BP* 738,982; 749,677; H-W. Schwechten, R. Neeff, and O. Bayer, *Chem. Ber.* **90**, 1129 (1957); see also Bayer and Co., *DRP* 268,592.

fluoroanthraquinones, and dyes derived from them.[11] A simple intermediate of considerable interest is 1-amino-6,7-dichloroanthraquinone, providing a relatively cheap route to dyes derived from 1-aminoanthraquinone and 1,4-diaminoanthraquinone. Dyes built from 1-amino-6,7-dibromoanthraquinone and the bromo-chloro compounds are also covered by patents.[12] 1-Amino-6,7-difluoroanthraquinone is the subject of a Russian patent.[13]

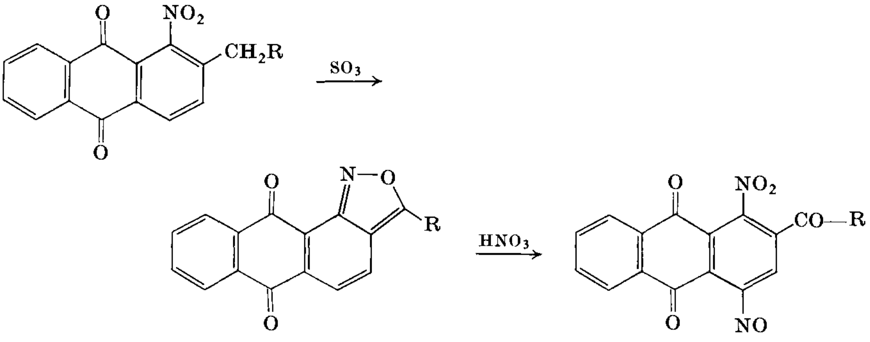
1-Amino- and 1,4-diaminoanthraquinones carrying a COOH or a CHO, $COCH_3$, or COPh group in the 2-position are useful intermediates for vat and disperse dyes. They can be prepared by treatment of 1-nitro-2-methyl-, ethyl-, or benzylanthraquinone with oleum to give the isoxazole (II). Hydrolysis or acid reduction of (II) gives 1-aminoanthraquinone-2-carboxylic acid or aldehyde or ketone; and treatment of (II) with nitric acid gives the 1-nitro-4-nitroso compound (III),



(I)



(IV)



(II)

(III)

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[11] G. Valkanas and H. Hopff, *J. Org. Chem.* **27**, 3680 (1962); *J. Chem. Soc.* p. 1923 (1963); see also Stauffer Chemical Co., *USP* 3,113,141.

[12] W. Jenny, W. Kern, and CIBA, *USP* 2,614,108–9; *DBP* 836,066; M. Staeuble and CIBA, *USP* 2,749,341; *DBP* 952,120; CIBA, *SP* 290,508–9; 291,732–5; *BP* 679,588; 680,378; 737,016; 736,437; 764,332; 761,066.

[13] N. S. Dokunikhin, B. V. Salov, and V. P. Piskareva, *RP* 166, 366.

which can be reduced to the diamine.[14] 4-Hydroxy-7,8-phthaloylcinnoline is obtained by treatment of 2-acetyl-1-aminoanthraquinone with nitrous acid.[15] 1-Amino-2-halogenoacetylanthraquinones can be prepared by halogenation of 1-amino-2-acetylanthraquinone in sulfuric acid.[16] By heating 1-amino-2-bromoacetylanthraquinone in dimethyl sulfoxide, which acts as a solvent and oxidizing agent, at 110° for a few hours, 6,7-phthaloylisatin is obtained.[17]

A series of aminoanthraquinone carboxylic acids, such as 1-aminoanthraquinone-3-carboxylic acid and 1,2-diaminoanthraquinone-4-carboxylic acid, have been synthesized.[18]

1,4-Diamino-2,3-dicyanoanthraquinone, which dyes polyacrylonitrile and polyester fiber a fast blue, is a useful intermediate for vat dyes and the subject of several patents. One method of preparation is to treat 1,4-diaminoanthraquinone-2-sulfonic acid or 2,3-disulfonic acid with sodium cyanide in aqueous solution in presence of an oxidizing agent.[19]

The introduction of alkyl or aryl sulfonyl groups into azo and other dyes is a well-known device for attempts to improve dyeing and fastness properties, and many examples were cited in *CSD I* and *II* (see, for instance, among acylamidoanthraquinones, p. 889). They can also be used for influencing the orientation of substituents. Thus the nitration of 2-methylsulfonylanthraquinone gives a mixture of the 5- and 8-nitro derivatives, and reduction with sodium hydrosulfide yields a separable mixture of 1-amino-6-methylsulfonylanthraquinone and 1-amino-7-mercaptoanthraquinone.[20] The preparation of 1- and 2-anthraquinonyl *p*-tolyl sulfone and their derivatives, useful as vat dyes or as intermediates for vat and azo dyes, has been described.[21] Vat dyes containing allylmercapto and allyl sulfone groups are the subject of a patent. *p*-Mercaptobenzoic acid is condensed with allyl chloride, the product heated with thionyl chloride, and the resulting *p*-allylthiobenzoyl chloride then used for acylating aminoanthraquinones. Allyl chloride

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[14] BASF, *BP* 769,183; 719,282; 718,882; F. Ebel *et al.*, and BASF, *DBP* 1,065,545.

[15] BASF, *BP* 709,614.

[16] BASF, *DBP* 1,127,911.

[17] H. Weidinger, H. G. Haese, and BASF, *DBP* 1,123,325.

[18] H. Hopff, J. Fuchs, and K. H. Eisenmann, *Ann. Chem.* **585**, 161 (1954).

[19] M. Kugel and G, *USP* 1,938,029; BASF, *BeP* 592,155; *BP* 901,059; *DBP* 1,108,704; D. B. Pattison and DuP, *USP* 2,795,593; J. D. Hildreth and Toms River Corp., *USP* 3,203,751; *BP* 1,022,220; Y. B. Shteinberg *et al.*, *RP* 148,066.

[20] CIBA, *BP* 738,650.

[21] E. Klingsberg, *J. Org. Chem.* **24**, 1001 (1959); E. Klingsberg and CCC, *USP* 2,995,584; see also, W. Jenny, W. Kern, and CIBA, *USP* 2,610,194; 2,644,824; CIBA, *SP* 274,709–20; *BP* 689,279.

may also be directly condensed with a vat dye such as 4,10-dimercaptoanthanthrone.[22]

Anthranol-10-aldehydes, useful intermediates for acedianthrones, are obtained by blowing air through solutions of anthraquinone derivatives (not containing amino groups) in dimethyl sulfoxide in the presence of alkali.[23] The reaction proceeds through (IV), resulting from the attack of the powerful anion of dimethyl sulfoxide on one of the carbonyl groups.

1-Anthraquinonyldiazonium borofluorides with halogen, nitro, and other substituents in the 4-position can be used for the preparation of 1-arylanthraquinones by the Gomberg-Bachmann-Hey reaction. 2-Arylanthraquinones with suitable substituents are useful disperse dyes, and 1-arylanthraquinones are claimed to be useful for the preparation of vat dyes.[24]

III. General Properties and Reactions

A. CHROMATOGRAPHIC ANALYSIS AND STRUCTURE DETERMINATION

In the production of many vat dyes the progress of the reaction can be followed by paper chromatography (PC) or thin-layer chromatography (TLC). This is especially true of reactions such as halogenation, the methylation of 16,17-dihydroxyviolanthrone, and cyclizations (anthrimides to carbazoles, diacylhydrazides to oxadiazoles, etc.).

Refinements in chromatographic analysis have facilitated the isolation of compounds in the pure state; and classical methods of structure determination can now be supplemented or largely replaced by NMR and mass spectral analysis. The first step obviously is to accumulate data on the known vat dyes. Color reactions are very useful for identification,[25] but they should be supplemented by spectral data. Ultraviolet-visible spectra may be determined in (a) an organic solvent, (b) conc. sulfuric acid, and (c) aqueous alkaline solution as the leuco derivative, stabilized by the addition of alcohols or amines. In determining and interpreting such spectra it is necessary to keep in mind several factors, such as the formation of a true solution, stability of the dye to sulfuric acid and to reducing conditions, and the dependence of the wavelength

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[22] CIBA, *BP* 966,497.

[23] E. Schwamberger, H. von Brachel, and CFM, *DBP* 1,232,567; cf. M. Chaykovsky and E. J. Corey, *J. Org. Chem.* **28**, 254 (1963).

[24] Deutsche Gold- und Silber-Scheidenanstalt and G. Valkanas, *DBP* 1,167,808; G. Valkanas and H. Hopff, *J. Org. Chem.* **29**, 489 (1964).

[25] D. A. Derrett-Smith and J. Grey, "The Identification of Vat Dyes on Cellulosic Materials." Pergamon Press, Oxford, 1967.

and the intensity of absorption on the concentration in sulfuric acid solution.

Infrared spectra are useful for characterization, as shown by McClure *et al.*,[26] who have recorded the IR spectra of 96 organic pigments including 10 anthraquinonoid and related dyes. Durie, Lack, and Shannon[27] have reported and discussed the IR spectra of violanthrone, isoviolanthrone, 16,17-dimethoxy- and diethoxyviolanthrone, pyranthrone, flavanthrone, and dibromoanthanthrone; and there is a need for published data on a much wider range of quinonoid vat dyes.

The isolation of the main constituent of a commercial vat dye involves separation from intermediates and by-products of the reactions by which it was synthesized, other vat dyes and diluents added for shading and standardization, and dispersing agents. Vat dyes in highly dispersed form with uniform particle size are marketed under such names as "liquid", "microfine," "microdisperse," "ultradisperse," and "colloisol" for application by continuous dyeing techniques (such as the pad-steam process) and for package dyeing[28]; various methods of dispersion are described in patents. After breaking up colloidal dispersions by suitable treatment, the dyes are recovered by vatting (under prescribed conditions to avoid over-reduction, dehalogenation and hydrolysis of amide groups), filtering and reoxidizing by air; nitrated violanthrone is exceptional and will be recovered as the corresponding amine after alkaline reduction. Because of the sparing solubility of the anthraquinonoid vat dyes in organic solvents, chromatographic separation has to be carried out at high temperatures, using solvents such as *o*-dichlorobenzene, 1,2,4-trichlorobenzene, molten naphthalene, phenol, cresols, dimethyl sulfoxide, and dimethylformamide at temperatures of 100–150°. A simple apparatus for this purpose has been described in which interchangeable ground-glass joints permit columns of different diameters and quantities of the adsorbent (alumina being generally suitable) varying from 5 to 100 g to be handled.[29]

Solutions of the leuco derivatives of vat dyes in aqueous sodium hydroxide are unsuitable for paper chromatography, because of their

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[26] A. McClure, J. Thomson, and J. Tannahill, *J. Oil. & Colour Chemists' Assoc.* **51**, 580 (1968).

[27] R. A. Durie, R. E. Lack, and J. S. Shannon, *Australian J. Chem.* **10**, 429 (1957).

[28] M. R. Fox [*J. Soc. Dyers Colourists* 78, 393 (1962)] has discussed the practical aspects of vat dyeing of cotton yarn packages [see also E. Atherton, A. C. Cooper, and M. R. Fox, *ibid.* **80**, 521 (1964)].

[29] M. K. Unni and K. Venkataraman, *J. Sci. Ind. Res.* **19B**, 355 (1960); see also R. Meier and J. Fletechinger, *Angew. Chem.* **68**, 373 (1956); E. Lederer and M. Lederer, "Chromatography," p. 15. Elsevier, Amsterdam, 1957.

rapid oxidation to the insoluble quinones and also the preferential retention of the alkali in the cellulose, resulting in a gradual reduction of pH as the front moves forward; but when sodium hydroxide is replaced by aqueous tetraethylenepentamine, $NH_2(CH_2CH_2NH)_3CH_2CH_2NH_2$, reduction with sodium dithionite yields a clear and very stable vat. The solution can be submitted to paper or thin-layer chromatography or chromatographed on a column of cellulose powder, the same reagents in aqueous solution being employed for developing the chromatogram.[30]

Although the simultaneous reduction of quinones with zinc and alkali and methylation of the leuco compounds with methyl *p*-toluenesulfonate has been known for a long time,[31] it has not been used as a method for isolating anthraquinonoid vat dyes in the pure state. When vat dyes are converted to the methyl ethers or acetates of the leuco compounds, the derivatives have greatly increased solubility in benzene and other common solvents, and are amenable to TLC and PLC (preparative layer chromatography). They can be crystallized from the common organic solvents, and some have adequate solubility in tetramethylurea for the determination of NMR spectra,[32] and volatility for mass spectra; but it may be necessary to prepare allyl, benzyl, trityl, and trimethylsilyl ethers and alkyl carbonates of the leuco compounds. Such derivatives of anthraquinone and a few anthraquinonoid vat dyes have been prepared[33] and the applicability of the methods to others is under investigation. There are experimental difficulties, and specific procedures have to be developed for particular dyes. The general procedure for obtaining the reductive methylation product is to reduce a vat dye with aqueous sodium dithionite and sodium hydroxide at the appropriate temperature and shake the solution vigorously with dimethyl sulfate (about 6 moles) with cooling if necessary, until the product separates. In a second method, the calculated amount of hydrogen is absorbed in a suspension of the quinone in a mixture of dimethylacetamide and triethylamine in presence of Adams platinum oxide catalyst. After filtration or decantation from the catalyst, the mixture is treated with sodium hydroxide solution and dimethyl sulfate and the leuco ether separates. The parent vat dyes are readily recovered from the leuco ethers by dissolving in conc. sulfuric acid and precipitating with water.

[30] N. R. Rao, K. H. Shah, and K. Venkataraman, *Current Sci.* (*India*) **19**, 149 (1950); **20**, 66 (1951); E. Klingsberg, *J. Soc. Dyers Colourists* **70**, 563 (1954); see also J. Šramék, *ibid.* **78**, 326 (1962); *J. Chromatog.* **11**, 524 (1963); E. G. Kiel and G. H. A. Kuypers, *Tex* **22**, 162 (1963); H. Tajiri, *Kogyo Kagaku Zasshi* **69**, 2169 (1966).

[31] P. Nawiasky *et al.*, and IG, *DRP* 470,184; *Frdl.* 16,1133.

[32] P. M. Nair, T. G. Manjrekar, A. V. Rama Rao, and K. Venkataraman, *Chem. & Ind.* (*London*) p. 1524 (1967).

[33] T. G. Manjrekar, A. V. Rama Rao, and K. Venkataraman, unpublished work.

Many of the sodium salts of the sulfuric esters of the leuco compounds, available as commercial products (CI Solubilized Vat Dyes) or readily obtainable from the parent vat dyes, dissolve in dimethylacetamide, and of course in deuterium oxide, and can be submitted to NMR spectroscopy, but relatively few have given perfect spectra so far because of difficulties in purifying the leuco sulfates and obtaining them in a crystalline form. The leuco sulfates of indigoid and anthraquinonoid vat dyes are separable from each other and as individual compounds by TLC on silica gel and two solvent systems: (a) dimethylformamide–isopropyl alcohol–water (1:8:1) and (b) DMF–ethanol–isoamyl alcohol (1:1:8).[34]

Physical methods of structure determination are of special value for the polycyclic quinonoid vat dyes, because of their great stability and the consequent difficulty in the isolation and characterization of smaller fragments produced by chemical degradation. Hydrolysis of aroylamido groups, destruction of outer rings (such as the oxidation of indanthrone to 2,3-dihydroxy-5,6-phthaloylquinoxaline, and of violanthrone to 2,2′-bianthraquinonyl-1,1′-dicarboxylic acid),[35] and drastic alkali fusion (such as the fission of 3,4-phthaloylacridone to acridone-3-carboxylic acid,[36] and of pyrazolanthrone to 3-*o*-carboxyphenylindazole)[37] are the few reactions which may be used for the breakdown of vat dyes, but their scope is very limited.

B. Reactivity of Polycyclic Quinones

Dibenzopyrenequinones, pyranthrone, flavanthrone, acedianthrone, violanthrone, and isoviolanthrone yield useful dyes by halogenation and other reactions. The orientation of the substituents has often remained undetermined, and possible experimental techniques for investigating such problems have been mentioned earlier. Hopff and Schweizer[38] have applied a known method for the calculation of localization energies to polycyclic quinones, taking into account the influence of the CO resonance integral and the Coulomb integral of the oxygen atoms with appropriate corrections. The correction factor $\delta\alpha_h$ for the difference between the Coulomb integrals of oxygen and carbon was roughly determined as 1.6β, no distinction being made between electrophilic

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[34] T. G. Manjrekar, Ph.D. Thesis, University of Bombay (1968); see also J. Šramék, *J. Chromatog.* **12**, 453 (1963); J. Kolsek, F. Mlakar, and M. Perpar, *Z. Anal. Chem.* **188**, 345 (1962).

[35] *CSD II*, pp. 934, 943, and 966.

[36] B. S. Joshi, N. Parkash, and K. Venkataraman, *J. Sci. Ind. Res.* (*India*) **14B**, 325 (1955).

[37] W. Bradley and K. W. Geddes, *J. Chem. Soc.* p. 1636 (1952).

[38] H. Hopff and H. R. Schweizer, *Helv. Chim. Acta.* **45**, 312; 1044 (1962); H. R. Schweizer *ibid.* p. 1934 (1962).

and nucleophilic reactions. For the simple quinones the calculated values of reactivity were in excellent agreement with available experimental data. For the more complex quinones, such as the dibenzopyrenequinones, pyranthrone, and violanthrone, the available experimental results are undependable, contradictory, and in poor agreement with the calculated reactivity.

C. Nucleophilic Substitution

Electrophilic substitution, notably halogenation, is frequently used for the preparation of derivatives with modified shades or improved fastness properties, starting from a parent vat dye, both among indigoids and anthraquinonoids. The importance of nucleophilic substitution, especially in connection with the mechanism of the reactions and the formation of by-products when anthraquinone derivatives are submitted to alkali fusion, has long been recognized and reference to relevant patents and publications will be found in *CSD II*. Nucleophilic substitution of benzanthrone was studied by Perkin and Spencer[39] and by Bradley and Robinson.[40] The action of potassium hydroxide (and oxidizing agents), sodium anilide, etc., on pyrazolanthrones, anthanthrone, pyranthrone, and other polycyclic quinones has been investigated by Bradley and his collaborators.[41] Thus it was found that by the action of potassium hydroxide on 3-benzoyl-, 3-*m*-nitrobenzoyl-, and 3-α-naphthoylbenzanthrone three concurrent reactions occurred: (a) hydrolysis of acyl groups; (b) cyclization to the corresponding dibenzopyrenequinones; and (c) nuclear hydroxylation.[42] The cyano group can be introduced into the phthaloylacridone, pyridanthrone, dibenzopyrenequinone, anthanthrone, and other polycyclic quinone systems by treatment with potassium cyanide in a glycol or other inert solvent, followed by oxidation with hypochlorite or bichromate.[43]

D. Introduction of Solubilizing Groups

An important advance described in Ciba patents is the introduction of solubilizing groups into vat dyes, as distinct from the sulfation of the leuco compounds. The objects are to facilitate vatting and to improve penetration and level dyeing properties. Anthraquinonoid vat dyes of all types are used. One method is to introduce one or more sulfonic groups

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[39] A. G. Perkin and G. D. Spencer, *J. Chem. Soc.* **121**, 479 (1922).

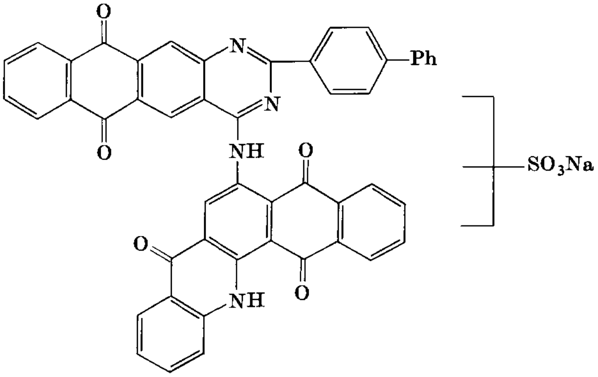
[40] W. Bradley and R. Robinson, *J. Chem. Soc.* p. 1254 (1932).

[41] W. Bradley *et al.*, *J. Chem. Soc.* pp. 1630 and 1636 (1952); pp. 1894 and 4506 (1954); p. 3778 (1953).

[42] A. J. Backhouse and W. Bradley, *J. Chem. Soc.* p. 849 (1955).

[43] H.-W. Schwechten, O. Bayer, and FBy, *USP* 3,047,577.

per a certain number of moles of a known vat dye,[44] a procedure which was not unknown for some of the older vat dyes, such as CI Vat Blue 12 (CI 69840) (Indanthrene Brilliant Blue 3G) which consists of indanthrone and a substantial amount of its monosulfonic acid. Apart from direct sulfonation, one method of introducing a sulfonic group is to treat a vattable amine with *p*-sulfobenzoyl chloride in the presence of pyridine; even if the dichloride of a sulfobenzoic acid is used, the carbonyl chloride undergoes preferential condensation and the sulfonyl chloride can then be hydrolyzed to the sulfonic acid.[45] Another approach is exemplified by the condensation of isophthaloyl chloride with 1 mole each of 1-amino-5-benzamidoanthraquinone and 1-aminoanthraquinone-5-sulfonic acid.[46] In one patent numerous dyes are mentioned which contain at least one vat-stable sulfonic and/or carboxyl group, and an example is (V), which dyes cotton a very fast green.[47] Other methods



(V)

involve the introduction of alcoholic groups which are then sulfated; the condensation of an aminoanthraquinone with cyanuric chloride and then with an arylamine sulfonic acid, or an arylamine or an ethanolamine (followed, respectively, by sulfonation or sulfation); and the formation of Bunte salts (Dye—S—SO_3Na).[44] Phosphorylation has also been

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[44] CIBA, *BP* 923,740; 927,019; 927,278; 927,713; 929,745; 931,944; 935,595; 952,798; 956,590; 961,424; 961,690; 962,142; 962,353; 969,569; 979,773; 979,900; 981,527; 981,531; 982,430; 983,124; 986,556; 987,965; 989,747; 991,026; 991,625; 991,811; 991,976; 996,244; 1,000,206; 1,021,194; 1,023,705; 1,025,915.

[45] CIBA, *BeP* 610,861; *BP* 982,430.

[46] CIBA, *BeP* 631,054.

[47] CIBA, *BP* 1,027,565; see also CIBA, *BeP* 618,825.

suggested.[48] Notwithstanding the intense patenting activity, the precise technical advantages are not clear, because the vat dyes in the commercial range present no serious difficulties in application and there are patents in which the introduction of solubilizing groups is supplemented by the addition of dispersing agents.[49]

E. CHLOROMETHYLATION

The conversion of copper phthalocyanine to basic dyes (e.g., Alcian Blue 8GX; CI Ingrain Blue 1; CI 74240) was followed by the application of similar reactions of chloromethylation and quaternary salt formation with alkylthioureas, triethylamine, etc., to the anthraquinonoid vat dyes.[49a] Nakazawa[50] has studied these processes and has discussed the dyeing properties of the products. He was thus able to introduce 2,4-chloromethyl and the corresponding pyridinium (or isothiuronium) chloride groups into anthanthrone. There are patent claims for the use of the chloromethyl derivatives themselves as vat dyes[51]; chlorine is lost during vatting and the method, therefore, is to effect *C*-methylation. Thus two methyl groups can be introduced into Indanthrene Navy Blue R (CI Vat Blue 25), and the product dyes stronger shades.[52]

F. REDUCTION OF POLYCYCLIC QUINONES TO HYDROCARBONS

The aromatic polycyclic hydrocarbons and their heterocyclic analogs are of interest for their carcinogenic and other physiological properties, chemical reactivity, electronic structure, and absorption spectra. A striking effect of several aromatic hydrocarbons, which "permits analysis of mechanisms of causes and cure of breast cancer," is that a single feeding of one of them produces tumors, predominantly of the breast, in the albino rat.[53] This simple procedure for the induction of cancer should also enable more rapid and accurate estimates to be made of carcinogenic activity from the point of view of the influence of structural variations. In his two monumental volumes on polycyclic hydrocarbons[54] Clar, a pioneer in this area, has given a comprehensive survey of their nomenclature; aromatic character; physical, chemical, and carcinogenic prop-

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[48] A. K. Wick and CIBA, *DBP* 1,265,896.

[49] CIBA, *BP* 992,857.

[49a] *CSD II*, p. 1140.

[50] S. Nakazawa and T. Matsumato, *Yuki Gosei Kagaku Kyokai Shi* **20**, 925 (1962); S. Nakazawa, *ibid.* 930, 1084, and 1091; **21**, 49 and 53 (1963).

[51] D. I. Randall, T. A. Martin, and G, *USP* 2,691,022; 2,666,767; see also D. I. Randall, E. E. Renfrew, and G, *USP* 2,645,645.

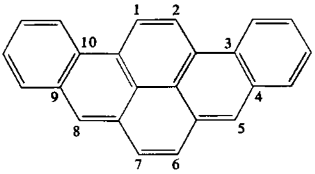
[52] D. I. Randall and G, *USP* 2,619,487; 2,647,899.

[53] C. Huggins and N. C. Yang, *Science* **137**, 257 (1962).

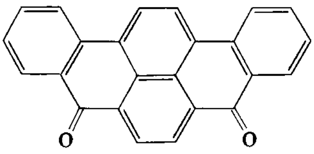
[54] E. Clar, "Polycyclic Hydrocarbons," Vols. 1 and 2. Academic Press, New York, 1964.

erties; and methods for their preparation. Clar's book is also invaluable for its treatment of polycyclic quinones, including the recent work of M. Zander, A. Zinke, and others.

Since many polycyclic quinones are available as commercial anthraquinonoid vat dyes and others are accessible by known synthetic reactions, it is useful to have a variety of methods for the reduction of polycyclic quinones to the corresponding hydrocarbon derivatives. Alternatives to the well-established Clar reduction of quinones to hydrocarbons are less drastic procedures, such as Raney nickel reduction of the sulfuric esters of the leuco compounds,[55] modifications of the Meerwein-Ponndorf reduction,[56] and reduction by cyclohexyl *p*-toluenesulfonate.[57] Anthraquinone and some of its derivatives undergo reduction to the corresponding anthracene derivatives by prolonged refluxing with sodium borohydride and diglyme; reduction with sodium borohydride in the presence of boron fluoride or aluminum chloride is another useful method, although it has certain limitations.[58] Thus 3,4,9,10-dibenzopyrene (VI), one of the most potent carcinogens, can be prepared readily from the commercially available 5,8-quinone (VII) by one of several methods.[59]



(VI)



(VII)

G. Vatting and Dyeing

When anthraquinonoid dyes are treated with alkaline dithionite, the $SO_2^{\cdot(-)}$ radical-ion appears to play an essential part. The first stage is the addition of dithionite to the ketonic carbon, the product then breaking down rapidly to the leuco compound and sulfite.[60] Nabar and

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[55] N. B. Desai, V. Ramanathan, and K. Venkataraman, *J. Sci. Ind. Res.* (*India*) **14B**, 330 (1955); **15B**, 279 (1956).

[56] S. Coffey and V. Boyd, *J. Chem. Soc.* p. 2468 (1954).

[57] W. Kelly and J. S. Shannon, *Australian J. Chem.* **13**, 103 (1960).

[58] C. J. Sanchorawala, B. C. Subba Rao, M. K. Unni, and K. Venkataraman, *Indian J. Chem.* **1**, 19 (1963).

[59] B. D. Tilak, M. K. Unni, and K. Venkataraman, *Tetrahedron* **3**, 62 (1958).

[60] U. Baumgarte, *Textilveredlung* **2**, 896 (1967); see also *Melliand Textilber.* **47**, 1153 (1966).

Shenoi[61] found that cold dyeing vat dyes dissolved completely in aqueous alkaline dithionite at pH 12.50, and the warm or hot dyeing dyes at pH 14. Introduction of electronegative groups and increase in complexity of the dye structure resulted in a lowering of the pH required for complete solubilization. They have described a modified method for the potentiometric titration of reduced vat dyes and have related the reduction potentials to ease of reduction and tendering behavior.

Meybeck[62] has obtained and discussed for 16 vat dyes the data on leuco potentials, cellulose affinity, $\lambda_{\max}$ and $\epsilon_{\max}$ in solution and on the fiber, lightfastness, and sensitization of photodegradation of the substrate. Müller[63] has attempted to correlate the constitution of anthraquinonoid and indigoid vat dyes with their behavior in solution and their dyeing properties. Sekido and Matsui[64] have studied the kinetic behavior of vat dyes on a cellulose substrate. The monosodium salts of some reduced vat dyes have higher substantivity to cotton than the disodium salts or the vat acids, as shown by a kinetic study of dyeing at various pH values.[65] Wegmann has discussed the limitations of earlier quantitative theories of the substantivity of vat and direct dyes.[66]

Numerous patents have appeared on modifications or replacements of the usual alkaline dithionite method for reducing vat dyes and applying them in dyeing and printing.[67] One object of such additions is to avoid over-reduction.[68] Another is to improve solubility and level-dyeing properties.[69] Ferrous complexes (e.g., with triethanolamine) are recommended as valuable reducing agents.[70] A mixture of sodium dithionite and an alkanesulfinic acid derivative such as $N(CHMe—SO_2Na)_3$ is a very efficient and economical reducing agent for vat and sulfur dyeing.[71] If a redox catalyst (a chelate complex of a transition metal)

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[61] G. N. Nabar and V. A. Shenoi, *Indian J. Technol.* **1**, 27 (1963); **4**, 182 (1966); *Textile Res. J.* **33**, 471 (1963).

[62] J. Meybeck, *Teintex* **31**, 699 (1966).

[63] J. Müller, *Melliand Textilber.* **45**, 1253 (1964); see also M. I. Artym and P. V. Moryganov, *Izv. Vysshikh Uchebn. Zavedenii, Tekhnol. Tekstil'n. Prom.* No. 3, p. 110 (1961).

[64] M. Sekido and K. Matsui, *J. Soc. Fiber Sci. Technol., Japan* **20**, 778, 783, and 786 (1964).

[65] V. G. Abozin, M. G. Romanova, N. V. Blokh, and L. G. Grebenkina, *Izv. Vysshikh Uchebn. Zavedenii, Tekhnol. Tekstil'n. Prom.* No. 4, p. 108 (1963).

[66] J. Wegmann, *Melliand Textilber.* **48**, 59 and 183 (1967).

[67] See, e.g., J. Rzymkoski and BASF, *DBP* 896,335; T. Wegmann, H. P. Schaub, A. Litzler, and CIBA, *SP* 414,566; D. Goerrig, *BP* 954,597; I. Von and CCC, *USP* 2,660,580; BASF, *BP* 936,644.

[68] E. Roessler and Chemische Fabrik Pfersee G.m.b.H., *DBP* 1,260,430.

[69] S. R. Buc and G, *USP* 2,953,423; CIBA, *SP* 451,078; BASF, *BP* 834,393.

[70] H. Waibel, J. Rzymkoski, and BASF, *DBP* 946,285; *BP* 767,644.

[71] BASF, *BP* 1,015,526.

is added to the printing paste, 30% less of the reducing agent and of the steaming time required for development are necessary.[72] The addition of 0.01 g/liter of 1,5-diaminoanthraquinone-2-sulfonic acid as a vatting accelerator greatly improves the color yield.[73] Thiourea dioxide (CI Reducing Agent 11; Manofast, HH) can be used as a reducing agent for vat dyes, especially in discharge printing on cellulose acetate, triacetate, and wool, because it is stable under acid conditions.[74]

One part of sodium borohydride (SBH) can replace several hundred parts of dithionite; the former probably functions as a stabilizer for dithionite against oxidation.[75] Using disodium nickel tetracyanate as initiator, SBH can entirely replace dithionite. It has been stated that plant trials have been completed and that a process using a hydride reducing agent is in commercial use.[76] The addition of leucoquinizarin reduces the time of reduction.[77] Impregnation with the dye and sodium bisulfite and then with sodium hydroxide and SBH is a method by which dyeing with vat dyes can be carried out. Vat dyes can be applied safely to wool, silk, and synthetic fibers by using an acidic solution of dithionite and an "amine borane," such as *N*-methylmorpholine borane. Such a vat is stable for long periods.[78] Baumgarte and Keuser[79] find that SBH is distinctly inferior to dithionite as a reducing agent for vat dyes under the conditions they studied. Nair and Shah[80] have discussed the contradictory claims on the effect of SBH as a partial substitute for dithionite in vat dyeing. A suitable redox titration procedure was standardized and the effect of SBH in various vat dyebaths studied. An analysis of the redox curve gave valuable data on the stability of the reducing agent system, leucopotential of the dye, and the overall stability of the dyebaths. SBH did not improve the stability of the dyebath against oxidation. In higher quantities, it showed adverse effects. The results indicated that SBH cannot be a total or partial substitute for dithionite in vat dyeing by the current practice.

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[72] G. Zirkev *et al.* and BASF, *BP* 1,007,781; ICI, *BP* 975,967.

[73] CFM, *BP* 1,095,459.

[74] See also HH, *BP* 900,936.

[75] C. E. Neale and Southern Bleachery and Print Works, *USP* 3,127,231.

[76] Ventron Corp., *BP* 1,174,797; W. F. Harrison and A. A. Hinckley, *Can. Textile J.* **80**, 49 (1963).

[77] D. Goerrig, *NethP* 6,409,224.

[78] Metal Hydrides, *USP* 3,124,411; *BP* 982,500; 937,273; see also D. Goerrig, *BP* 872,998; F. Schubert, D. Goerrig, M. Söll, and FBy, *DBP* 1,041,462; R. A. Fleming and DuP, *USP* 2,992,061.

[79] U. Baumgarte and U. Keuser, *Melliand Textilber.* **47**, 286 (1966).

[80] G. P. Nair and R. C. Shah, *Textile Res. J.* **40**, 303 (1970).

Several patents[81] describe methods for the preparation of vat acids in fine dispersion.

A Japanese patent claims the preparation of "meso-dichloro compounds of semi-leuco compounds" of vat dyes containing more than one anthraquinone nucleus by treatment of the semileuco compound with phosphorus pentachloride; but the stability of the chlorine atoms under dyeing conditions and the advantages of the suggested reaction are not clear from the available abstract.[82]

Polypropylene can be dyed with vat dyes by applying them as the vat acids of particle size not larger than 3μ, and reoxidizing after heat fixation.[83]

Anodized aluminum can be dyed with a vat dye dissolved in 98% sulfuric acid by subsequent treatment with water or water vapor to insolubilize the dye in the oxide coating.[84]

H. BEHAVIOR ON TEXTILE SUBSTRATES

Cotton or viscose dyed with vat dyes is usually submitted to a final soaping treatment.[84a] While this improves washing fastness, there is also an alteration in shade with many vat dyes, probably as the result of aggregation and change in crystal habit. An entire book has appeared in which the relevant theories are reviewed.[85] Warwicker[86] has shown by a comparison of the X-ray powder photographs of different samples of 10 anthraquinonoid vat dyes that polymorphism is a common phenomenon. Wegmann[87] has reviewed the literature on color changes accompanying the soaping of vat dyes. He has presented interesting data, supported by color photographs, on the effect of soaping (before and after drying) on the hues of cotton dyed with a series of 1,4-bis(benzamido)anthraquinones in which the benzoyl groups were substituted by Cl, SO_2NMe_2, and SO_2NEt_2. Structural changes in a molecule (mainly prototropic shifts, hydrogen bonding, changes in the relative contribution of resonance structures) by interaction with a solvent or substrate are well known, and they may be responsible for the color changes exhibited by some

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[81] BASF, *BP* 694,473; 707,681.

[82] Y. Nagai, *JP* 5275/1959.

[83] BASF, *BP* 940,495; see also Hercules Powder Co., *USP* 3,056,643.

[84] Aluminum Co. of America and Koppers Co., *USP* 3,058,855.

[84a] *CSD II*, p. 874.

[85] L. M. Golomb, "Physicochemical Principles Underlying the Final Operations of Vat Dyeing," Light Industry Press, Moscow, 1964.

[86] J. O. Warwicker, *J. Textile Inst.* **50**, T443 (1959). see also D. G. Drummond and J. O. Warwicker, *ibid.* p. 487.

[87] J. Wegmann, *J. Soc. Dyers Colourists* **76**, 282 (1960); *Am. Dyestuff Reptr.* **51** No. 8, 46 (1962); see also G. S. Egerton and F. Galil, *Nature* **181**, 1399 (1958).

dyes; but there is no evidence for Wegmann's "working hypothesis" of "a new type of isomerism, termed contact isomerism."

The photochemistry of the anthraquinonoid vat dyes has been discussed by H. Meier in *CSD IV*.[88] The Kunz hypothesis[88a] that vat dyes possessing basic character because of the presence of pyridine or pyrimidine rings are nontendering by the action of light on dyed cellulose is now known to be of limited validity. In this context, derivatives of 1-aza-anthraquinone have been recently studied, but the results did not lead to especially nontendering dyes or extensions of the Kunz hypothesis.[89]

Preliminary work[90] seems to show that 2,3,6,7-dibenzopyrene-1,8-quinone, pyranthrone, and violanthrone "offer a range of protection, as measured by tensile strength, for certain cotton and cotton/polyester blends against degradation from gamma radiation."

IV. Anthraquinone Derivatives

A. ACYLAMIDOANTHRAQUINONES

Cibanone Yellow 2GW (CI Vat Yellow 23; CI 65420) is an isomer of CI Vat Yellow 13 (CI 65425[90a]); they are prepared by condensing 1-amino-5-benzamidoanthraquinone with isophthaloyl and terephthaloyl chloride, respectively. Several patents[91] describe precise conditions for the preparation of CI Vat Yellow 13. A heterocyclic carboxylic acid is used in the preparation of Indanthrene Yellow 4GF (CI Vat Yellow 20; CI 68420). The analog from 1-amino-4-methoxyanthraquinone is a useful orange pigment for coloring plastics and cement.[92] Cibanone Brilliant Pink 2R (CI Vat Red 44), which dyes a very clear pink shade, has the indicated structure.[93] Indanthrene Rubine GR (CI Vat Red 21; CI 61670) dyes a dull bluish red.

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[88] See also N. K. Bridge, *J. Soc. Dyers Colourists* **76**, 484 (1960); F. Dörr, *in* "Optische Anregung Organischer Systeme," p. 732. Verlag Chemie, Weinheim, 1966; E. H. Daruwalla, A. P. D'Silva, and G. N. Tandon, *Textile Res. J.* **37**, 160 (1967); V. A. Titkov, T. A. Kolobolotskaya, and I. D. Plentev, *J. Appl. Chem. USSR* (*English Transl.*) **36**, 805, 1061 (1963); E. W. Abrahamson and I. D. Panik, *Proc. 4th Intern. Meeting Mol. Spectry, Bologna, 1959*, Vol. I, p. 354; P. J. Baugh, G. O. Phillips, and N. N. Worthington, *J. Soc. Dyers Colourists* **86**, 19 (1970).

[88a] *CSD II*, p. 1247.

[89] M. Yokote, S. Ishigaki, and S. Suzuki, *J. Chem. Soc. Japan, Ind. Chem. Sect.* **58**, 932 (1955); H. Höpff and V. Kappeti, *Chimia* (*Aarau*) **19**, 228 (1965).

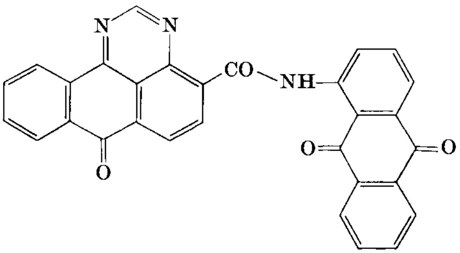
[90] C. J. Westberry and W. L. Hyden, *Am. Dyestuff Reptr.* **56**, P2 (1967).

[90a] *CSD II*, p. 885.

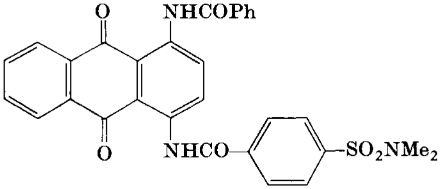
[91] E. Moergeli and CIBA, *USP* 2,763,667; *BP* 762,752; *DBP* 974,670.

[92] BASF, *BP* 976,071; *BeP* 587,166.

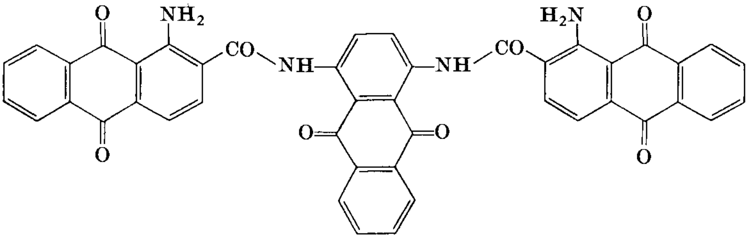
[93] O. Bayer, "Die Neuere Entwicklung der Farbenchemie," p. 13, Leverkusen, 1958.



Indanthrene Yellow 4GF
(CI Vat Yellow 20)



Cibanone Brilliant Pink 2R
(CI Vat Red 44)



Indanthrene Rubine GR (CI Vat Red 21)

Introduction of a methyl group in 1-acylamidoanthraquinones results in "lower dyeing power" and in a bathochromic or hypsochromic shift in λ_{max} according as the substitution is in the 4- or 2-position.[94] In contrast to the amides from 1-aminoanthraquinones and anthraquinone-2-carboxylic acids, which are useful vat dyes, the analogs from anthraquinone-1-carboxylic acids have poor affinity, probably because of a nonplanar structure.[95] Hayashi and Shibata[96] have studied the effects of substituents (NO_2, Cl, OMe, NH_2, SO_2NMe_2) in the acyl group of 1-benzamido- and 1,4-, 1,5-, and 1,8-bis(benzamido)anthraquinones on the vatting and dyeing properties, the light fastness on cotton, and the visible and IR spectra. Several phenazine carboxylic acids have been synthesized by improved methods in order to examine the dyeing and fastness properties of the anthraquinonylamides; some gave useful shades on cotton, but the fastness to soda boil was only moderate.[97] Tundo[98] has prepared a large number of acylamidoanthraquinones

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[94] N. S. Dokunikhin and V. Ya. Fain, *Zh. Prikl. Khim.* **39**, 473 (1966).

[95] N. S. Dokunikhin and V. Ya. Fain, *J. Appl. Chem. USSR* (*English Transl.*) **36**, 2686 (1963).

[96] T. Hayashi and R. Shibata, *Bull. Chem. Soc. Japan* **34**, 1116 (1961).

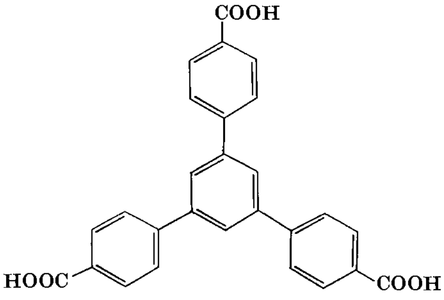
[97] H. Hopff and C. Ziegler, *Chimia* (*Aarau*) **12**, 112 (1958).

[98] A. Tundo, *Ann. Chim.* (*Rome*) **47**, 291 (1957), and earlier papers.

derived from 1-amino-4-arylamino- or 4-arylmercaptoanthraquinones and dicarboxylic acids such as furan-2,5-dicarboxylic acid. Phenyl isocyanate and isothiocyanate react smoothly at 100° with aminoanthraquinones in the presence of aluminum chloride, yielding the corresponding ureas and thioureas. The phenylthiourea from 1 aminoanthraquinone and the phenylureas and phenylthioureas from 1,4-, 1,5-, and 2,6-diaminoanthraquinones are yellow to orange and red-violet vat dyes with good fastness to light and chlorine.[99]

Because of the ease of preparation, acylamidoanthraquinones continue to figure in numerous patents. They can be prepared in a single apparatus and in purer state by treating the condensation product of an aminoanthraquinone and thionyl chloride in an inert solvent such as *o*-dichlorobenzene with a mono- or dicarboxylic acid and pyridine ($AQNH_2 + SOCl_2 \rightarrow AQ{-}N{=}SO$; $AQ{-}N{=}SO + ArCOOH \rightarrow AQNHCOAr + SO_2$).[100]

The main disadvantage of the acylamidoanthraquinones is their low substantivity, and this is one direction in which improvements are sought. Increased affinity is claimed for the very bright golden yellow dye obtained by condensing 2 moles of 1-aminoanthraquinone with 1 mole of stilbene-4,4′-dicarboxylic acid.[101] The acid (VIII) is used for acylating 3 moles of 1-aminoanthraquinone or other vattable amine [e.g., the acridone derivative (XLIX) or 16-aminoviolanthrone] to produce greenish yellow to blue and green-blue "hot dyeing" vat dyes of excellent fastness.[102]



(VIII)

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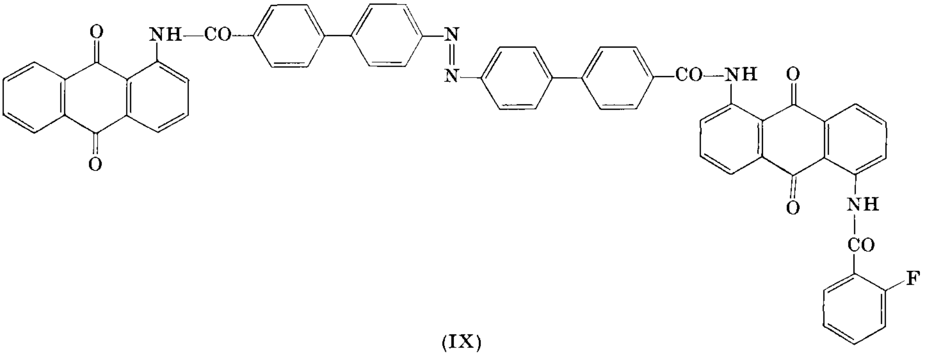
[99] R. D. Desai, *J. Indian Chem. Soc.* **45**, 196 (1968); see also N. S. Dokunikhin, *Zh. Prikl. Khim.* **29**, 930 (1956).

[100] T. Pfliegel and L. Hruška, *CzechP* 97,943; see also A. Michaelis, *Ann. Chem.* **274**, 178 (1893); H. Z. Lecher, D. R. Eberhart, and CCC, *USP* 2,479,943.

[101] CCC, *USP* 2,903,450.

[102] Gy, *BP* 853,969.

The need for bright yellow (and greenish yellow) vat dyes with maximum lightfastness is reflected by a larger number of patents. The condensation product of 1-aminoanthraquinone and 5-fluoroisophthalic acid is a fast lemon yellow dye,[103] and fluorine figures in many patents on acylamidoanthraquinones.[104] The condensation of 2 moles of 1-amino-5-(2′-fluoro-5′-chloro)benzamidoanthraquinone with one of azobenzene-3,3′-dicarboxylic acid gives a bright yellow dye.[105] An unusual intermediate is 1-nitro-2-methylanthraquinone-3-carboxylic acid; when it is condensed with 1-aminoanthraquinone and reduced, the amine dyes cotton orange; benzoylation gives a bright greenish yellow.[106] Acylation of 1-amino-5-benzamidoanthraquinone with fluorenone-2-carboxylic acid gives a bright golden yellow dye.[107] CI Vat Yellow 10 (CI 65430) contains an azo group, and other azobenzene derivatives[105, 108] have been suggested. Azobiphenyl-4,4′-dicarboxylic acid is an important intermediate for bright yellow light-fast dyes. The dye (IX) dyes cotton greenish yellow fast to light and chlorine.[108] The condensation product



(IX)

of thiophene-2,5-dicarboxylic acid and 1-aminoanthraquinone dyes cotton a very fast greenish yellow, and also gives fast coloration in polyvinyl chloride and stoving enamels.[109] Another fast yellow dye is the condensation product of thianthrene dicarboxylic acid (mentioned

[103] Gy, *BP* 923,530.

[104] CIBA, *SP* 292,689–692; *BP* 735,855; W. Jenny, W. Kern, and CIBA, *USP* 2,685,591; *BP* 712,837; 712,889; E. Moergeli and CIBA, *USP* 2,705,709; *BP* 706,737; 718,524; W. Zerweck, E. Heinrich, and CFM, *BP* 791,304; FH, *BP* 703,528; H. Greune, M. Corell, and FH, *DBP* 889, 340.

[105] CIBA, *SP* 308,793–6; E. Moergeli and CIBA, 350,398.

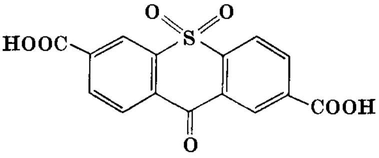
[106] E. Jutz and BASF, *DBP* 936,589.

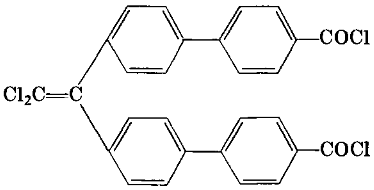
[107] W. Zerweck, E. Heinrich, and CFM, *BP* 777,789.

[108] CIBA, *BP* 834,456; F. Frister and CFM, *DBP* 1,098,647.

[109] CIBA, *BP* 974,036.

in several earlier patents) and 1-amino-5-(2′-fluoro-4′-chloro)benzamidoanthraquinone.[110] When thioxanthone dioxide (thioxanthone sulfone) 3,7-dicarboxylic acid (X), obtained by heating diphenyl sulfone-2,5,4′-tricarboxylic acid with oleum, is condensed with 1-amino-5-benzamidoanthraquinone, the product dyes cotton a fast yellow.[111] Two other examples are (a) the greenish yellow dye from 1,5-diaminoanthraquinone condensed with 1 mole of quinoline-8-carboxylic acid and 0.5 mole of terephthalic acid or 1 mole of pyrimidanthrone-3-carboxylic acid[112]; and (b) the yellow dye from pyrimidanthrone-3-carboxylic acid and 1-amino-3-chloroanthraquinone.[113] Treatment of 1-aminoanthraquinone with an excess of phthaloyl chloride gives a fluorescent, bright greenish yellow product, useful for mass pigmentation.[114]


(X)


(XI)

Isothiazolanthrone-3-carbonyl chloride gives a yellow dye with 1-amino-6,7-dichloroanthraquinone and a red-orange dye with 1-amino-4-methoxyanthraquinone; they are also useful as pigments for PVC.[115] The reddish yellow dye from 2 moles of 1-amino-6,7-dichloroanthraquinone and one of (XI) has excellent fastness properties.[116] The amide from 1,2-phthaloylpyrrocoline-3-carboxylic acid and 1-amino-4-benzamidoanthraquinone dyes cotton reddish orange.[117] Anthrapyridone-4-carboxylic acid gives a yellow-green dye with α-aminoanthraquinone, and a red-brown with 1-amino-4-benzamidoanthraquinone.[118] The condensation products of 1-aminoanthraquinone-2-carboxylic acid and

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[110] P. Hindermann, J. P. Jung, and Gy, *SP* 306,548; 306,888–91.

[111] W. Braun, O. Trauth, and BASF, *DBP* 1,046,803–4.

[112] H. Schwechten and FBy, *USP* 2,830,989; *BP* 801,687.

[113] K. Akamatsu, M. Hazue, and NSK, *JP* 76/59; for orange and brown dyes from this acid, see CIBA, *BP* 1,170,899.

[114] D. I. Randall, J. Taras, and G, *USP* 2,914,542. cf. IC, *USP* 2,727,044.

[115] F. Graser and BASF, *DBP* 1,162,015; F. Graser, E. Daubach, and BASF, *DBP* 1,164,002.

[116] Gy, *BP* 851,557.

[117] D. I. Randall, W. Schmidt-Nickels, and G, *USP* 2,773,873.

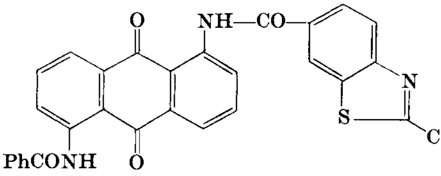
[118] P. Kienzle, and Fran, *FP* 1,055,425.

1-amino-5-arylmercaptoanthraquinones are red dyes of good fastness to light and wet treatments.[119] Good leveling power and light fastness are claimed for the red vat dye from 1-amino-4-chloroanthraquinone and 1-aminoanthraquinone-2-carboxylic acid.[120]

Several patents cover the preparation of benzamidoanthraquinones in which one or more of the benzene rings carry SO_2NR_2 (including sulfonylmorpholide) groups,[121] alkyl and aryl sulfonyl groups, or both sulfone and sulfonamido groups.[122] An equimolar mixture of 1,4-bis(benzamido)-anthraquinone and 1-benzamido-4-(*p*-dimethylsulfamoyl)benzamidoanthraquinone dyes viscose a fast violet, whereas the former gives a dull red-orange and the latter a bright red.[123]

1,4-Diamino-2-benzoylanthraquinone can be readily monoacylated in the 4-position, and the *p*-chlorobenzoyl derivative dyes cotton reddish blue.[124] *N*-Aroyl derivatives of 1,5-diamino-4,8-dihydroxyanthraquinone are well-known commercial dyes[124a]; CI Vat Violet 15 (CI 63355) is the dibenzoyl derivative. A very recent patent claims the preparation of the *p*-bromo analog.[125] Diaminoanthraquinones may be condensed first with esters of 2,5-dibromoterephthalic acid and then with other acid chlorides or cyanuric chloride.[126]

The introduction of a *p*-hydroxymethyl group into benzamidoanthraquinone yields dyes especially suitable for printing. Thus 1-*p*-hydroxymethylbenzamido-5-benzamidoanthraquinone gives "strong clear gold yellow prints."[127] The yellow vat dye (XII) containing a



(XII)

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[119] CIBA, *BP* 1,017,870; *USP* 3,360,532.

[120] BASF, *BP* 766,407.

[121] See, e.g., M. Stäuble and CIBA, *USP* 2,763,663; *BP* 718,566; CIBA, *SP* 285,007–9; W. Jenny, W. Kern, and CIBA, *USP* 2,614,109; *DBP* 965,260.

[122] CIBA, *SP* 293,893–919.

[123] J. Wegmann, W. Kern, W. Jenny, and CIBA, *USP* 2,883,312; *BP* 775,885.

[124] CIBA, *SP* 280,188; see also F. Ebel, W. Rupp, W. Keller, and BASF, *USP* 2,731,464; *BP* 719,282.

[124a] *CSD II*, p. 887.

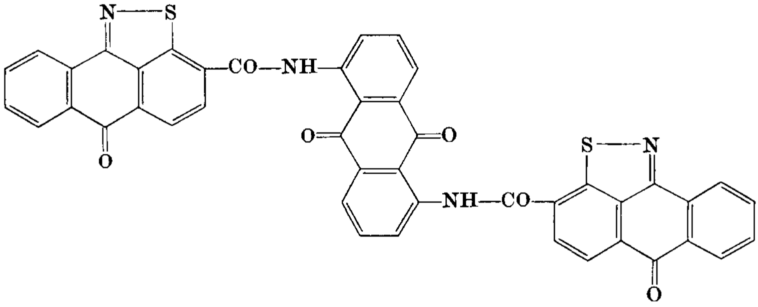
[125] W. Zerweck, E. Heinrich, and CFM, *DBP* 1,276,846.

[126] N. S. Dokunikhin *et al.*, *RP* 197,837.

[127] FBy, *BP* 762,888; see also CIBA, *BP* 890,172; H. Thielert, K. Weinand, and FBy, *DBP* 935,988.

reactive chlorine atom represents a general type for which high fastness to dry cleaning and migration is claimed.[128] Another example is the acylation of dyes of several types containing free amino groups in α-positions of anthraquinone nuclei with the dichloride of *p*-sulfobenzoic acid under conditions in which benzamides with free SO_2Cl groups are formed.[129]

1-Methacrylylamidoanthraquinone and similar monomers can be polymerized *in situ* for coloring plastics yellow to red.[130] The dye (XIII) has lightfastness 5–6 as a vat dye on cotton, but lightfastness 7–8, high color value, and good fastness to plasticizers and solvents as a pigment.[131] Pigments with very high fastness to light are obtained by condensing 2 moles of 1-amino-4-*p*-chlorobenzamidoanthraquinone with 1 mole of azobenzene or azoxybenzene-4,4′-dicarboxylic acid.[132]



(XIII)

B. Derivatives of Cyanuric Chloride and Related Compounds

Three commercial dyes prepared by condensing 1-aminoanthraquinone and its derivatives with cyanuric chloride (CC) were mentioned in *CSD II*[132a]: Cibanone Orange 6R, Red G, and Red 4B. Cibanone Orange 6R (CI Vat Orange 18; CI 65705) is the product obtained by condensing 1 mole of CC with 2 moles of 1-amino-4-methoxyanthraquinone; the structure of Red G (CI Vat Red 28; CI 65710) is confirmed; and Red 4B (CI Vat Red 24) has no CI constitution number.

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[128] CIBA, *BP* 977,807.

[129] K. Weber *et al.*, and CIBA, *SP* 427,103.

[130] T. Seiyaku and Co., *BP* 1,036,700.

[131] BASF, *BP* 998,704; see also F. Graser and BASF, *BP* 1,004,076.

[132] FBy, *BP* 1,132,818.

[132a] *CSD II*, p. 891.

Whelen[133, 134] assigns structures to the following Cibanone dyes; the amines condensed with 1 mole of CC are specified. None of them is confirmed in CI, and only Yellow 2GR, Red G, and Red 4B are in the current Cibanone pattern card.

Yellow 2GR	2 moles 1-aminoanthraquinone + 1 mole aniline
Orange RN	1 mole 1-aminoanthraquinone + 1 mole 1,5-diaminoanthraquinone
Orange 2R	1.5 mole 1-aminoanthraquinone + 0.5 mole 1,8-diaminoanthraquinone
Orange 3R	2 moles 1,4-diaminoanthraquinone
Orange 6R	1 mole 1-aminoanthraquinone + 1 mole 1-amino-4-methoxyanthraquinone
Red B	2 moles 1-amino-4-benzamidoanthraquinone + 1 mole 1-amino-4-methoxyanthraquinone
Red 4B	3 moles 1-amino-4-benzamidoanthraquinone (as in *CSD II*)
Red G	2 moles 1-amino-4-methoxyanthraquinone + 1 mole aniline
Red 3G	1 mole 1-amino-4-benzamidoanthraquinone + 1 mole 1-amino-4-methoxyanthraquinone

Large quantities of CC are used at the present time for the production of reactive dyes and optical brighteners, and it is readily available at a low price. Perhaps for this reason, the patent literature reveals a renewal of interest in vat dyes based on *s*-triazine. Thus a yellow vat dye of very good fastness is obtained by condensing CC with 2 moles of 6-chloro-1-aminoanthraquinone; replacement of the third chlorine in CC by NH_2 or NHEt gives a golden yellow dye.[135] Greenish yellow dyes are obtained by condensing 2 moles of 1-amino-3-chloroanthraquinone and 1 mole of 2-amino or mercapto benzothiazole or benzimidazole with CC.[135a] Examples of other intermediates for such condensation are 1-amino-6- and 7-methoxyanthraquinone,[136] 1,4-diamino-2-aroylanthraquinones (for blue dyes),[137] aminoacedianthrones,[138] and *N*,*N'*-diphenylperylene-

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[133] PB 74772, Frames 3855–3926 (cited by M. S. Whelen in Lubs[134, p.523]).

[134] H. A. Lubs, ed., "The Chemistry of Synthetic Dyes and Pigments." Reinhold, New York, 1955.

[135] CIBA, *BP* 831,880; see also *BP* 972,957.

[135a] P. Ulrich and CIBA, *Ger. Offen.* 1,906,841.

[136] K. Weber and CIBA, *USP*, 2,985,656.

[137] CIBA, *BP* 887,753.

[138] P. Kenzle and Fran, *FP* 1,098,647.

3,4,9,10-tetracarboxylic diimide in which each phenyl carries an amino group.[139] Replacement of the third chlorine by an alkoxy group leads to dyes with improved dyeing properties and increased fastness to alkali.[140] The third chlorine can be reacted with 2-*p*-aminophenyl-6-methylbenzothiazole,[141] and it also affords a device for the introduction of a sulfonic group via a phenoxy or phenylmercapto or anilino group (see also Section III, D).[142] When 2,6-dichloro-4-phenoxy-*s*-triazine is condensed with 2 moles of 1-aminoanthraquinone or 1-amino-4-aroylamidoanthraquinone, yellow to red vat dyes are obtained, which are also useful as pigments and for application to polyester fiber by the thermosol process.[143] The dyes prepared by condensing CC with 1 mole of *p*-aminoazobenzene (or its derivatives) and 2 moles of 1-aminoanthraquinone (or its derivatives) can be used as vat dyes on cotton or for coloring PVC.[144] When the reaction product from 1,4-diamino-2-acetylanthraquinone (1 mole) and 2,6-dichloro-4-phenoxytriazine (1 mole) is heated with 1,4-diaminoanthraquinone, a blue dye with very good fastness properties on cellulose is obtained.[145] Condensation of 2 moles of 2-amino-3,4-phthaloylacridone (XLIX) and 1 mole of phenol with CC gives a reddish blue dye[146]; replacing phenol by 3-amino-4-chlorobenzotrifluoride, the blue vat dye has good fastness to light and wet processing.[147]

Vat dyes, such as (XIV) and (XV) and analogs in which the hydroxyl groups are sulfated, have the interesting feature of a reactive chlorine atom.[148] When they are applied to cotton by a method in which vatting and dyeing are carried out under conditions designed to avoid hydrolysis of the chlorine atom, the dyes are "substantially irremovable from the fiber with hot dimethylformamide so that it is probable that they are chemically bound on the fiber." Dyes based on *s*-triazine, but which

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[139] Cf. M. Stäuble, K. Weber, and CIBA, *BP* 883,337; *USP* 2,914,531 (concerning reactive dyes of this type).

[140] Y. E. Gerasimenko, V. Z. Maslosh, and Scientific Research Institute of Organic Intermediates and Dyes (Rubezhan Branch), *RP* 187,910.

[141] F. Graser and BASF, *DBP* 1,149,476.

[142] CIBA, *BP* 1,000,206; 981,527; H. Altermatt and CIBA, *SP* 454,321 (add'n. to *SP* 407,373).

[143] CFM, *BP* 1,029,444; see also *FP* 1,410,547; *DBP* 1,274,069; 1,191,060; R. C. Conn, J. M. Campbell, and CCC, *USP* 3,040,045.

[144] P. Ulrich, C. Frey, and CIBA, *DAS* 1,904,433.

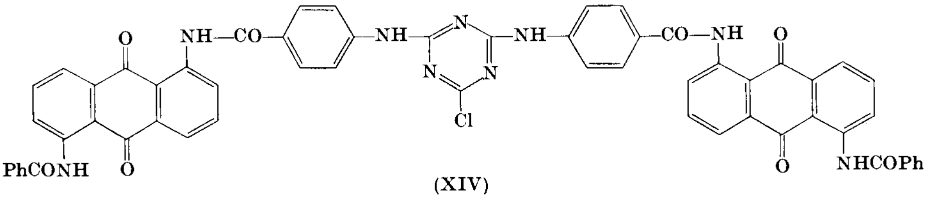
[145] CFM, *BP* 1,063,159.

[146] CIBA, *BP* 982,905; see also *BeP* 632,847; 626,819.

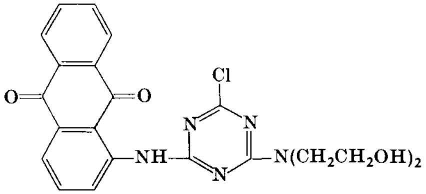
[147] CIBA, *BP* 957,148.

[148] CIBA, *BP* 891,794; 892,382; see also *BP* 915,266; *BP* 923,740 (cf. reference 44); G. A. Gamlen, C. Morris, D. F. Scott, H. J. Twitchett, and ICI, *BP* 950,327; 937,182.

contain an $SO_2NHCH_2CH_2Cl$ group attached to an aryl or anthraquinone nucleus, have also been patented.[149]



(XIV)



(XV)

Although the condensation of dyes or intermediates containing amino groups is without doubt the most convenient route to dyes containing the *s*-triazine nucleus, methods involving the construction of the *s*-triazine ring have been suggested. Thus 1-chloro- or 1,3-dibromoanthraquinone can be condensed with dicyandiamide.[150] Russian patents also suggest the use of melamine or 2,4-diamino-6-aryltriazine, condensed with 1-chloroanthraquinone and its derivatives.[151]

Useful properties are claimed for vat dyes based on 2,6-dichloro-4-aryl-1,3,5-triazines instead of CC. The former intermediates can be prepared by several methods, such as the condensation of nitriles of aromatic acids with dicyandiamide, followed by treatment with phosphorus pentachloride.[152]

The yellow pigment (XVI) (AQ = α-anthraquinonyl) is very resistant to heat and fast to light, and is particularly suitable for the mass pigmentation of synthetic polymers.[153] The analog in which AQ is 4-aminoanthraquinone-3-carboxylic ester dyes a fast reddish blue.[154] A fast red-

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[149] M. Stäuble, K. Weber, and CIBA, *SP* 397,120; CIBA, *SP* 449,155; *BP* 973,910.

[150] V. A. Titkov and I. D. Pletnev, *RP* 120,625; 121,520; 130,596.

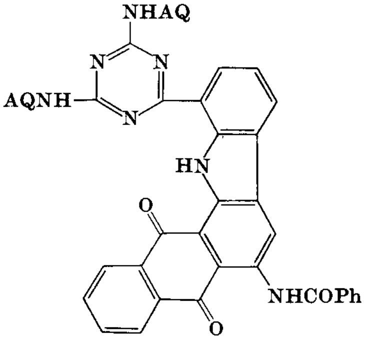
[151] V. A. Titkov and I. D. Pletnev, *RP* 132,740.

[152] BASF, *BP* 784,926; F. Ebel, H. Weidinger, and BASF, *USP* 2,832,779; *DBP* 1,026,456; A. W. Joyce and CCC, *USP* 2,694,709; CCC, *BP* 750,861.

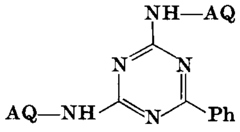
[153] CIBA, *BP* 953,155; see also *BP* 915,266.

[154] W. Kern, J. Koch, and CIBA, *USP* 3,079,389; *BP* 934,583; see also F. Ebel, W. Rupp, W. Keller, and BASF, *USP* 2,735,849.

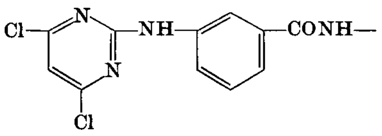
brown dye is obtained when Ph is replaced by 2-hydroxy-1-naphthyl and AQ by 5-benzamidoanthraquinone.[155] If Ph in (XVI) is replaced by *o*-chlorophenyl, the chlorine atom is labile enough to condense with 1-amino-4-benzamidoanthraquinone; aluminum chloride cyclization then gives the olive green dye (XVII).[156]



(XVII)



(XVI)



(XVIII)

Homogeneous compounds can be obtained by condensing 2,6-dichloro-4-phenyl-*s*-triazine stepwise with two different aminoanthraquinone derivatives. When such dyes are mixtures of products which result when the two aminoanthraquinones are used simultaneously, they have unattractive hues and unequal exhaustion rates.

Another general type of vat dye containing reactive chlorine is represented by anthraquinone derivatives containing the group (XVIII) in an α-position. They can be prepared by the condensation of the chloride of 2-*m*-carboxyanilino-4,6-dichloropyrimidine with an α-aminoanthraquinone. Thus the analog of Indanthrene Golden Orange 3G (CI 69025[156a]) dyes cotton yellow-brown from a hydrosulfite vat.[157]

In addition to cyanuric chloride and trichloropyrimidine, other intermediates for reactive dyes have been used for the preparation of vat dyes. Thus 2,3-dichloroquinoxaline-6-carboxylic acid and 1-aminoanthraquinone give the golden orange dye (XIX). With the acridone derivative (XLIX), only one chlorine atom reacts, and the product dyes

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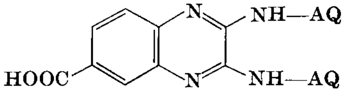
[155] CIBA, *BP* 933,170; see also CCC, *BP* 691,506; CIBA, *BP* 914,798; R. A. Gadea, W. P. Munro, and CCC, *USP* 2,691,020; *DBP* 926,976; V. A. Titkov and I. D. Pletnev, *RP* 119, 640; 130,595.

[156] A. W. Joyce and CCC, *USP* 2,729,638.

[156a] *CSD II*, p. 902.

[157] CIBA, *BP* 925,998.

cotton olive green.[158] Another reactive intermediate used for this purpose is 1-(*p*-carboxyphenyl)-4,5-dichloro-6-pyridazone. Other examples of acylating or reactive bridging units are 2,4-dichloroquinazoline (or its 6-chloro or 6,8-dichloro derivative) and 2-aryl-4-chloroquinazoline.[159] The condensation products of aminoanthraquinones with 2-phenyl-4-chloroquinazoline are recommended for application to polyamide fiber.[160] The condensation product of 1-aminoanthraquinone and 2,4,6-trichloroquinazoline dyes cotton orange.[161] Compound (XX), in which AQ and AQ′ represent suitably substituted anthraquinone derivatives, dye cotton bright yellow to blue-green of good color strength and fastness.[162] The azo group in these dyes is stable under normal vatting conditions. If benzoic acid is replaced by *o*-chlorobenzoic acid in Indanthren Green 4G (CI Vat Green 12; CI 70700[162a]), the chlorine atom can be condensed with an α-aminoanthraquinone (e.g., 1-amino-4-benzamidoanthraquinone) and the product cyclized to an olive green carbazole.[163] Yellow and green vat dyes with excellent fastness properties are obtained by heating (XXI) with about 2 moles of vattable amines such as 1-aminoanthraquinone and 1-amino-5-benzamidoanthraquin-



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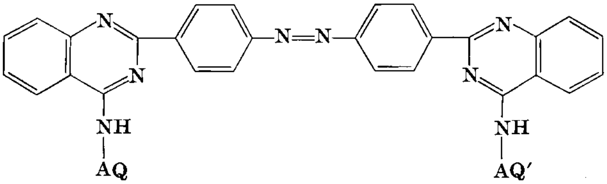

(XX)

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[158] K. Weber, I. Hari, and CIBA, *SP* 419,399; *AustP* 219,042.

[159] BASF, *BP* 829,699; W. Braun, H. Weissauer, and BASF, *DBP* 940,243; F. Ebel *et al.*, and BASF, *USP* 2,792,397; *BP* 771,347.

[160] F. Ebel, F. Schuhmacher, K. E. Kling, and BASF, *DBP* 1,046,565.

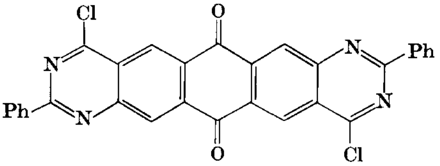
[161] F. Ebel, W. Kupp, O. Trauth, and BASF, *USP* 2,697,097; *BP* 743,034.

[162] BASF, *BP* 1,043,348; see also M. Scalera, A. W. Joyce, and CCC, *USP* 2,800,468; H. Weidinger, G. Haese, and BASF, *BP* 1,043,348.

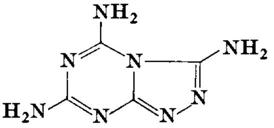
[162a] *CSD II*, p. 927.

[163] P. Sutter and CIBA, *USP* 2,840,560; *BP* 719,670.

one.[164] 2,4,7,8-Tetrachloroquinazoline and 2,4-dichloro-6-phenyl-1,3,5-triazine have been used to link two different aminoanthraquinones.[165]



(XXI)



(XXII)

Condensation of the triazolotriazine (XXII) with 3 moles of 1-chloroanthraquinone yields a yellowish orange dye which has good fastness properties and is much less photochemically active than the corresponding *s*-triazine derivative, being comparable to flavanthrone.[166]

C. ALDAZINES

Although Indanthrene Bordeaux B (CI Vat Red 18; CI 60705), the azine from 1-aminoanthraquinone-2-aldehyde, is unimportant, patents on derivatives and related dyes have appeared. Thus the 6,6′-dichloro derivative dyes cotton in strong red-violet shades.[167] 1-Aminoanthraquinone-3-aldehyde can be prepared from the 2-aldehyde by nitration, deamination, and reduction; and the *N*-benzoyl derivative of the azine dyes cotton greenish yellow shades.[168]

D. ANTHRIMIDES AND CARBAZOLES

1. *Anthrimides*

"Anthrimide" in this chapter refers to 1,1′-dianthraquinonylamine and AQ to 1-anthraquinonyl. Anthrimides are important as intermediates for the carbazoles and it is doubtful if any anthrimide is used as a dye at the present time. An anthrimide not mentioned in *CSD II* is CI V at Orange 20 (CI 65025) (Solanthrene Orange 5J, Fran), the condensation product of 1-benzamido-5-chloroanthraquinone and 1-aminoanthraquinone; but it is not in the commercial range. Trianthrimides, such as the condensation product of 1,5-dichloroanthraquinone and 1-aminoanthraquinone, yield dye compositions suitable for dyeing polymers in

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[164] BASF, *BP* 763,328; see also CIBA, *BP* 642,129.

[165] BASF, *BP* 829,699.

[166] V. A. Titkov and I. D. Pletnev, *RP* 122,227; *J. Gen. Chem. USSR* (*English Transl.*) **33**, 951 and 1324 (1963); see also D. W. Kaiser and CCC, *USP* 2,473,797.

[167] R. Neeff, H.-W. Schwechten, and FBy, *BP* 750,977.

[168] W. Eckert, H. Armand, and FH, *DBP* 936,945.

shades with good fastness to light and migration.[169] The trianthrimide from 1 mole of 1,8-diamino-4,5-bis(benzamido)anthraquinone and 2 moles of 2-chloroanthraquinone dyes cotton bluish olive green.[170] Anthrimides (and anthraquinonylaminobenzanthrones; see Section VI, D) can be prepared in aqueous medium.[171] An interesting synthesis of 1,2′- and 2,2′-anthrimides is to take advantage of the readiness with which isothiazolanthrone (XXIII; R = H) undergoes nucleophilic substitution, for instance, with 2-aminoanthraquinone to form (XXIII; R = 2-anthraquinonylamino); desulfurization then yields 2,2′-dianthrimide.[172]

2. *Carbazoles*

When an anthrimide is heated with aluminum chloride, cyclization to the carbazole takes place (see Section V for a discussion of the mechanism). Several carbazole derivatives of this type are largely used vat dyes of yellow, orange, khaki, brown, and olive shades.[172a, 173] Vigorous treatment with an oxidizing agent such as sodium hypochlorite is essential for the development of the pure shades.

The carbazole structures assigned to a few of the dyes have been confirmed.[174] For Indanthrene Khaki GG (CI Vat Green 8; CI 71050), prepared by condensing 1 mole of 1,4,5,8-tetrachloroanthraquinone with 4 moles of 1-aminoanthraquinone and heating the pentanthrimide (XXIV) with aluminum chloride, the tetracarbazole structure is usually assumed, but there has been some doubt if all the four anthrimide groups undergo cyclization. Jayaraman[175] synthesized and examined a series of anthrimides, corresponding carbazoles, and compounds such as (XXV) containing both anthrimide and carbazole groups. The simpler anthrimides and carbazoles could be distinguished on the basis of their absorption spectra in organic solvents, but Vat Green 8 was almost totally insoluble. The absorption spectra in sulfuric acid supported the tetracarbazole structure. Anthrimides showed two peaks at about 263 and 360 mμ; the carbazoles exhibited a peak at about 260 mμ and a broad

[169] A. Caliezi and CIBA, *DBP* 1,100,943.

[170] J. Koch, W. Kern, and CIBA, *USP* 2,657,221; *BP* 677,381.

[171] DuP, *USP* 3,040,063.

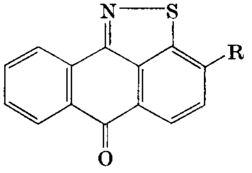
[172] K. H. Shah, "Proceedings of the Symposium on Contributions to the Chemistry of Synthetic Dyes and Mechanism of Dyeing," p. 1. Univ. of Bombay, 1968.

[172a] *CSD II*, p. 899.

[173] For a recent review, see J. Arient, V. Slavik, and J. Marhan, *Chem. Listy* **60**, 1509 (1966).

[174] W. Bradley and C. R. Thitchener, *J. Chem. Soc.* p. 1085 (1953); W. Bradley and P. N. Pandit, *ibid.* p. 3399 (1955).

[175] P. Jayaraman, Ph.D. Thesis, University of Bombay (1957).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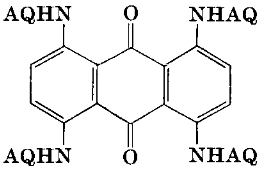
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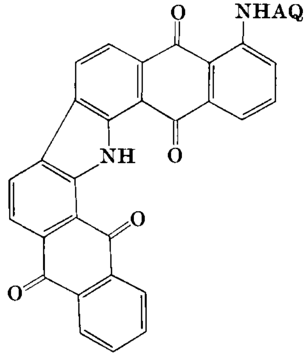
(XXV)

band at about 508 mμ; compounds such as (XXV) containing both anthrimide and carbazole groups exhibited absorption bands in all the three regions. Vat Green 8 in sulfuric acid showed absorption maxima at about 260 and 540 mμ, and the anthrimide peak at 360 mμ was absent. Infrared spectra also supported the tetracarbazole structure.[176] The NH groups in the anthrimides are involved in hydrogen bonding with the neighboring carbonyl groups, and all the anthrimides including anthrimide-carbazoles (XXV) showed two strong bonds at 1670–1664 and 1665–1630 cm^{-1}. In the carbonyl region the carbazoles, including Vat Green 8, showed only one band at about 1666 cm^{-1}. Bradley and Pandit[177] synthesized a compound which they believed to be the tetracarbazole, but by a series of reactions which gave amorphous intermediate products and which, in fact, provided no evidence concerning the structure of their ultimate product. Since their final product dyed a yellowish shade on cotton, it was presumably different from Vat Green 8, although this conclusion was not specifically stated.[177a]

[176] C. J. Sanchorawala, Ph.D. Thesis, University of Bombay (1963); C. I. Jose, C. J. Sanchorawala and, M. K. Unni, unpublished work (1963); see also J. Arient, J. Knizek, J. Marhan, and V. Slavik, *Collection Czech. Chem. Commun.* **33**, 3280 (1968).

[177] W. Bradley and P. N. Pandit, *J. Chem. Soc.* p. 819 (1957); p. 3399 (1955).

[177a] In a recent patent conditions are described for the preparation from pentanthrimide of the tricarbazole, which is a yellowish khaki vat dye (BASF, *BP* 1,172,192).

Shah[178] has used the spectral data discussed above to decide if cyclization of anthrimides to carbazoles has taken place in certain vat dyes. Thus the structure of Indanthrene Olive T (CI Vat Black 25; CI 69525) was confirmed; Indanthrene Grey M (CI Vat Black 8; CI 71000) contains an anthraquinonylamino and not a carbazole group; Indanthrene Grey BG (CI Vat Black 29; CI 65225) is a mixture of condensation products of dibromoanthanthrone with 1 and 2 moles of 1-amino-4-benzamidoanthraquinone.

Brodman *et al.*[179] have studied and standardized the preparation of a few anthrimides and carbazoles, using paper and thin-layer chromatography for following the reactions. Thus optimum conditions were determined for the preparation of CI Vat Orange 11 (CI 70805), CI Vat Brown 1 (CI 70800), and CI Vat Black 27 (CI 69005). Analytical control methods in the commercial production of CI Vat Orange 11 (1,5-diaminoanthraquinone + 2 moles 1-chloroanthraquinone; cyclize the trianthrimide to the dicarbazole) have also been discussed.

Dokunikhin *et al.* prepared analogs of CI Vat Orange 15 (CI 69025) and CI Vat Black 27 (CI 69005), the carbazoles from 5,5′- and 4,4′-bis(benzamido)anthrimide, in which the benzamido groups were replaced by PhNHCONH groups, and found that they dyed deeper shades, but with inferior fastness properties.[180]

An improvement in the carbazolization of 4,4′-bis(benzamido)-anthrimide to CI Vat Black 27 is to add water after the sulfuric acid treatment and oxidize directly with dichromate; the product dyes cotton a yellowish olive. In the preparation of CI Vat Green 8 oxidation of the crude product of carbazolization successively with hypochlorite (12% active chlorine) and permanganate gives a greener dye.[181] Dianthrimides containing free amino groups can be *N*-benzoylated and carbazolized in one step by adding benzoic acid to the solution in oleum or chlorosulfonic acid. In the latter medium the two reactions take place concurrently; and in oleum benzoylation occurs first. The dyes prepared in this manner have greater tinctorial value than CI Vat Black 27, and the reaction conditions can be varied to produce yellower or greener shades.[182] A fast red dye is obtained by acylating the carbazole from

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[178] K. H. Shah *et al.*, *Indian J. Chem.* **2**, 361 (1964); **3**, 273 (1965); see also CIBA, *BP* 771,748.

[179] F. Brodman *et al.*, *Rev. Chim.* (*Bucharest*) **14**, No. 4, 222 (1963); *Bull. Inform. Lab. Cent. Color* **3**, No. 7, 9 (Rom) (1967); *Rev. Chim.* (*Bucharest*) **19**, No. 1, 6 (Rom) (1968).

[180] N. S. Dokunikhin, A. M. Fomicheva, and N. I. Abramova, *J. Appl. Chem. USSR* (*Engl. Transl.*) **20**, 1009 (1956).

[181] J. S. Milazzo and G, *USP* 3,023,220; H. Klemme, F. Osterloh, and FH, *DBP* 1,144,424.

[182] J. J. Carr and ICI, *USP* 3,230,232.

5,5′-diaminoanthrimide with 1-aminoanthraquinone-2-carbonyl chloride.[183]

The trianthrimide from 1,4-diaminoanthraquinone and 1-chloroanthraquinone gives two dyes (CI Vat Brown 1, CI 70800; and CI Vat Brown 44, CI 70802) according to the reagent employed for carbazolization: aluminum chloride in pyridine or potassium hydroxide.[184] Both the dyes are assigned the same dicarbazole structure, and it was stated in *CSD II*[184a] that Indanthrene Brown BR (CI Vat Brown 1) is a purer brand of Indanthrene Brown GR (CI Vat Brown 44). The mechanism of the reactions and the structures of the dyes obviously need investigation.

Carbazolization of the trianthrimide from 1-aminoanthraquinone and 1,4-dichloro-5-methoxyanthraquinone with aluminum chloride in pyridine gives a brown dye, and with aluminum chloride–sodium chloride at 130–140° a blue dye[185]; in this patent of 27 pages many interesting reactions and products based on anthrimides and carbazoles from α-hydroxy- and methoxyanthraquinones containing 2–4 nuclear chlorine atoms are described. The dye obtained from 1-chloro-4-benzamidoanthraquinone and a mixture of 1,5- and 1,8-aminobenzamidoanthraquinone, followed by carbazolization, dyes cotton a bright brown shade of excellent fastness and is obtained in 90% yield.[186] When 1-amino-6,7-dichloroanthraquinone (see Section II) is converted to 4,5′-dibenzamido-6,7-dichloroanthrimide and then carbazolized, the product dyes cotton pure brown shades.[187]

During the cyclization of di- or polyanthrimides, using titanium(IV) halides as catalysts, the carbazole is produced as a stable Ti complex. A method[188] of breaking down this complex, giving a 2–5% increase in yield of dye and a reduction of the ash content to 2–6%, consists in successive treatment with dilute sodium hydroxide solution and hydrochloric acid at about 90°. A polyanthrimide may be cyclized to the corresponding polycarbazole in one step, or a stepwise synthesis through an intermediate carbazole may be carried out. Using aluminum chloride in pyridine, a fast gray dye can be thus obtained from 1,1′,4′,1″,4″,1‴-tetranthrimide.[189] When anthrimide is nitrated in the presence of boric

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[183] T. Holbro and CIBA, *USP* 2,778,837; *BP* 767,412.

[184] *FIAT* 1313, II, p. 101; K. J. Bradley and P. Kronowitt, *Ind. Eng. Chem.* **46**, 1146 (1954).

[184a] *CSD II*, p. 906.

[185] FBy, *NethP* 6,510,298.

[186] M. Scalera, H. W. Stewart, and CCC, *USP* 2,425,126.

[187] CIBA, *BP* 704,013.

[188] J. Arient, J. Marhan, and L. Musilova, *BP* 1,094,847.

[189] CIBA, *USP* 2,804,461; *BP* 792,036; M. Grelat *et al.*, and CIBA, *USP* 2,853,492; *BP* 784,396.

acid to a product containing 15–20% of the 4-nitro and 60–70% of the 4,4′-dinitro derivative, the remainder being a polynitro compound, reduced, benzoylated, and carbazolized with sulfuric acid, a green vat dye is obtained.[190] Gray vat dyes of good fastness and leveling power are obtained by cyclizing (preferably with aluminum chloride in pyridine at 120–125°) the aminopolyanthrimides obtained by treatment of 4-unsubstituted 1-aminoanthraquinones with manganese dioxide or potassium persulfate in sulfuric acid and reduction of the quinoneimines with stannous chloride.[191]

"Linear polyanthrimide-carbazoles" prepared from a 1,4-diaminoanthraquinone and a 1,4-dichloroanthraquinone in certain proportions are gray pigments and vat dyes of excellent fastness to chlorine and light.[192] Brown-gray dyes of this type can also be prepared by condensing 4-chloroanthrimide with 4-aminoanthrimide and heating the tetranthrimide with aluminum chloride in a tertiary base.[193] The introduction of 2.54% chlorine by treatment with sulfuryl chloride in nitrobenzene before carbazolization leads to compounds dyeing cotton fast neutral gray shades.[194] When the linear tetranthrimide from 4,4′-diaminoanthrimide and 2 moles of 1-benzamido-4-chloroanthraquinone is carbazolized by short heating at 138° with aluminum chloride in pyridine, the product dyes cotton in "fast bluish tints"; changes in the aroyl group lead to bluish gray and gray dyes.[195] Very fast brown, khaki, olive and gray dyes are produced by carbazolizing anthrimides containing aroylamido groups in the 4,5,8-positions,[196] or tetranthrimides in which one anthraquinone residue carries a benzamido group.[197] An olive green dye is obtained by carbazolizing 1-benzamido-4,5,1′,1″-trianthrimide, prepared from 1,8-dichloro-4-nitroanthraquinone and 2 mols of 1-aminoanthraquinone.[197a]

Several patents cover the use of *o*-fluorobenzamidoanthrimides.[198]

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[190] F. Brodman, *et al.*, *RomP* 49,330.

[191] CIBA, *BP* 829,527; 794,849; Dvorak *et al.*, *CzechP* 124,132; E. Mörgeli, M. Grelat, and CIBA, *SP* 332,488; 374,444.

[192] M. Grelat and CIBA, *BP* 835,714; *USP* 2,884,425; see also M. Grelat, W. Kern, and CIBA, *USP* 2,672,462; *BP* 703,502.

[193] M. Grelat *et al.*, and CIBA, *DBP* 972,957; *USP* 2,804,461; *BP* 693,075; see also *BP* 784,396; *DBP* 960,029.

[194] M. Grelat and CIBA, *USP* 2,790,809; *BP* 749,792.

[195] CIBA, *BP* 767,595; M. Grelat, W. Kern, and CIBA, *USP* 2,847,415; *DBP* 959,578.

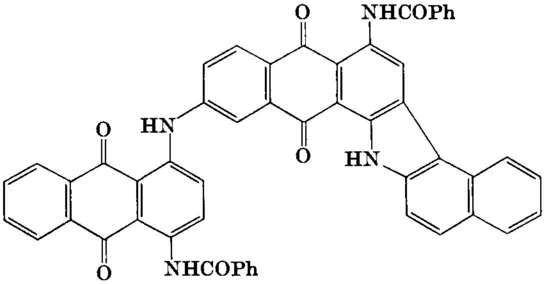
[196] FBy, *BP* 1,087,568; W. Holmann and FBy, *DBP* 1,232,296.

[197] FBy, *BP* 1,069,460.

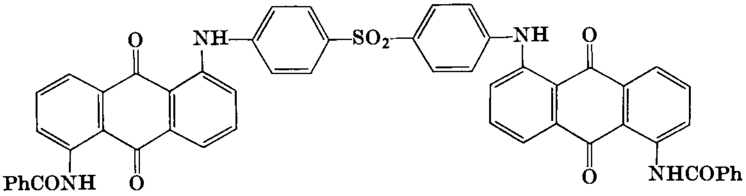
[197a] V. Hajek, *FP* 1,551,784; see also *FP* 1,553,270.

[198] See, e.g., E. Mörgeli and CIBA, *BP* 658,721–2.

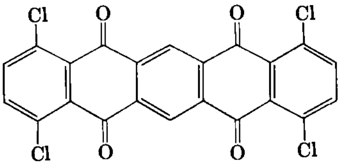
Examples were given in *CSD II*[198a] of dyes in which cyclization to a carbazole is carried out on secondary amines AQ—NH—Ar, Ar being a derivative of benzene, naphthalene, etc. Another example is the dark violet dye (XXVI), in which the major contributors to the color and dyeing properties are the benzamido groups and the 1,2′-anthrimide part of the molecule.[199] The sulfone (XXVII) dyes cotton a red-brown shade of excellent fastness; by fusion with aluminum chloride–sodium chloride (XXVII) can be cyclized to the bis-carbazole, which is a yellow-brown dye.[200] The tetracarbazole obtained from 4 moles of 1-aminoanthraquinone and 1 mole of tetrachloropentacenediquinone (XXVIII) dyes cotton



(XXVI)



(XXVII)



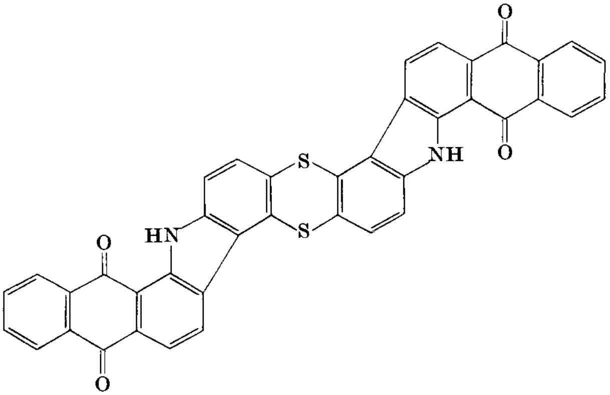
(XXVIII)

[198a] *CSD II*, p. 910.

[199] W. Mieg and FBy, *DBP* 909,385.

[200] T. A. Martin, D. I. Randall, and G, *USP* 2,908,684.

yellowish brown with lightfastness 6–7 and chlorine fastness 3.[201] Other variations involve the use of chloropyrimidanthrones, benzothiazoles, benzoxazoles, brasanquinones (from 2,3-dichloronaphthoquinone), etc., dyes containing one or more anthraquinone and one or more carbazole nuclei being ultimately produced.[202] Dyes of this series linked in an α-position of an anthraquinone to 2-aminobenzothiazole are gray, brown, or black dyes for cellulosic fibers with very good fastness to light.[203] The attachment of a benzoxazole or benzothiazole or benzimidazole in the 2-position to the 6-position of 1,4-diaminoanthraquinone improves the fastness properties of the vat dyes obtained by conversion to the dicarbazoles via the trianthrimides.[204] When 2,4-dichloroquinazoline is condensed with 1-amino-5-chloroanthraquinone, and the product is condensed with 1-amino-5-benzamidoanthraquinone, the resultant anthrimide dyes cotton corinth and the corresponding carbazole brown shades.[205] Aluminum chloride cyclization of the condensation products of 2,6-dibromothianthrene with 2 moles of 1-aminoanthraquinone or its 4- or 5-benzamido derivative yields products (XXIX), which dye cotton fast brown to maroon shades.[206] Presumably the leuco derivatives in alkaline solution have adequate substantivity for cellulose, notwithstanding the nonplanar character of the thianthrene molecule.



(XXIX)

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[201] J. J. A. Moll and Vond, *USP* 3,228,958.

[202] See, e.g., H. Weidinger *et al.*, and BASF, *BP* 1,023,703; W. Braun, H. Krantz, and BASF, *BeP* 636,653; J. A. Simonnet, L. Cabut, and Fran, *FP* 1,364,563; H. Leister, S. Bien, and FBy, *BeP* 671,894; M. F. Sartori and DuP, *USP* 2,893,998.

[203] FBy, *BP* 1,054,158.

[204] BASF, *BP* 989,049.

[205] F. Ebel, H. Weidinger, and BASF, *DBP* 1,064,174.

[206] W. Schmidt-Nickels and G, *USP* 3,106,563.

E. IMIDAZOLES, OXAZOLES, AND THIAZOLES

If an aminoanthraquinone carries an actual or potential amino, hydroxyl, or thiol group in an adjacent position, it can be acylated and cyclized to form an imidazole, oxazole, or thiazole. Several dyes of this type (XXX; or the 1,2- or 2,1-isomer), which can also be prepared by other methods, were described in *CSD II*.[206a] The oxazoles are the most important; the only two imidazoles in *Colour Index* (Algol Brilliant Orange FR, CI 66795; and Indanthrene Orange RRK, CI 66800) are obsolete.

Hida[207] has studied the synthesis of oxazoles and thiazoles of the type (XXX), as well as the 1,2- and 2,1-isomers, in which Ar = 2-anthraquinonyl with amino groups in the 1,4-positions (prepared by condensation of the appropriate aminohydroxyanthraquinone or aminomercaptoanthraquinone with 1,4-diaminoanthraquinone-2-carbonyl chloride) (cf. Indanthrene Blue CLG and CLB).[207a] He has also carried out the Ullmann condensation of 1- and 2-aminoanthraquinone with (XXX; Ar = *p*-bromophenyl) and has recorded the visible absorption spectra of the dyes and the shades on cotton.

The versatility of the reactions has led to many patents covering dyes of this series. There are patents covering all the three heterocyclic rings; but the essential points in some of the patents appear to involve the group Ar in (XXX) or the 2,1-type from 1-chloro-2-aminoanthraquinone. Thus some patents specify the use of 1-aminoanthraquinone-2-carboxylic acid in the form of 3,4-phthaloylisatoic anhydride,[208] 1-aminoanthraquinone-3-carboxylic acid,[209] and azobiphenyl-4,4′-dicarboxylic acid.[210] In one patent unsymmetrical compounds are prepared by condensing the last acid successively with a 1,2-diaminoanthraquinone and a 2-amino-3-chloroanthraquinone; the ultimate products, which are yellow dyes, contain both imidazole and oxazole rings.[211]

1. *Imidazoles*

The imidazole (XXXI) is a greenish yellow vat dye. Orange and green dyes and pigments of this type can be prepared by suitable variations

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[206a] *CSD II*, pp. 910, 911, and 914.

[207] M. Hida, *Yuki Gosei Kagaku Kyokai Shi* **20**, 266, 343, 348, and 473 (1962).

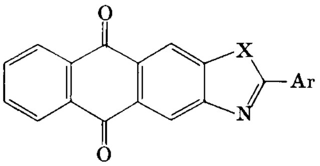
[207a] *CSD II*, p. 915

[208] F. Ebel, R. Randebrock, and BASF, *BP* 731,008; *USP* 2,717,898.

[209] BASF, *BP* 709,596.

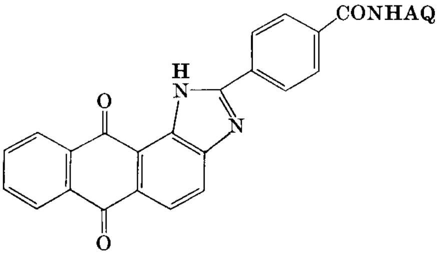
[210] H. E. Schroeder, J. Deinet, and DuP, *USP* 2,559,667–75; 2,587,908; J. Deinet and DuP, *USP* 2,719,838–42; *BP* 726,797.

[211] W. R. Demler and NAC, *USP* 3,367,928; see also T. Sasa *et al.*, and MDW, *JP* 2642/64.

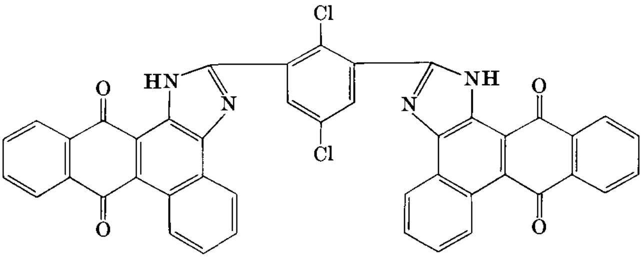


X = NH or O or S

(XXX)

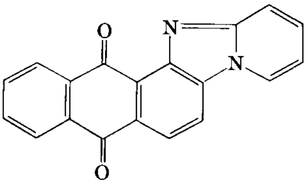


(XXXI)

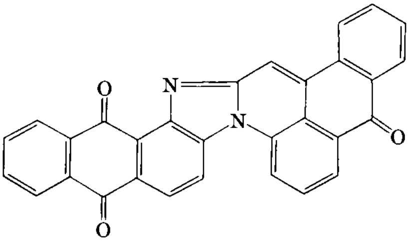


(XXXII)

in the monamine and diamine linked to terephthaloyl chloride.[212] The bis-imidazole from 1,2-diaminoanthraquinone and terephthalic acid dyes cotton yellow; it was mentioned in an IG patent application[213] and is also the subject of more recent patents.[214] The analog from biphenyl-4,4′-dicarboxylic acid dyes golden yellow. The bis-imidazoles (XXXII) are red to violet dyes with improved fastness to washing.[215]



(XXXIII)



(XXXIV)

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[212] CIBA, *BP* 1,073,617; see also CIBA, *BP* 1,033,780.

[213] IG, *DRP* Anm. J. 49,049.

[214] H. Geeren *et al.*, and BASF, *DBP* 1,137,817; CIBA, *BP* 1,033,780.

[215] BASF, *BP* 1,146,158; cf. H. Geeran *et al.*, and BASF, *BP* 867,160; *USP* 2,989,535.

When 1-chloro-2-nitroanthraquinone is heated with 2-aminopyridine in presence of copper acetate in ethylene glycol diacetate, the product is the imadazo[1,2-*a*]pyridine derivative (XXXIII), which dyes cotton orange.[216] When 1-amino-2,1′-anthrimide is treated with acetic anhydride the corresponding *N*-anthraquinonyl-2-methyl-4,5-phthaloylbenzimidazole is formed; hot sulfuric acid effects further cyclization to (XXXIV), which contains the imidazo[1,2-*a*]pyridine ring system and is also a derivative of 3-azabenzanthrone; it dyes cotton a fast orange shade.[217]

2. *Oxazoles*

CI Vat Red 10 is an important dye included in the vat dye range of several firms. Stilmar[218] has drawn attention to the fact that it has chlorine fastness 5 on cotton in spite of the free amino group. He suggests that "the remarkable resistance of the amino group in Indanthrene Red FBB to bleach may be explained by hydrogen bonding. One of the amino hydrogens is bonded to the peri carbonyl oxygen while the other amino hydrogen is bonded to either the nitrogen or oxygen of the oxazole ring. This principle of amino protection is also effective in thiazole combinations" (CI Vat Red 20; CI Vat Blue 30 and 31). Other vat dyes with high chlorine fastness which have free amino groups are CI Vat Red 31 (an oxadiazole; see Section IV,F) and CI Vat Red 21 [bis-1,4(1′-amino-2′-anthraquinonylamido)-anthraquinone; see Section IV,A]. Although hydrogen bonding of an amino group simultaneously with an anthraquinone carbonyl and a heterocyclic nitrogen or an amide carbonyl group is possible in all these dyes, it is very doubtful if the relative chlorine fastness of vat dyes attached to the cellulose molecule can be explained by hydrogen bonding. Indanthrone, in which the NH groups are powerfully hydrogen-bonded with the neighboring carbonyl groups (see Section IV,J), has chlorine fastness 1. Hydrogen bonding is clearly unable to prevent the oxidation of the dihydrophenazine to the phenazine. The two very similar dyes CI Vat Violet 15 and 17, the *N*-benzoyl and *N*-anisoyl derivatives of 4,8-diamino-1,5-dihydroxyanthraquinone, have chlorine fastness 5 and 3, respectively, because electron-donor substituents tend to decrease chlorine fastness. Vat Red 10 and the other dyes with free amino groups probably owe their chlorine fastness to the delocalization of the amino nitrogen lone-pair electrons by mesomeric interaction with C=O and C=N groups, as shown in the structures (A)

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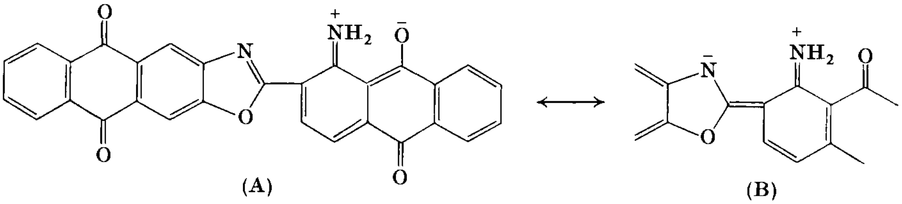
[216] W. L. Mosby, W. L. Berry, and CCC, *USP* 2,938,904.

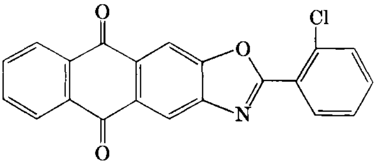
[217] M. Grelat, W. Jenny, and CIBA, *USP* 2,815,347; *BP* 787,311.

[218] F. B. Stilmar, *in* Lubs[134, p.473].



(A) (B)

CI Vat Red 10; CI 67000
Indanthrene Red FBB



(XXXV)

and (B) for Vat Red 10. It is also necessary to remember in this connection that the fastness of a dye to chlorine, light, or other agencies is a property of the solid dye–cellulose (or other dye–substrate) system.

CI Vat Red 10 is useful for the preparation of high-temperature grease.[219]

The hue of CI Vat Red 10 can be shifted to violet by introducing a benzamido group para to the amino group; thus 1,4-diamino-2-anthraquinonyl-2′,3′-anthraquinone-oxazole may be condensed with 2,5-dichlorobenzoyl chloride, when only the 4-amino group undergoes acylation.[220] Condensation of the diamine with 2,3-dihydroxy-7,8-phthaloylquinoxaline[220a] (see Section IV,H) gives a gray dye.[221]

A blue-violet dye is obtained by condensing 1-amino-4-benzamido-anthraquinone-2-carbonyl chloride with *o*-aminophenol. The bis-oxazole from this acid chloride (2 moles) and 4,6-dibromo-*m*-phenylenediamine dyes cotton blue-gray.[222] Another route to symmetrical and unsymmetrical bis-oxazoles involves the use of 2,5-diamino-*p*-benzoquinone.

In the oxazole (XXXV) the chlorine atom can be condensed with 1-amino-5-benzamidoanthraquinone and subsequently cyclized with aluminum chloride to a carbazole, which dyes cotton yellowish brown.[223]

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[219] F. Buehler and Socony Mobil Oil Co., *USP* 3,137,653.

[220] W. Braun, W. Ruppel, and BASF, *USP* 2,905,691; *BP* 825,033.

[220a] See also *CSD II*, p. 943.

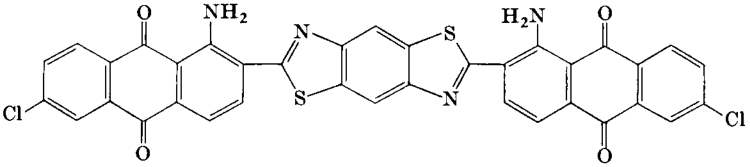
[221] F. Graser and BASF, *BP* 925,112.

[222] T. Holbro, W. Kern, and CIBA, *USP* 2,792,384; 2,807,622; *BP* 802,681.

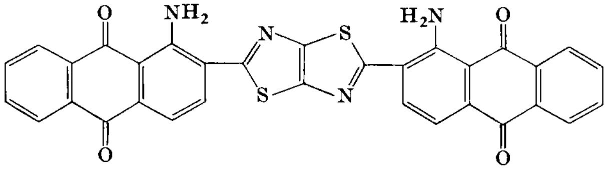
[223] W. Zerweck, E. Honold, and CFM, *DBP* 821,252.

3. *Thiazoles*

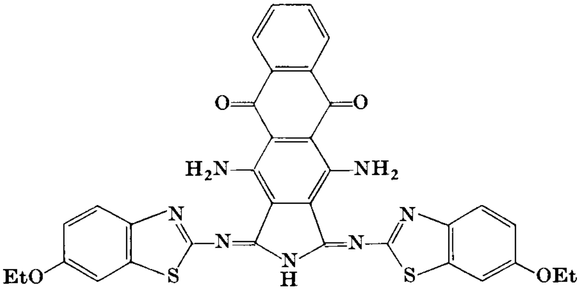
Yellow, red, blue, gray, and green vat dyes of especially high fastness to light and high color intensity are obtained by condensing 2 moles of an anthraquinone-2-aldehyde (or its anil) with 1 mole of 2,5-diamino-1,4-dithiobenzoquinone.[224] An example is the bluish bordeaux dye (XXXVI). Using 1-aminoanthraquinone-2-aldehyde and dithiooxamide, the product is (XXXVII), which dyes cotton a dark reddish blue. 1-Amino-4-benzamidoanthraquinone-2-aldehyde (conveniently used in the form of the anil obtained directly by heating the 2-methylanthraquinone derivative with aniline and potassium carbonate in nitrobenzene) is a useful intermediate, which can be converted to benzothiazoles and benzoxazoles carrying the 2-anthraquinonyl group in the 2-position. Grayish blue dyes are thus obtained.[225]



(XXXVI)



(XXXVII)



(XXXVIII)

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[224] FBy, *BP* 1,019,774; 1,010,235; see also R. Neeff and FBy *DBP* 1,164,003.

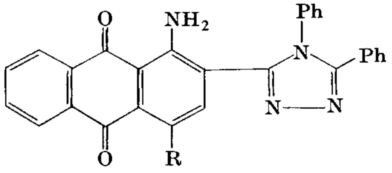
[225] R. Neeff and FBy *USP* 2,868,799; *BP* 811,386.

Vat dyes and pigments of considerable interest containing isoindole ring systems can be prepared by condensing 1,4-diamino-2,3-dicyanoanthraquinone with 2-aminobenzothiazole or imidazole or oxazole. An example is (XXXVIII), which dyes greenish gray from an emerald green vat.[226]

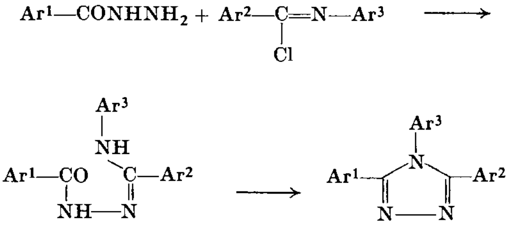
F. TRIAZOLES AND OXADIAZOLES

1. *Triazoles*

By appropriate reactions starting with 1-aminoanthraquinone-2-carboxylic acid the red dye (XXXIX; R = H), the blue dye (XXXIX; R = PhCONH), and analogous dyes can be prepared.[227] Thus an anthraquinonyl carbohydrazide can be condensed with an aroylarylide chlorimide in an inert solvent above 120° (cf. the synthesis of oxadiazoles[228, 229] The anthraquinone residue can be in either of the two reactants. The reaction product may spontaneously cyclize to the 1,2,4-triazole (XLI), but if it stops at the amidrazone stage (XL), ring



(XXXIX)



$$Ar^1—CONHNH_2 + Ar^2—\underset{\substack{|\\ Cl}}{C}=N—Ar^3 \longrightarrow$$

(XL) (XLI)

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[226] F. Baumann and FBy, *DBP* 1,151,335; see also FBy, *USP* 2,945,861; *BP* 879,240.

[227] E. Klingsberg and CCC, *USP* 2,884,424; 2,898,343; see also H. Weidinger and J. Kranz, *Chem. Ber.* **96**, 1064 (1963).

[228] For recent reviews of 1,3,4-oxadiazole chemistry, see A. Hetzheim and K. Mockel, *Advan. Heterocyclic Chem.* **7**, 183 (1966). E. P. Nesynov and A. P. Grekov, *Russ. Chem. Rev.* (*English Transl.*) **33**, 508 (1964).

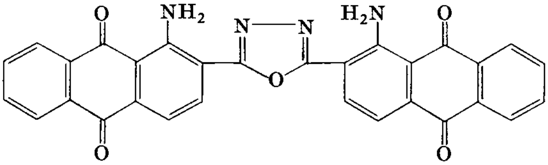
[229] H. Weidinger and J. Kranz, *Chem. Ber.* **96**, 1049 (1963).

closure is effected by heating with thionyl chloride or phosphorus oxychloride or chlorosulfonic acid.

Vat dyes derived from 1,2,4-triazole can also be prepared by (a) condensation of 3,5-diamino-1,2,4-triazole with 1-aminoanthraquinone-2-aldehyde or its anil[230]; and (b) the action of arylamines on anthraquinone α-chloro- or α,α'-dichloroaldazines, which can be prepared by the chlorination of the aldazine or treatment of the diacyl hydrazide with phosphorus pentachloride, which is specific for this purpose and irreplaceable by thionyl chloride.[231]

2. *Oxadiazoles*[228]

There was a passing reference in *CSD II*[231a] to red vat dyes containing the 1,3,4-oxadiazole ring and to a du Pont patent. Indanthrene Red F3B (Caledon Brilliant Red 5B; CI Vat Red 31) is a 1,3,4-oxadiazole derivative, and such oxadiazoles are important vat dyes now described in many patents.[232–236]



Indanthrene Red F3B (CI Vat Red 31)

The first du Pont patent (1949) referred to the lack of desirable shades of red in the anthraquinonoid vat dye series, and covered the preparation of a dye of the indicated structure by the condensation of hydrazine in two steps with 2 moles of 1-aminoanthraquinone-2-carbonyl chloride, followed by cyclization in trichlorobenzene at 205° in the presence of

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[230] H. Klappert, J. Eibl, and FBy, *DBP* 1,060,527.

[231] E. Klingsberg and CCC, *USP* 2,863,883.

[231a] *CSD II*, p. 914.

[232] P. L. Belshaw, F. Irving, and ICI, *DBP* 831,432; *BP* 676,699; 705,920; 705,928; P. Belschaw, A. C. Robson, and ICI, *BP* 705,929.

[233] CIBA, *USP* 2,838,520; *BP* 762,149; 954,410; 1,006,157; 1,009,929; K. Weber, P. Hugelshofer, and CIBA, *SP* 439,534.

[234] H. W. Schwechten, J. Singer, and FBy, *DBP* 825,111; H. W. Schwechten, R. Neeff, J. Singer, and FBy, *BP* 746,379; *USP* 2,749,352; H. W. Schwechten and FBy, *BP* 733,456; 680,364; *USP* 2,759,948; 2,616,891.

[235] F. Ebel, R. Randebrock, and BASF, *BP* 731,008; *DBP* 955,174; O. Trauth and BASF, *DBP* 1,049,025; H. Weidinger, J. Kranz, and BASF, *BP* 855,721; *DBP* 1,067,439.

[236] F. B. Stilmar and DuP, *USP* 2,464,831; 2,511,018-9; 2,567,132; 2,601,179; 2,628,230; 2,650,926.

p-toluenesulfonic acid.[236] Subsequent patents have described the preparation of the diacylhydrazide in one step, modified conditions for the cyclization, and the preparation of numerous derivatives of 2- and 2,5-bis(β-anthraquinonyl)oxadiazole. Cyclization to the oxadiazole can be effected by a variety of reagents, such as oleum containing 0.5–5% SO_3,[232] thionyl chloride, phosphorus oxychloride, and polyphosphoric acid.[237] In the preparation of CI Vat Red 31, 1-aminoanthraquinone-2-carbonyl chloride can be replaced by the corresponding isatoic anhydride.[235] CI Vat Red 31 can be chlorinated or brominated in the 4,4′-positions of the anthraquinone nuclei.[236] The analog of CI Vat Red 31 from 1-amino-6-chloroanthraquinone-2-carboxylic acid dyes ruby red shades.[234]

Substitution in the 4,4′-positions of the anthraquinone nuclei in CI Vat Red 31 is an obvious method of modifying the hue and other properties. Nitration of CI Vat Red 31, followed by reduction with sodium sulfide, is feasible[234]; or 1-amino-4-nitroanthraquinone-2-carboxylic acid can be used as starting material.[232, 233] Cyclization of the diacylhydrazide to the oxadiazole and reduction of NO_2 to NH_2 can be effected in one step by treatment with sulfur in oleum.[235] If the two substituents are NHCOPh, a bright blue dye results,[232] which can also be prepared from 1-amino-4-benzamidoanthraquinone-2-carbonyl chloride.[238] If the benzene rings carry *p*-SO_2Cl groups, reddish blue dyes of very good fastness to light and washing are obtained.[233] If the two substituents are NHCOAr, in which one Ar is heterocyclic, strong greenish to reddish blue shades of excellent fastness are obtained. Dyes in which one or both of the acyl groups are acetyl, or one is acetyl and the other benzoyl, have greater tinctorial strength than the bis-benzamido derivatives. Using the two-step condensation technique, a benzamido group can be introduced para to the amino group in one anthraquinone nucleus to produce a violet dye.[232]

One anthraquinone nucleus is adequate to give useful vat dyes. Thus (XLII) is a scarlet vat dye.[234] A method suitable for the preparation of unsymmetrical 2,5-diaryloxadiazoles is to melt together a hydrazide ($ArCONHNH_2$) with an acid chloride (Ar′COCl) until the evolution of hydrogen chloride ceases.[239]

A fast greenish yellow dye is obtained by condensing (XLIII) with 2 moles of α-aminoanthraquinone[240]; (XLIII) can be prepared by

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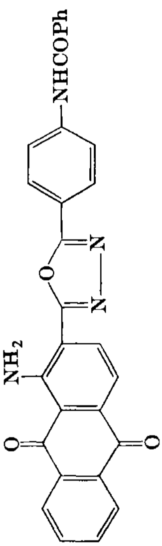
[237] *J. Chem. Soc.* p. 3503 (1964); *Chem. & Ind. (London)* p. 752 (1964).

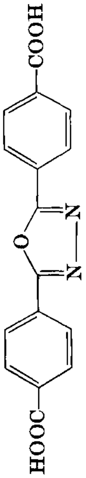
[238] T. Akamatsu and NSK, *JP* 5048/62.

[239] T. R. Vakula, T. V. Saraswathi, and V. R. Srinivasan, *Indian J. Chem.* **6**, 172 (1968).

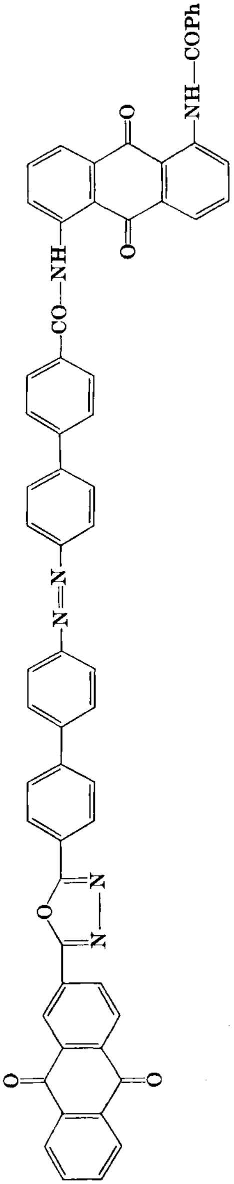
[240] E. Mörgeli *et al.*, and CIBA, *USP* 2,741,621; *BP* 762,149; *DBP* 1,134,782.



(XLII)



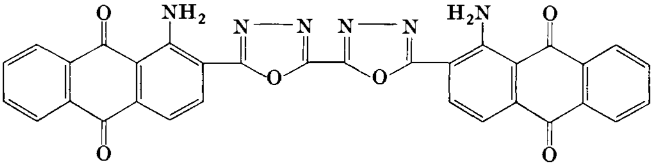
(XLIII)



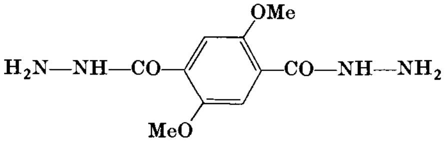
(XLIV)

chromic acid oxidation of 2,5-bis(*p*-tolyl)-1,3,4-oxadiazole.[241] The sophistication possible in a patent for a yellow vat dye is shown by (XLIV).[242]

Starting from 1-nitroanthraquinone-2-carboxylic acid, condensing 2 moles of the monohydrazide with oxalyl chloride, cyclizing by treatment with thionyl chloride in nitrobenzene at 170° and replacing the nitro by amino groups by passing ammonia through a solution in nitrobenzene at 180°, the final product (XLV) dyes cotton bluish red. A similar series of reactions can be performed in which oxalic acid is replaced by terephthalic or thiophene-2,5-dicarboxylic acid.[236] A Japanese patent[243] protects the preparation of an analog of (XLV) by the condensation of 2 moles of 1-aminoanthraquinone-2-carbonyl chloride with 1 mole of (XLVI).



(XLV)



(XLVI)

A general method for the synthesis of 2,5-diaryl(alkyl)-1,3,4-oxadiazoles is the interaction of acid hydrazides with imido esters or their hydrochlorides. Bis-oxadiazoles are formed from bis-imidoester hydrochlorides. If the free ester is used, an intermediate amidrazone may be formed, and it can be cyclized with the elimination of ammonia.[229, 235]

Oxadiazoles can also be prepared by heating aromatic acid hydrazides with *N*-alkyl imidochlorides in a basic solvent; the alkylamine hydrochloride is eliminated.[244] However, these procedures have no advantage over the cyclization of the diacylhydrazides (ArCONHNHCOAr), so far as vat dyes are concerned.

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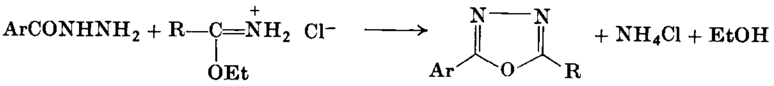
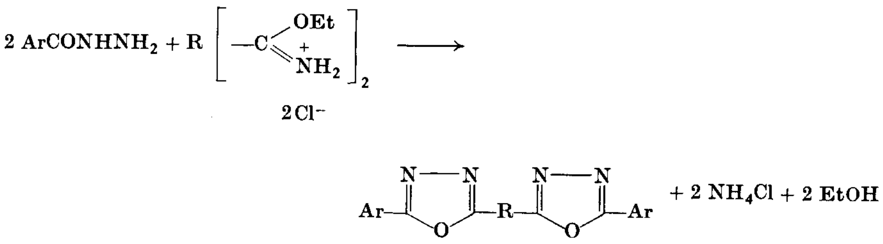
[241] K. Saftien, E. Anton, and BASF, *DBP* 923,028.

[242] T. Sasa *et al.*, and MDW, *JP* 2643/64.

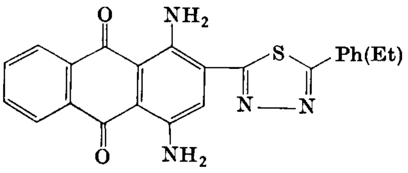
[243] A. Akamatsu, M. Hazue, and NSK, *JP* 7080/57.

[244] H. Weidinger, H. Eilingsfeld, and BASF, *DBP* 1,113,053.





Closely related to the oxadiazoles are the thiadiazoles, which can be prepared by the action of phosphorus pentasulfide on the bis-acylhydrazides. Condensation of the thiadiazole (XLVII) with terephthaloyl or isophthaloyl chloride gives a fast blue vat dye; the amino group not adjacent to the heterocyclic ring reacts preferentially.[245]



(XLVII)

G. ACRIDONES[246]

Indanthrene Khaki GR (CI Vat Brown 16[246a]) has the indicated structure (CI 70910).

Bradley and Kaiwar[247] have examined the light absorption and other properties of a series of phthaloylacridones synthesized by known methods; *N*-methylation produced a hypsochromic shift and reduced the affinity for cotton. The UV-visible and IR spectra of 1,2- and 3,4-phthaloylacridones have been discussed.[248] Methods for the degradation of (XLVIII) and its derivatives have been studied.[36] They are stable

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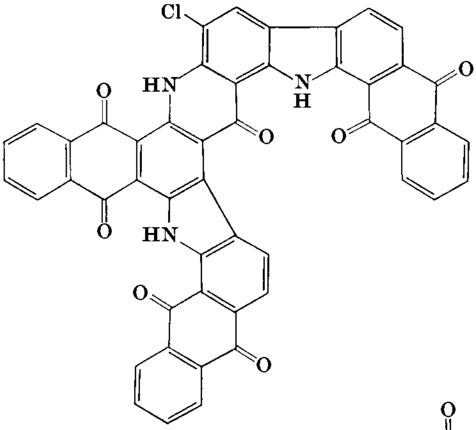
[245] H. Weidinger, L. Eilingsfeld, L. Moebius, and BASF, *DBP* 1,248,833.

[246] For a review, see C. F. H. Allen, *Chem. Rev.* **54**, 3418 (1960).

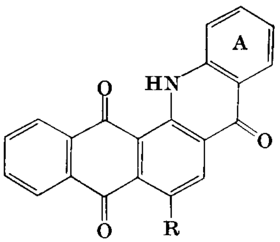
[246a] *CSD II*, p. 930.

[247] W. Bradley and H. Kaiwar, *J. Chem. Soc.* p. 2859 (1960).

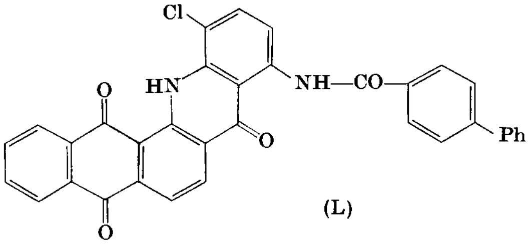
[248] T. Hayashi and J. Maehara, *Bull. Chem. Soc. Japan* **35**, 1690 (1962).



CI Vat Brown 16; CI 70910



(XLVIII; R = H)
(XLIX; R = NH_2)



(L)

to nitric acid and other oxidizing agents, but break down by caustic potash fusion; thus (XLVIII) yields benzoic acid and acridone-3-carboxylic acid, and the bis-acridone (Indanthrene Violet RN; CI Vat Violet 13; CI 68700) from 1,5-dichloroanthraquinone gives only the latter acid. A comparison of 1-amino-2-benzoylanthraquinone and its derivatives with the corresponding phthaloylacridones has shown that in the acridones there is a bathochromic shift of λ_{max} by 9 to 37 mμ.[249]

In the preparation of Indanthrene Red RK (CI Vat Red 35; CI 68000[249a]), β-naphthylamine, a potent carcinogen, can be replaced by its 1-sulfonic acid for the condensation with 1-nitroanthraquinone-2-carboxylic acid.[250] New conditions for the condensation of 1,5-dichloroanthraquinone and anthranilic acid[251] and for the subsequent cyclization[252] to the bis-acridone (CI Vat Violet 13) have been described. The mixture of tri- and tetraamino compounds obtained by nitration and reduction of (XLVIII) dyes cotton dark bluish green.[253] When 1-chloro-3,4-phthaloylacridone is heated with urea in nitrobenzene, chlorine is

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[249] N. S. Dokunikhin, S. M. Shein, and I. L. Boguslavskaya, *Zh. Obshch. Khim.* **34**, 1565 (1964).

[249a] *CSD II*, p. 923.

[250] R. S. Barnes, W. Smith, and ICI, *BP* 691,118; *USP* 2,689,247.

[251] T. Sasa *et al.*, and MDW, *JP* 22,465/65.

[252] L. H. Ulich and DuP, *USP* 2,726,242.

[253] Y. Hosoda, O. Teramachi, and MDW, *JP* 25,847/63.

replaced by NH_2, and the product is a red dye.[254] Wine red shades on cotton are produced by (L).[255] Similarly substituted dyes in which the acid used for acylation is 1-aminoanthraquinone-2-carboxylic acid have good affinity for cellulose and yield brown shades.[256] However, Indanthrene Bordeaux BB (CI 67815*), a dye of this type, is obsolete. Treatment of the acridone from 1-chloroanthraquinone and *p*-phenylenediamine-2-carboxylic acid with oxidizing agents leads to dimerization to a phenazine, which dyes cotton red-brown shades of high fastness.[257]

Dyes of the Indanthrene Turquoise Blue GK type[257a] [CI Vat Blue 32; CI 67910; analog of (XLIX) from 2-amino-4-chlorobenzoic acid] yield deep turquoise blue prints and dyeings of very good fastness on polyester fabrics by padding.[258] Analogous dyes from bromo- and fluoroanthranilic acids have been described.[259]

The amine (XLIX), in which ring A may be chlorinated, is a useful intermediate from which other vat dyes can be prepared. Indanthrene Blue CLN (CI Vat Blue 39) is stated[260] to be the *p*-chlorobenzoyl derivative of (XLIX) and "a specialty color suitable for high temperature dyeing." *N*-Aroyl derivatives of (XLIX) can be prepared by aroylation of (XLIX) or from 1-aroylamido-4-chloroanthraquinone and the appropriate anthranilic acid.[261] Acylation of (XLIX) and its chloro derivatives with cyclohexylcarbonyl chloride gives valuable bluish gray dyes.[262] Condensation of (XLIX) with 1-*m*-bromobenzamidoanthraquinone gives (LI), which dyes cotton a clear yellowish green shade.[263] Yellow-green dyes can also be obtained by condensing azobenzene- or azobiphenyl-4,4′-dicarboxylic acid with 2 moles of (XLIX) or 1 mole of (XLIX) and 1 mole of 1-aminoanthraquinone.[264] Condensa-

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[254] A. Schuhmacher, A. Ehrhardt, and BASF, *BP* 964,767.

[255] K. Weber, *et al.*, and CIBA, *BP* 961,690.

[256] CCC, *BP* 860,384.

[257] J. Haase and J. Filipi, *CzechP* 89,848; J. Haase and M. Pokorny, *CzechP* 98,220.

[257a] *CSD II*, p. 924.

[258] W. Zerweck, E. Heinrich, and CFM, *DBP* 1,135,415; *BP* 919,270.

[259] FBy, *BP* 775,802; H. Schlichenmaier and FH, *DBP* 1,027,346; F. Baumann and FBy, *DBP* 1,032,452.

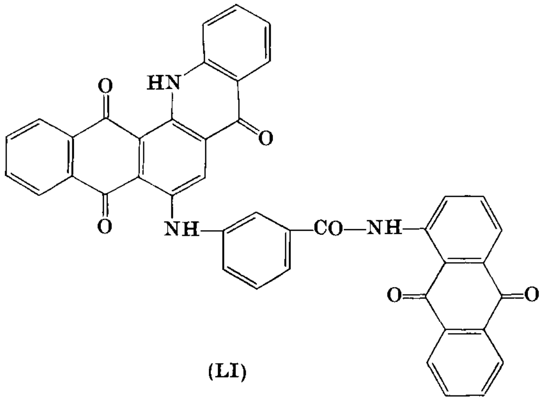
[260] M. S. Whelen, *in* Lubs[134, p.506].

[261] Ya. E. Berezin and V. V. Vanifat'ev, *RP* 183,857.

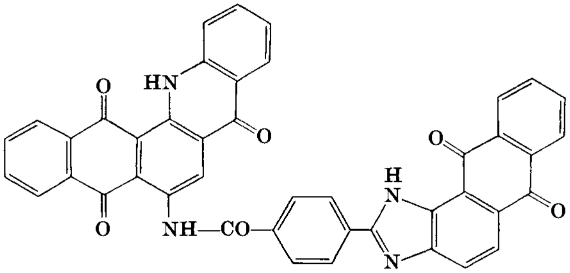
[262] W. Zerweck, E. Heinrich, and CFM, *USP* 2,623,047; *BP* 707,576; see also CFM, *BP* 713,512.

[263] W. Zerweck and CFM, *BP* 767,004; *USP* 2,752,349; W. Zerweck, E. Heinrich, and CFM, *DBP* 955,173; 1,081,584; W. Eckert, W. Dauner, and FH, *DBP* 955,084; F. Baumann, H. S. Bien, and FBy, *DBP* 1,056,306; P. L. Belshaw *et al.*, and ICI, *BP* 737,586.

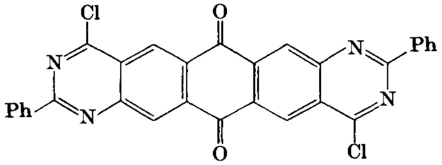
[264] P. Nawiasky, L. D. Barrick, and G, *USP* 2,729,631; W. Zerweck, *et al.*, and CFM, *DRP* 1,060,072.



(LI)



(LII)



(LIII)

tion of terephthaloyl chloride with 1 mole of (XLIX) and 1 mole of 1,2-diaminoanthraquinone results in the green dye (LII).[265] Numerous other acids have been suggested for the acylation of (XLIX).[266] A patent[267] mentions that the condensation of (XLIX) with 1,3,5-, 1,2,3-, or 1,2,4-trichlorobenzene gives the dichloroanilino derivative, which dyes cotton brilliant green; but 1,3,5-trichlorobenzene will

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[265] CIBA, *BeP* 668,789.

[266] W. Zerweck *et al.*, and CFM, *DBP* 936,943; 946,735; *USP* 2,727,894; *BP* 761,687.

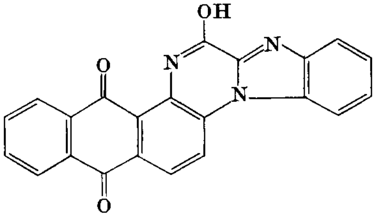
[267] A. Vilsmeier and BASF, *BP* 892,402.

require much more stringent conditions than the 1,2,4-isomer. When 4,4′-dibromobenzophenone is condensed with 1 mole each of (XLIX) and 1-amino-4-benzamidoanthraquinone, a blue-black dye is obtained.[268] Products of the condensation of (XLIX) with 1,8-dichloroanthraquinone are fast gray dyes for cotton; after carbazolization, they produce "extremely fast dyeings in dark shades."[269] Vat dyes can be produced by condensing (XLIX) with cyanuric chloride and other compounds containing reactive chlorine, and then with another vattable amine.[270] The product obtained by condensing 2 moles of (XLIX) with (LIII) dyes cotton green. [271]

Complex carbazole-acridones, mainly brown, khaki, gray, and olive dyes, continue to attract attention.[271a, 272]

H. *Quinoxalines*

Condensation of 2,3-dihydroxy-5,6-phthaloylquinoxaline[272a] with anthranilic acid in boiling phenol gives (LIV); both this product and its methyl ether are bright scarlet dyes.[273] When the same quinoxaline derivative is first converted to the chloride by means of thionyl chloride, and then condensed with 1-aminoanthraquinone-6-carboxylic acid, the product (cf. Indanthrene Brilliant Scarlet RK; CI 68300) dyes cotton a golden orange shade.



(LIV)

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[268] W. Eckert, W. Dauner, and FH, *DBP* 955,084.

[269] CIBA, *BP* 686,422.

[270] F. Ebel, H. Weidinger, and BASF, *BP* 829,699; *USP* 2,951,842; see, e.g., K. Klemm *et al.*, and FBy, *BP* 993,257; *USP* 3,167,557; FH, *BP* 837,298.

[271] BASF, *BP* 763,328.

[271a] Cf. *CSD II*, p. 929.

[272] See, e.g., FH, *BP* 837,298; F. Lodge and ICI, *USP* 2,414,155; *BP* 566,872; M. Grelat *et al.*, and CIBA, *USP* 2,837,523; *BP* 733,372; CIBA, *SP* 298,380–8; P. Sutter and CIBA, *BP* 727,826; 719,670; *USP* 2,722,530; F. Graser and BASF, *FP* 1,371,077; W. Zerweck, E. Heinrich, and CFM, *DBP* 1,084,404; K. Klemm, F. Baumann, H. S. Bien, and FBy, *USP* 3,167,557; FBy, *BP* 993,257.

[272a] *CSD II*, p. 943.

[273] A. Oken and DuP, *USP* 2,751,385.

I. PHENAZINES (INDANTHRONES)

1. *Mechanism of Indanthrone Formation*

A brief reference was made in *CSD II*[273a] to Bradley's extensive experimental work on the chemistry of indanthrone, later described in a series of 13 papers.[274–278] Numerous compounds were prepared in addition to those which had relevance to the mechanism of indanthrone formation. Bradley did not study the actual reaction (alkali fusion of 2-aminoanthraquinone in the presence of an oxidizing agent) by which indanthrone is manufactured, and he did not attempt to isolate the intermediate products.

Scholl and Eberle[279] suggested the enolization of 2-aminoanthraquinone (LV) to (LVa) (which he wrote as the enol and not the anion) and the addition of (LV) to the quinone system of (LVa), to form (LVI), shown here as the dianion; a repetition of the reactions then led to indanthrone (see Chart 1). The Michael reaction type of addition of (LV) to (LVa), which contains an α,β-unsaturated carbonyl group, is quite feasible. Bradley ruled out the enolization of (LV) to (LVa), because the compound in which the imino group of (LVIII) was replaced by NMe could be cyclized to *N*-methylindanthrone; but this does not exclude the Scholl mechanism for the first stage leading to the formation of (LVIII) or its *N*-methyl analog.

Bradley considered that (LV) yields the anion (LVb), which then attacks (LV) to form (LVII); (LVII) undergoes "dehydrogenation by air, alkali nitrates, or the quinones, for example 2-aminoanthraquinone, which are always present in the alkali melt" to give (LVIII); by a similar series of reactions (LVIII) leads to indanthrone. Bradley also observed that the cyclization of (LVIII) to indanthrone occurs with great ease under acid, neutral, and alkaline conditions.

Bradley found that 2-aminoanthraquinone was formed in unspecified yield by vigorous reduction of 2-nitro-1,2′-dianthraquinonylamine with alkaline dithionite and he offered this as evidence for the reversibility of step (a) and the formation of alizarin.[275] It is unlikely that step (a) is reversible when a strong base and an inorganic oxidizing agent or amino-

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[273a] *CSD II*, p. 932.

[274] W. Bradley and E. Leete, *J. Chem. Soc.* pp. 2129 and 2147 (1951).

[275] W. Bradley, E. Leete, and D. S. Stephens, *J. Chem. Soc.* pp. 2158 and 2163 (1951).

[276] W. Bradley and H. E. Nursten, *J. Chem. Soc.* pp. 2170 and 2177 (1951); p. 3027 (1952); p. 924 (1953).

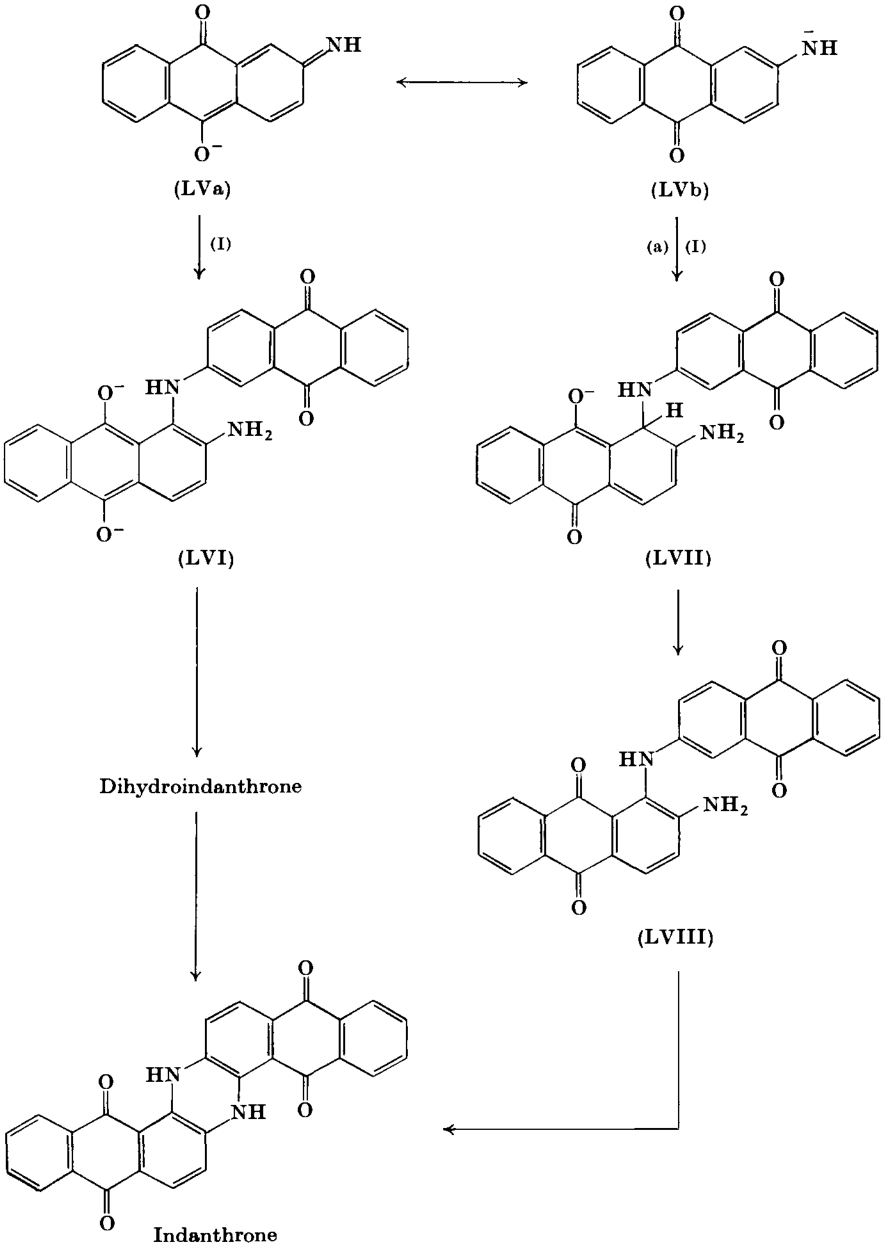
[277] W. Bradley, R. F. Maisey, and C. R. Thitchener, *J. Chem. Soc.* p. 272 (1954).

[278] M. C. Clark, *J. Chem. Soc.*, *C* pp. 277; 2081; and 2090 (1966); p. 936 (1967).

[279] R. Scholl and F. Eberle, *Monatsh. Chem.* **32**, 1035 (1911).

CHART 1

Formation of Indanthrone from 2-Aminoanthraquinone
(Ionic Mechanism)



anthraquinone are present. At the lower temperatures which lead to alizarin the ionization of 2-aminoanthraquinone probably does not take place, and there is a nucleophilic attack of OH^- on the 1-position and subsequent replacement of NH_2 by OH.

It is difficult to explain the attack of the anion (LVa) on the 1-position of 2-aminoanthraquinone, which is not an electron-deficient center vulnerable to attack by a nucleophile. Appropriately substituted aniline derivatives do not undergo a similar reaction leading to a phenazine, and the unique character of aminoanthraquinone in this context has to be remembered. Bradley has cited the preparation of 2-*p*-nitroanilinoanthraquinone by the action of 2-aminoanthraquinone (LV) on nitrobenzene in presence of alkali[280] as an example of the ability of (LV) to function as a substituting agent, but our concern is with the activation of the 1-position in (LV) for attack by the anion (LVa).

Mechanisms involving radical intermediates need to be considered, because we are dealing with a quinone in presence of aqueous alkali and oxygen or an oxidizing agent, and in the overall reaction four atoms of hydrogen have to be removed. However, these can only be speculative in the absence of experimental evidence. If we assume (see Chart 2) that in the alkali melt OH^- attacks (LV) to give (LIX), the latter can undergo a homolytic fission to give the semiquinone ion (LX). The ion (LX) can give rise to the tautomeric form (LXI) and the resonance structure (LXII), and these two radical anions can then combine to give (LXIII). Oxidation of (LXIII) will generate (LVIII), which undergoes cyclization to indanthrone by repetition of the same sequence of reactions. Dimerization of (LXII) and subsequent cyclization will yield flavanthrone; and the reaction of (LXII) with $OH^\bullet$ can give 1-hydroxy-2-aminoanthraquinone, which will lead to alizarin.

Preliminary experiments on ESR spectra showed that a radical mechanism might well be involved, but it has not yet been possible to identify specific radical intermediates. When a mixture of 1-aminoanthraquinone, potassium hydroxide, acetate, and nitrate was heated at 200°, the melt was conducting and could not be examined for an ESR signal; but on being cooled to room temperature, the bluish black solid exhibited a strong free-radical ESR signal, which was indefinitely stable. A partial solution of the amine and potassium hydroxide in tetramethylurea behaved similarly. Interpretation of the results became more difficult when it was observed that indanthrone itself, after isolation by the usual method through the sparingly soluble disodium salt of the dihydro derivative or by regeneration from the chromatographically

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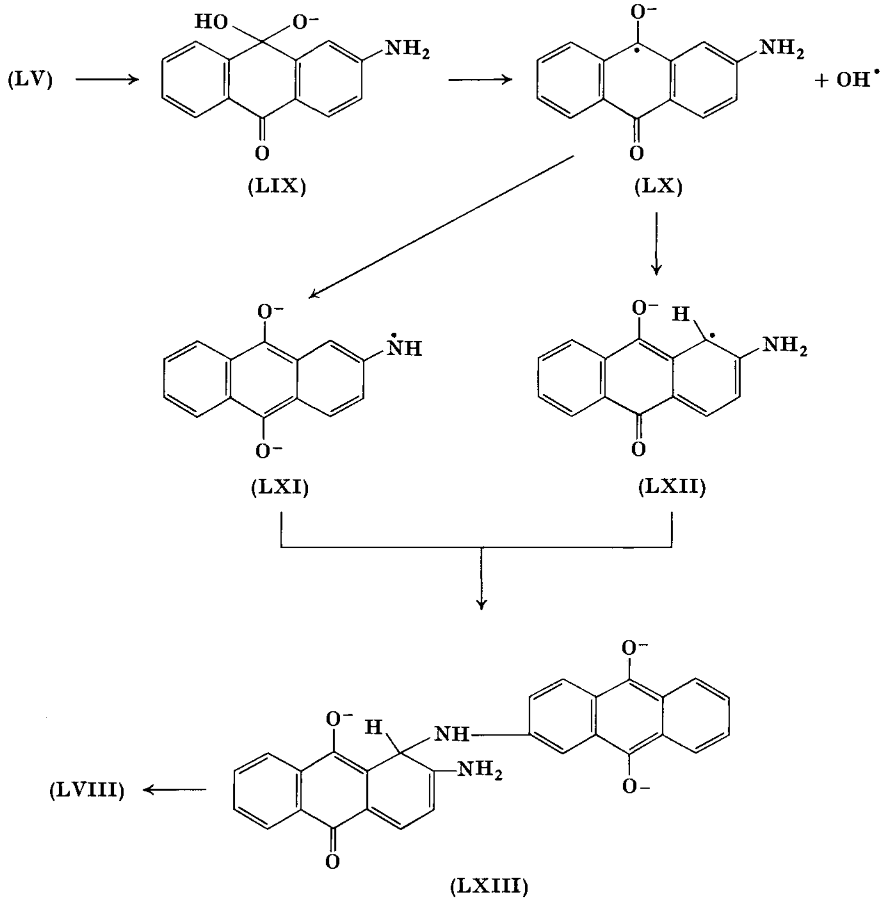
[280] *FIAT* 1313, III, p. 82.

homogeneous and recrystallized dihydroindanthrone dimethyl ether, gave in the solid state a very broad ESR signal and a very narrow signal indicating a free radical. Dihydroindanthrone dimethyl ether in the solid state showed no ESR signal.[281]

On the basis of inadequate chemical evidence, indanthrone B (a by-product formed in the absence of an oxidizing agent) has been assigned

CHART 2

Radical Mechanism for Indanthrone Formation



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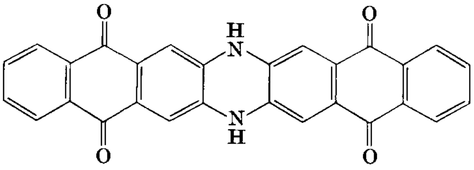
[281] A. V. Rama Rao, B. Venkataraman, and K. Venkataraman, unpublished work (1969).

the structure of a mono- or dihydroxy derivative of linear indanthrone (LXIV).[275]



(LXIV)

Clark's papers[278] on linear indanthrone, the constitution of the reduction products of indanthrone, the azines corresponding to indanthrone and the linear isomer, and the constitution of indanthrone B have not added to our knowledge obtained from earlier work. No new attempts to purify the complex products through derivatives more soluble and more amenable to chromatographic analysis were made. Further, confirmation or modification of the structures assigned by earlier workers necessarily involves mass spectrometry and NMR spectroscopy; and as a preliminary, appropriate derivatives having the requisite purity, volatility, and solubility have to be prepared.

Leete[282] has shown that Clark's two syntheses of linear indanthrone (LXIV) do not yield the authentic compound, and he has synthesized (LXIV) by two methods: (a) ferric chloride oxidation of 3,3′-diamino-2,2′-dianthraquinonylamine; and (b) refluxing 2,3-diaminoanthracene in *o*-dichlorobenzene, oxidation of the product (probably a tetrahydro-7,16-diazaheptacene) to the anthraquinone-azine, and reduction to (LXIV). Linear indanthrone (LXIV) is olive green in color and gives a reddish brown vat. The dyeing properties were not recorded.

Wyman[283] suggested an enolic structure for indanthrone by an erroneous interpretation of the IR spectrum. Subsequently Weinstein and Merritt[284, 285] concluded from a study of the UV-visible and IR spectra of indanthrone and related compounds that "indanthrone in the solid state and in inert solvents exists primarily in a keto form." However, there is no justification for the statement in the opening sentence of their paper that "the structure of indanthrone ... has been a subject of controversy for many years." The Bohn structure, in which two CO groups of two anthraquinone nuclei are strongly hydrogen-bonded with the two NH groups of a 1,4-dihydropyrazine, is fully supported by chemical

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[282] E. Leete, O. Ekechukwu, and P. Delvigs, *J. Org. Chem.* **31**, 3734 (1966).

[283] G. M. Wyman, *J. Am. Chem. Soc.* **78**, 4599 (1956).

[284] J. Weinstein and C. Merritt, *J. Am. Chem. Soc.* **81**, 3759 (1959).

[285] See also R. A. Durie and J. S. Shannon, *Australian J. Chem.* **11**, 189 (1958).

evidence and more recently, by X-ray analysis[286]; and the IR spectrum cannot be interpreted to make individual bond assignments in the indanthrone molecule except, of course, for the C═O bonds.

Indanthrone is polymorphic; the crystal structure of the stable α-form was determined, and a slight departure of the molecule from planarity was established.[286] The two rings at each end of the molecule are planar, but there is a slight staggering of the atoms of the three central rings. The two outer C═O bond lengths are 1.21 Å, and the two inner C═O bonds are slightly longer, 1.23 Å. The C—N bonds have the same length of 1.39 Å, and similar shortening of the normal C—N single-bond lengths of 1.47 Å has been found in other heterocyclic compounds. The nitrogen atom is intramolecularly hydrogen-bonded to the adjacent oxygen atom, the N—H bond length being 1.01 Å.

2. *The Blue Vat of Indanthrone*

The normal blue vat, from which a sparingly soluble disodium salt separates, corresponds to dihydroindanthrone. Partly because the compound (LXV) is blue in color, Scholl[286a] gave the disodium salt of dihydroindanthrone the structure (LXVI). Appleton and Geake[287] submitted the blue vat in 50% pyridine to oxidative titration, and found the normal potential to be −292 mV. Titration of the brown vat was not possible because of the very low potential at which it was oxidized, but "the conclusion was drawn that the normal potential of its oxidation to the blue vat cannot be above −700 mV." A recent polarographic study[288] has shown that the fully reduced vat of indanthrone obtained by reduction with zinc and aqueous sodium hydroxide gives two reversible anodic waves of equal height separated by 390 mV, corresponding to a two-stage oxidation through the dihydro derivative to the parent indanthrone. The blue vat (obtained by reduction with aluminum and alkali) gives an anodic and a cathodic step of equal height, corresponding to oxidation to indanthrone and reduction to the tetrahydro derivative.[289]

Gill and Stonehill[290] suggested a structure for dihydroindanthrone involving the reduction of the two outer nonbonded carbonyl groups,

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[286] M. Bailey, *Acta Cryst.* **8**, 182 (1955).

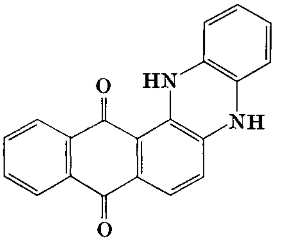
[286a] *CSD II*, p. 935.

[287] D. Appleton and A. Geake, *Trans. Faraday Soc.* **37**, 60 (1941).

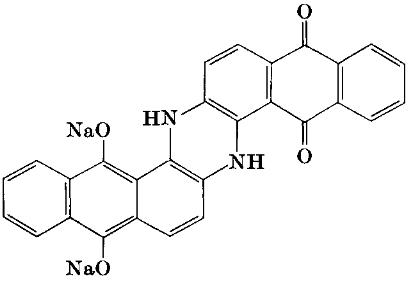
[288] P. S. Shetty, C. J. Sanchorawala, T. G. Manjrekar, and P. R. Subbaraman, *Indian J. Chem.* **4**, 340 (1966).

[289] The dependence of the shape of redox-potential curves of vat dyes on the solubility of the oxidized dye and on possible association equilibria in the solution has been evaluated on the basis of a simple theoretical model [H. H. Buehler, B. Milićević, and F. Kern, *Helv. Chim. Acta* **45**, 1811 (1962)].

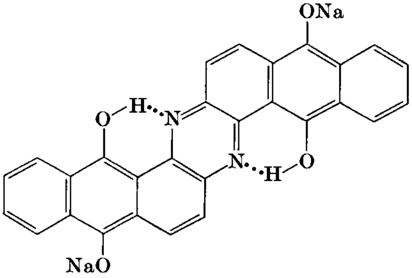
[290] R. Gill and H. I. Stonehill, *J. Soc. Dyers Colourists* **60**, 183 (1944).



(LXV)



(LXVI)



(LXVII)

shown in (LXVII) as the disodium salt in a slightly modified form to indicate the double bonds and the fact that the product has to be an azine. The ready formation and the sparing solubility of the disodium salt are the result of the very strong hydrogen bonding between the OH groups and the azine nitrogen atoms, favored by the rigid spatial arrangement in the planar molecule.

The IR spectrum in Nujol mull of the disodium salt from the blue vat shows no C=O absorption. Treatment of the disodium salt in aqueous sodium hydroxide with dimethyl sulfate and crystallization of the precipitate from *o*-dichlorobenzene gives red-violet needles of the dimethyl ether corresponding to (LXVII).[291] The IR spectrum shows no C=O absorption. In the mass spectrum the molecular ion is at *m/e* 472 (17%) and the base peak is at *m/e* 442 ($M - 2CH_3$) corresponding to indanthrone ion. Although the product is chromatographically homogeneous, the mass spectrum indicates the presence of a trace of the trimethyl ether.

An error in *CSD II*[291a] is the structure assigned to Indigosol Blue IBC (CI Solubilized Vat Blue 6; CI 69826), which is the azine (LXVIII)

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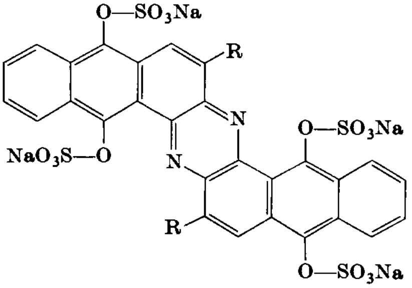
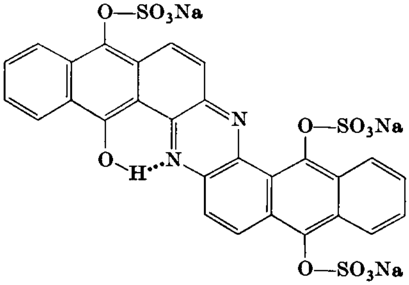
[291] M. R. R. Bhagwanth and A. V. Rama Rao, unpublished work (1968).

[291a] *CSD II*, p. 1049.

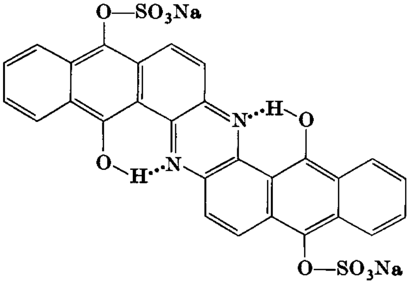
and not the dihydroazine. The corresponding derivative of indanthrone[(LXIX); Indigosol Blue IRS; CI Vat Blue 4; CI 69801] can be prepared by the method used for (LXVIII): oxidation of the disulfuric ester of leuco-2-aminoanthraquinone. In aqueous solution (LXIX) is yellow with a bright green fluorescence; it undergoes reduction with dithionite to the dihydroazine (brown nonfluorescent solution), which however, is readily reoxidized by air. Acidification of (LXIX) with acetic



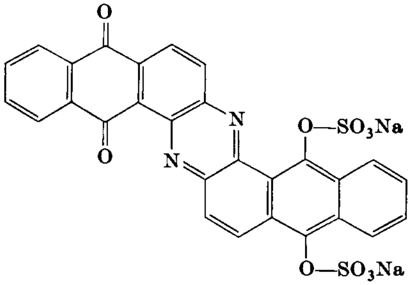
(LXVIII; R = Cl)
(LXIX; R = H)



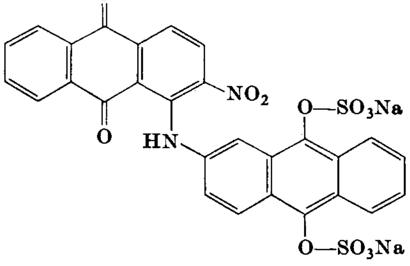
(LXX)



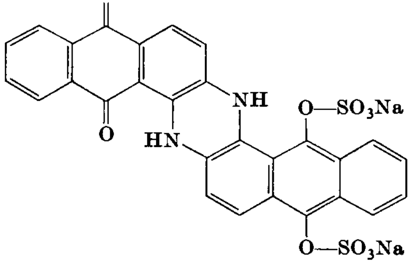
(LXXI)



(LXXII)



(LXXIII)



(LXXIV)

acid and immediate neutralization with alkali gives the red triester (LXX); but with mineral acid the product is the violet diester, to which Dokunikhin[292] assigns the structure (LXXI). Contrary to Dokunikhin, however, the formation of (LXXI) from (LXIX) involves only hydrolysis and no oxidation by the azine. The triester (LXX) can be oxidized in alkaline solution to the red diester (LXXII), described in an IG patent[293]; it is synthesized by an Ullmann condensation of 1-chloro-2-nitroanthraquinone with the disulfuric ester of leuco-2-aminoanthraquinone to form (LXXIII), reduction with sodium sulfide (apparently to the nitroso compound which tautomerizes to the isonitroso form and cyclizes), and air oxidation. The ester (LXXII) is very sensitive to acid hydrolysis, because the corresponding hydroquinone isomerizes immediately to indanthrone; and the reaction has been used for the detection of organic acids on a paper chromatogram.[294] The fact that (LXXII) is not directly convertible to the violet diester is cited by Dokunikhin as evidence for the azine structure (LXXI), and against the dihydroazine structure (LXXIV); he therefore concludes that the normal blue vat of indanthrone is the disodium salt (LXVII) of dihydroindanthrone.

3. *Production Methods*

An excellent yield of oxidized indanthrone of high quality is obtained by washing the cake of the crystalline leuco compound (sodium salt) with 1% aqueous sodium bicarbonate until the pH of the filtrate is below 10, and then washing with water to neutral.[295]

A statistical study of the optimum conditions for the alkali fusion of 2-aminoanthraquinone to indanthrone has been made.[296]

Nagai[297] has described a continuous method for the alkali fusion of 2-aminoanthraquinone to reduce foaming and local overheating and the consequent formation of by-products. A yield of 65.9% was claimed, but the process does not appear to be used technically.

There have been two important patent claims in recent years: (a) the use of 1-aminoanthraquinone and (b) the use of solvents, notably dimethyl sulfoxide (DMSO), enabling the alkali fusion to be effected at about 120°. Fusion of 1-aminoanthraquinone (100 parts) with potassium

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[292] N. S. Dokunikhin, *Trans. 8th Conf. Aniline Dye Chem. Techn. 1947* p. 121. Acad. Sci. U.S.S.R., 1950.

[293] J. Haller and G. Rösch, *DRP* 739,819.

[294] K. Schlögl, *Naturwissenschaften* **46**, 447 (1959).

[295] CCC, *USP* 2,898,337.

[296] S. Balasubramanian and L. K. Doraiswamy, *Brit. Chem. Eng.* **12**, No. 3, 377 (1967); V. N. Iyer, Ph.D. Thesis, University of Bombay (1968).

[297] Y. Nagai, *Kogyo Kagaku Zasshi* **62**, 485 (1959); *DBP* 1,239,042.

phenate (90% KOH, 100 parts, in phenol, 150), sodium acetate (40), sodium chlorate (5–20), and ferric or manganese dioxide (1) at 200–210° for 2.5–7 hours and further processing of the product, gives indanthrone in 70% yield with a 10% recovery of starting material[298]; air and a catalyst (MnO_2 or $FeCl_3$) can be used as oxidizing agent.[299] But commercial production continues to be based on the β-isomer. In a recent Polish paper a yield of 67% is claimed when the alkali fusion of 1-aminoanthraquinone is carried out under optimum conditions determined by a statistical evaluation of experimental data. Phenol and potassium nitrate were used in a ratio of 3:2 and 1:13 in relation to 1-aminoanthraquinone.[300]

Treatment of 1- or 2-aminoanthraquinone with 50% aqueous potassium hydroxide in DMSO at 115–120° for 7 hours, with or without the addition of vanadium pentoxide and other oxidizing agents, gives indanthrone[301] in unspecified yield. The advantages of using DMSO (and similar sulfoxides and sulfones) are stated to be (a) the relatively low temperature at which there is only a slight danger of substituents being changed by side reactions, and (b) the possibility of using 1,4-diaminoanthraquinone, aminoviolanthrone, and other complex amines to form "higher cyclic derivatives" of indanthrone.

A more recent patent[302] describes the production of indanthrone from 1- or 2-aminoanthraquinone, 45% potassium hydroxide and tetramethylurea[303] at 115–125° in a current of air.

Indigosol Blue IBC is prepared[303a] by the lead peroxide oxidation of the sulfuric ester of leuco-2-acetamido-3-chloroanthraquinone; indanthrone itself can be regenerated by acid oxidation of the solubilized vat dye (CI Solubilized Vat Blue 4; CI 69801) similarly prepared from 2-acetamidoanthraquinone, and a 68% yield of pure indanthrone is claimed.[304]

A 50% yield of indanthrone can be obtained from 2,9,10-triaminoanthracene by treatment with permanganate in pyridine. Treatment of

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[298] FBy, *BP* 703,377; H. Thielert, F. Baumann, and FBy, *USP* 2,693,469; CIBA, *BP* 787,908.

[299] FBy, *BP* 741,341.

[300] J. Prochazka, *Chem. Prumysl* **19**, 407 (1969).

[301] CFM, *FP* 1,376,198; *BP* 992,568.

[302] CFM, *DBP* 1,264,648.

[303] For a review of the properties of this solvent, see A. Lüttringhaus and H. W. Dirksen [*Angew. Chem. Intern. Ed. Engl.* **3**, 260 (1964)].

[303a] *CSD II*, p. 1048.

[304] Y. Bansho, K. L. Huang, S. Suzuki, and I. Saito, *Kogyo Kagaku Zasshi* **64**, 1066 (1961).

2,4,9,10-tetraaminoanthracene with cupric oxide in liquid ammonia gives 4,4′-diaminoindanthrone.[305]

4. *Indanthrone Derivatives*

Several patents and a paper have appeared on the preparation of chlorinated indanthrones, both by direct chlorination and by the self-condensation of 1-bromo-2-amino-3-chloroanthraquinone.[306, 307] 3,3′-Dibromo-*N*,*N*-dimethylindanthrone dyes cotton violet-blue from an orange-red vat; the shade is fast to hypochlorite.[308] The condensation of 3,3′-dichloroindanthrone with thiophenol gives a greenish blue vat dye; sulfonation gives a blue direct cotton dye.[309] 3,4,3′,4′-Tetramethylindanthrone, a blue dye, can be prepared from 2-amino-1-bromo-3,4-dimethylanthraquinone.[310] Greenish blue and green vat dyes (and acid dyes by sulfonation) are obtained by the self-condensation of 1-amino-2-bromoanthraquinone derivatives carrying an NHAr or O–Ar or S–Ar or SO_2Ar group in the 4-position.[311] A similar Ullmann condensation of 1-amino-2-bromo-5-benzamidoanthraquinone (an orange dye for polyester fiber) with itself yields 5,5′-bis(benzamido)indanthrone, a bluish green vat dye.[312] A blue-green dye is obtained by condensing indanthrone with hydroxylamine hydrochloride in presence of aluminum chloride at 105–110°.[313]

5. *Uses Other than Textile Applications*

Indanthrone is useful as a pigment and it is a permitted food color in some countries. Because of its great stability, indanthrone can be incorporated in greases to withstand high temperatures.[314] A paint

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[305] S. Tanabe and K. Suzuki, *JP* 3240/55.

[306] J. A. McSheehy, W. A. Raimond, and CCC, *USP* 2,742,471; A. Caliezi, W. Kern, T. Holbro, and CIBA, *USP* 2,862,930; *BP* 820,171; *DBP* 1,058,661; G. R. Genta and NAC, *USP* 2,995,552; *BeP* 665,732; S, *FP* 1,448,922.

[307] G. G. Yakobson, A. E. Ioffe, and N. N. Vorozhtsov, Jr., *Izv. Sibirsk Otd. Akad. Nauk SSSR., Ser. Khim. Nauk* No. 1, p. 156 (1963).

[308] W. Bradley, E. Leete, and H. E. Nursten, *J. Soc. Dyers Colourists* **68**, 117 (1952).

[309] CIBA, *BeP* 609,670; *BP* 981,527; 974,518.

[310] N. S. Dokunikhin and T. N. Kurdyumova, *Sb. Statei Obshch. Khim.* **2**, 1411 (1953).

[311] A. Tundo, *Ann. Chim. (Rome)* **47**, 291 (1957); *Boll. Soc. Fac. Chim. Ind. Bologna* **14**, 109 (1956); **15**, 80 (1957).

[312] CIBA, *BP* 1,095,087.

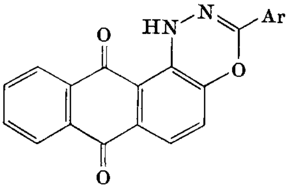
[313] W. B. Braun and BASF, *DRP* 825,866; *BP* 680,511.

[314] A. J. Haltner and C. S. Olives, *J. Chem. Eng. Data* **6**, 128 (1961); J. R. A. Handschy, J. W. Armstrong, and B. E. Gordon, *Lubrication Eng.* **14**, 293 (1958); J. W. Armstrong, H. A. Woods, and Shell Development Co., *USP* 2,848,417; N. V. de Bataafsche Petroleum Maatschappij, *BP* 840,199; Dow Corning Corp., *BP* 893,399; R. J. Dupzyk, H. A. Woods, and Shell Oil Co., *USP* 2,940,928.

containing indanthrone and a vinyl copolymer gives effective protection against radiation.[315] Nonluminescent compositions reflecting light in the IR (7000–100,000 Å) comprise indanthrone and two or more metal derivatives.[316]

J. OXADIAZINES

The oxadiazine derivatives (LXXV) are vat dyes prepared by condensing 1-chloro-2-nitroanthraquinone with an aroylhydrazide, and cyclizing in the presence of a base. When Ar = Ph, the dye is violet; and when Ar = 1-amino-2-anthraquinonyl, it is reddish black.[317]



(LXXV)

V. The Scholl Reaction

Cyclizations using aluminum chloride, such as the conversion of 3-benzoylbenzanthrone and 1,5-dibenzoylnaphthalene to 2,3,7,8-dibenzopyrene-1,6-quinone (CI Vat Yellow 4; CI 59100), were mentioned in *CSD II* as the Scholl reaction, which is defined by Gowan and Wheeler[318] as the cyclodehydrogenation of polyaryl ketones by heating with anhydrous aluminum chloride. The Scholl and related reactions were reviewed for the first time by Balaban and Nenitzescu,[319] who prefer to give the Scholl reaction the wider definition of "the elimination of two aryl-bound hydrogens accompanied by the formation of an aryl–aryl bond under the influence of Friedel-Crafts catalysts." However, the two aspects of the Scholl reaction are distinct insofar as ketones or quinones are invariably the compounds submitted to cyclization in the synthesis of dyes. It is reasonable to assume that the carbonyl and

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[315] E. Abe, S. Nishida, and Dai Nippon Paints Co., *JP* 336/60.

[316] Eltro and Co., *BP* 795,464.

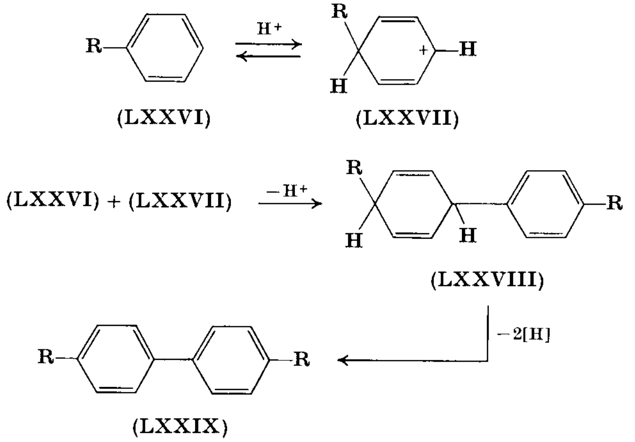
[317] W. L. Berry, W. L. Mosby, and CCC, *USP* 3,012,031.

[318] J. E. Gowan and T. S. Wheeler, "Name Index of Organic Reactions," p. 223. Longmans, Green, New York, 1960.

[319] A. T. Balaban and C. D. Nenitzescu, *in* "Friedel-Crafts and Related Reactions" (G. A. Olah, ed.), Vol. II, p. 979. Wiley (Interscience), New York, 1964.

quinone groups play an essential role in the Scholl condensations used in the synthesis of polycyclic quinones and in the conversion of anthrimides to carbazoles. This restricted Scholl reaction and the more generalized Scholl reaction can well proceed through different mechanisms.

Balaban and Nenitzescu have reformulated the mechanism proposed by Baddeley,[320] in which the generalized Scholl reaction is regarded as a normal electrophilic substitution of an aromatic (LXXVI) by its conjugate acid (LXXVII), proceeding through the dihydro derivative (LXXVIII), which is subsequently dehydrogenated to the biaryl (LXXIX).



(LXXVI) (LXXVII)

(LXXVIII)

(LXXIX)

Nenitzescu and Balaban[321] studied the intermolecular Scholl reaction of 1-ethoxynaphthalene and aluminum chloride, which succeeds only in nitrobenzene as solvent. Reduction of nitrobenzene (to phenylhydroxylamine) is considered to take place by a hydride ion abstraction from a dihydrobiaryl such as (LXXVIII). The oxidizing agent which accepts hydrogen may be a reducible group, such as C=O in the same molecule.

Tilak[322] has suggested the mechanism shown in Chart 3, which involves hydride ion abstraction, for the cyclization of 1,5-dibenzoylnaphthalene to CI Vat Yellow 4 (CI 59100); but since the cyclization does not proceed in the absence of oxygen and the product has to be oxidized by sodium hypochlorite for obtaining the vat dye, a radical mechanism, especially in the final step of hypochlorite oxidation, is more probable.

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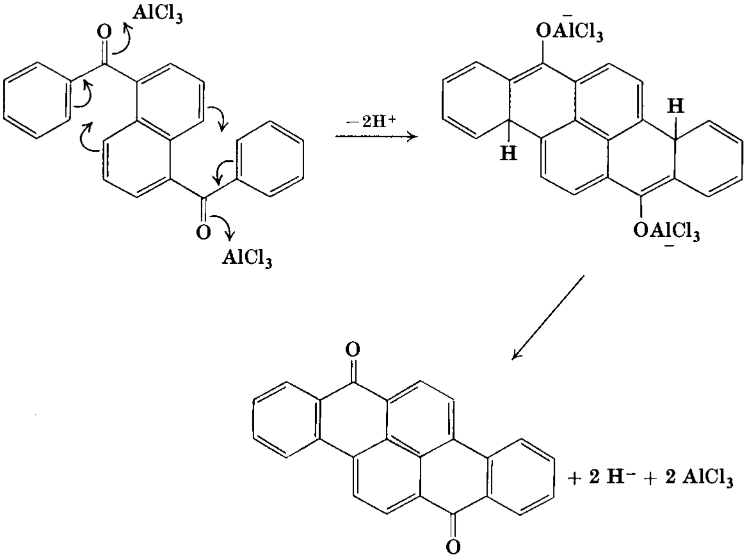
[320] G. Baddeley and J. Kenner, *J. Chem. Soc.* p. 307 (1935).

[321] C. D. Nenitzescu and A. T. Balaban, *Chem. Ber.* **91**, 2109 (1958).

[322] B. D. Tilak, *Chimia* (*Aarau*) **20**, 272 (1966).

CHART 3

Scholl Reaction on 1,5-Dibenzoylnaphthalene



Rooney and Pink[323] postulate radical cations as the active intermediates in ring closure reactions of aromatic hydrocarbons catalyzed by anhydrous aluminum chloride, based solely on the observation that solutions of anthracene or chrysene in carbon disulfide or chloroform give ESR spectra in the presence of aluminum chloride or bromide. Clowes[324] has recently studied the oxidation of 1-ethoxynaphthalene and related compounds to give biaryl coupling products under a variety of Scholl reaction conditions, and he has interpreted the results in terms of two complementary mechanisms, one involving conventional ionic intermediates and the other radical cation intermediates. He has also discussed the significance of electron-transfer processes in electrophilic aromatic substitution.

No mechanistic study of the conversion of anthrimides to carbazoles by heating with aluminum chloride at 150–250° has been recorded.[325]

Anthrimides containing benzamido groups in the 4- or 5-positions [and anthrimides from the acridone (XLIX)] undergo facile cyclization to the corresponding carbazoles by treatment with concentrated sulfuric

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[323] J. J. Rooney and R. C. Pink, *Proc. Chem. Soc.* p. 142 (1961).

[324] G. A. Clowes, *J. Chem. Soc., C* p. 2519 (1968).

[325] See, however, W. Bradley and C. R. Thitchener, *J. Chem. Soc.* p. 1085 (1953).

acid at 30°, followed by oxidation with aqueous sodium chlorate or dichromate and sulfuric acid at about 90°. Several important vat dyes are thus obtained.[325a]

Anthraquinone in concentrated sulfuric acid shows paramagnetic resonance absorption, providing evidence for the presence of free radicals.[326] Bianthrone is thermochromic; this property can also be induced by sulfuric acid and it has been explained by assuming an equilibrium between a protonated molecule and a diradical cation. In view of these observations, Bradley[327] has suggested that the cyclization of 4,5′-bis(benzamido)anthrimide to a carbazole (CI Vat Brown 3; CI 69015) by treatment with concentrated sulfuric acid at about 30° involves a diradical dication in which the carbonyl groups adjacent to the benzamido groups are protonated. There is no evidence for the formation of diradicals when an anthraquinone derivative is dissolved in sulfuric acid. More recent work suggests that ESR spectra obtained from sulfuric acid solutions arise from oxidation products.[328]

Gopalan and Sunthankar[329] confirmed that two acylamido groups in the 4,4′- or 4,5′- or 5,5′-positions are necessary for carbazolization by sulfuric acid[330]; powerful electron-withdrawing substituents in the acyl groups hinder cyclization. They have outlined a mechanism in which the very improbable dication (LXXX) undergoes intramolecular disproportionation to (LXXXI), which cyclizes, loses two protons, and finally undergoes an anthrahydroquinone → anthraquinone oxidation to form the diphthaloylcarbazole.

Hammett and Deyrup[331] have shown that in sulfuric acid solutions of anthraquinone one molecule each of both reagents participates in the protolytic reaction, the proton being attached to one of the CO groups. In connection with the quantitative determination of boron, selenium(IV), and tellurium(IV) with anthrimides in sulfuric acid, Arnesen and Langmyhr[332] examined solutions of anthrimide in sulfuric acid

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[325a] *CSD II*, pp. 901 and 905.

[326] J. M. Hirshon, D. M. Gardner, and G. K. Fraenkel, *J. Am. Chem. Soc.* **75**, 4115 (1953).

[327] W. Bradley, "Recent Progress in the Chemistry of Dyes and Pigments," p. 8. Roy. Inst. Chem., London, 1968.

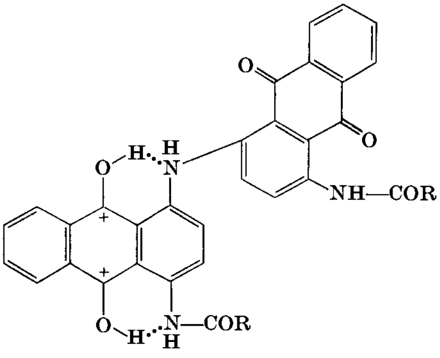
[328] For references, see D. J. E. Ingram, "Free Radicals as Studied by Electron Spin Resonance," p. 149. Butterworth, London and Washington, D.C., 1958.

[329] R. Gopalan and S. V. Sunthankar, *J. Soc. Dyers Colourists* **85**, 372 (1969).

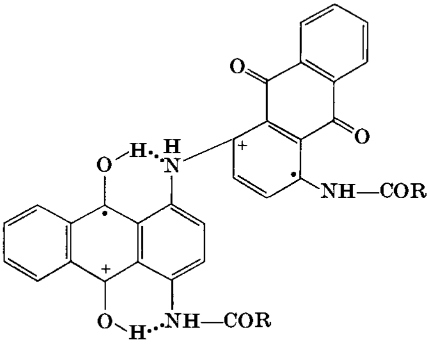
[330] See also K. H. Shah and K. M. Shah, *Bull. Chem. Soc. Japan* **39**, 2023 and 2041 (1966).

[331] L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.* **55**, 1900 (1933).

[332] R. T. Arnesen and F. J. Langmyhr, *Acta Chem. Scand.* **18**, 2400 (1964); see also F. J. Langmyhr and O. B. Skaar, *ibid.* **13**, 2107 (1959).



(LXXX)



(LXXXI)

conductometrically and concluded that one molecule of anthrimide takes up three protons, the NH group protonating first.

The function of the two benzamido groups in an anthrimide is to favor protonation of the two amide CO groups. This species first present in sulfuric acid may therefore be assumed to be (LXXXII). Enolization of the amide groups, protonation of the adjacent quinone carbonyls, and subsequent oxidation by sulfuric acid result in the transformations (see Chart 4) which ultimately lead to the carbazole derivative (LXXXIII). The role of sulfuric acid as an oxidant is confirmed by the fact that hot phosphoric acid only effects hydrolysis of the amide groups, and not cyclization to the carbazole.[333]

1. *Fusion with Aluminum Chloride in Pyridine*

Aluminum chloride in pyridine is technically important for the cyclization of certain anthrimides to carbazoles.[334] Wick[335] recently carried out a thermal analysis of this system and proved the existence of a 1:2 complex. He also reexamined[336] and confirmed Mieg's patent[337] on the dimerization of 1-aminoanthraquinone to 1,1′-diamino-2,2′-bianthraquinonyl in 75% yield by fusion with aluminum chloride in moist pyridine at about 80° in the presence of copper. Using anhydrous conditions, Wick found that 1-aminoanthraquinone-2-sulfonic acid

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[333] W. Bradley and J. V. Butcher, *J. Chem. Soc.* p. 2311 (1954).

[334] W. Mieg and IG, *DRP* 451,495.

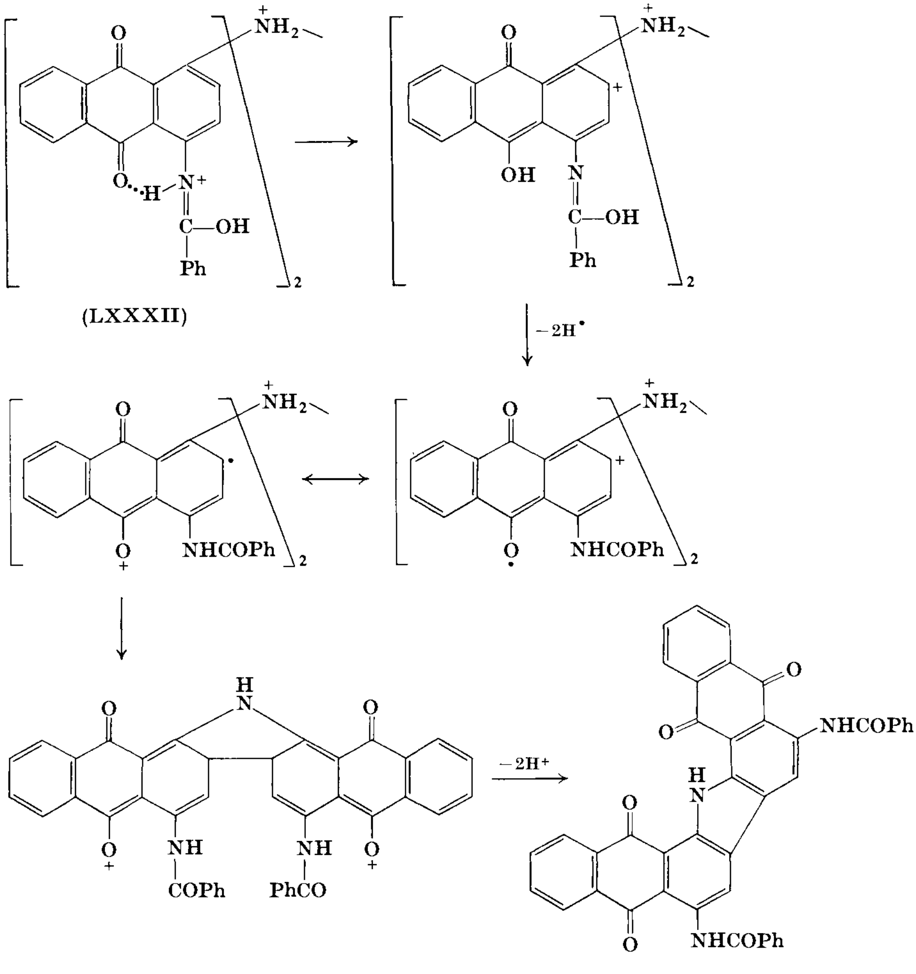
[335] A. K. Wick, *Helv. Chim. Acta.* **51**, 85 (1968); see also A. K. Wick and CIBA, *Ger. Offen.* 1,813,729.

[336] A. K. Wick, *Helv. Chim. Acta.* **49**, 1748; 1755 (1966); **50**, 377 (1967).

[337] W. Mieg and IG, *DRP* 470,550; PB Report 70339, frame 11438.

CHART 4

Cyclization of 4,4′-Bis(benzamido)anthrimide to the Carbazole



(LXXXII)

(LXXXIII)

gave a 70% yield of the corresponding 4,4′-bianthraquinonyl.[338] A byproduct in the reaction, obtained in 40% yield from a mixture of 1-aminoanthraquinone and the 2-sulfonic acid, had the structure (LXXXIV), containing a new semi-flavanthrone type of chromophore.[339] The amine obtained by desulfonation yielded useful pigments

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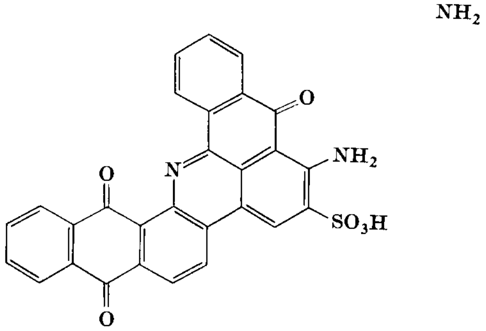
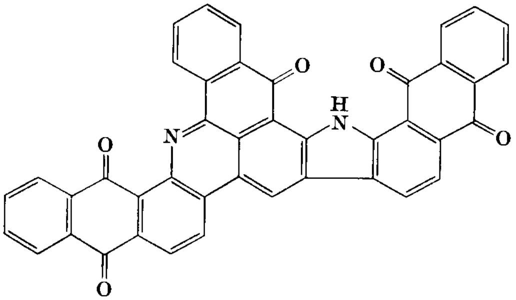
[338] CIBA, *FP* 1,416,980; *BP* 1,032,319.

[339] CIBA, *BP* 1,138,431.

and dyes by acylation.[340] Removal of the NH_2 and SO_3H groups gave the parent compound, crystallizing in olive green needles.



(LXXXIV)



(LXXXV)

Mieg[337] isolated a new orange vat dye by the fusion of 1-aminoanthraquinone with aluminum chloride in anhydrous pyridine, and in the course of this recent work, Wick demonstrated its structure as (LXXXV). Wick has also shown that the imidazopyridine derivative (XXXIII) is obtained by heating 1-aminoanthraquinone with aluminum chloride and ferric chloride in pyridine or 1-amino-2-bromoanthraquinone with aluminum chloride in pyridine.

Arient has recently studied the cyclization of 1-anilinoanthraquinones to acridines (ceramidonines[340a]) or carbazoles using aluminum chloride as a sodium chloride melt or in pyridine.[341] In the melt reaction ceramidonines were obtained in high yield; exceptions were *p*- and *m*-nitroanilinoanthraquinones, which gave phthaloylcarbazoles with simultaneous reduction to the amine and chlorination.

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[340] CIBA, *BP* 1,188,378.

[340a] Cf. *CSD II*, p. 1247.

[341] J. Arient and V. Slavik, *Collection Czech. Chem. Commun.* **34**, 3576 (1969).

VI. Anthrone Derivatives

A. PYRANTHRONES

Pyranthrone is prepared in crystalline form of high purity by fusing a mixture of 2,2′-dimethyl-1,1′-bianthraquinonyl with 5% of its weight of sodium sulfide and ethanolic potassium hydroxide in an autoclave, separating the leuco compound, and oxidizing.[342] A quantitative yield of pyranthrone from 2,2′-dimethyl-1,1′-bianthraquinonyl is obtained by heating it with caustic soda in water and diethylene glycol monomethyl ether under specific conditions.[343] Pyrene can be condensed with benzoyl chloride to form the 1,6- and 1,8-dibenzoyl derivatives, using copper powder as a catalyst; both the diketones yield pyranthrone by Scholl cyclization.[344] Difluoropyranthrone, which dyes cotton a clear orange, is obtained in 50–60% yield by condensing pyrene with *m*-fluorobenzoyl chloride in the presence of aluminum chloride.[345] When pyranthrone is heated with selenium dioxide in an $AlCl_3$–NaCl melt, an orange dye containing Se_2 and Cl_3 is obtained. This is a general reaction applicable to homocyclic and heterocyclic quinones.[346] When dibromopyranthrone is condensed with 1-aminoanthraquinone-2-aldehyde in the presence of sodium carbonate and copper oxide in molten naphthalene, the product, assumed to be an acridine derivative, dyes cotton red-brown.[347]

Pyranthrene sublimes as a yellow or brown powder, depending on the vacuum and the rate of heating. The two forms have the same structure, but different degrees of crystallinity and different semiconductor properties.[348]

B. DIBENZOPYRENEQUINONES

The attractive shade of CI Vat Yellow 4 (CI 59100)[348a] is adversely affected if more than 1% of thc 1,8-isomer is present in the 1,5-dibenzoylnaphthalene submitted to Scholl cyclization. The desired purity is obtained by repeated washing with chlorobenzene and is followed by the UV-visible absorption spectrum in sulfuric acid. Sodium *m*-nitrobenzenesulfonate is a convenient oxidizing agent in the cyclization process. Bromination of Vat Yellow 4 gives CI Vat Orange 1 (CI 59105). The

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[342] M. H. Fleysher and Allied Chemical and Dye Corp., *USP* 2,787,622.

[343] W. Dettwyler and DuP, *USP* 2,855,408.

[344] J. Arient and J. Marhan, *Collection Czech. Chem. Commun.* **26**, 1941 (1961).

[345] W. Eckert, E. Dietz, and FH, *DBP* 1,006,989.

[346] W. Braun and BASF, *DBP* 890,402.

[347] K. Saftien, A. Vilsmeier, and BASF, *USP* 2,603,644; *BP* 668,103.

[348] M. Sano and H. Akamatsu, *Bull. Chem. Soc. Japan* **36**, 1695 (1963).

[348a] *CSD II*, p. 954.

orientation of the bromine atoms depends on the conditions of bromination.[348b] Bromination in oleum gives a mixture which can be separated into a bright orange vat dye and a much less useful yellow component by slurrying with 93–97% sulfuric acid in which the latter dissolves.[349] When bromination is carried out in molten aluminum chloride and urea at 120°, the bromine atoms probably enter the 2,9-positions.[350] Bromo-iodo derivatives can be prepared by treating the bromo compounds with alkali iodides in nitrobenzene in presence of copper or its salts.[351] Indanthrene Red Brown G (CI Vat Brown 39; CI 59270) is the condensation product of a monobromo derivative of Vat Yellow 4 with 1-amino-anthraquinone-2-aldehyde. Brown vat dyes are obtained by condensing a dihalo derivative of Vat Yellow 4 with the amino-acridone (XLIX), followed by treatment with aluminum chloride or its adducts with sulfuric acid.[352]

C. ANTHANTHRONES

Like benzanthrone, anthanthrone undergoes nucleophilic substitutions; thus treatment with potassium hydroxide and an oxidant yields 3,9-dihydroxyanthanthrone.[353] CI Vat Orange 3 (CI 59300)[353a] is the 4,10-dibromo derivative.[354] 4,10-Dibromoanthanthrone and other derivatives of anthanthrone, the first being the preferred compound, are useful for greases to withstand temperatures above 600°F.[355]

D. BENZANTHRONE DERIVATIVES

1. *Violanthrones and Isoviolanthrones*

a. Mechanism of Formation of Violanthrone. The mechanisms outlined by (a) Lüttringhaus and Neresheimer[356] and (b) Bradley and Sutcliffe[357] for the condensation of two molecules of benzanthrone to 4,4′-bibenzanthronyl (an intermediate stage in the formation of violanthrone) by

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[348b] *CSD II*, p. 955.

[349] DuP, *USP* 3,024,254.

[350] W. A. Fisher, W. R. Demler, and NAC, *USP* 2,921,943.

[351] Ya. E. Berezin and V. V. Vanifat'ev, *RP* 192,994.

[352] H. Schlichenmaier, J. Stallman, and FH, *BP* 837,298.

[353] W. Bradley and J. Waller, *J. Chem. Soc.* p. 3778 (1953); cf. F. Baumann and IG, *DRP* 530,497.

[353a] *CSD II*, p. 956.

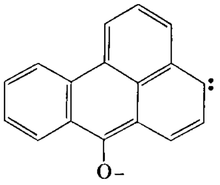
[354] T. Maki and H. Hashimoto, *Bull. Chem. Soc. Japan.* **26**, 348 (1953); W. Bradley and J. Waller, *J. Chem. Soc.* p. 3783 (1953).

[355] J. L. Zakin and Socony Mobil Oil Co., *USP* 3,102,861; see also IG, *DRP* 507,33 *BP* 288,957.

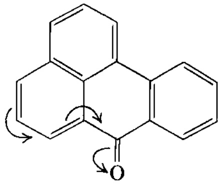
[356] A. Lüttringhaus and H. Neresheimer, *Ann. Chem.* **473**, 259 (1929).

[357] W. Bradley and F. K. Sutcliffe, *J. Chem. Soc.* p. 708 (1954).

treatment with alkali are similar in principle,[357a] but differ in terminology, as suggested by Wanzlick and Ahrens.[358] This is also true of the mechanism they prefer in which the carbene anion (LXXXVI) undergoes a Michael addition to benzanthrone as the conjugated dienone (LXXXVII).



(LXXXVI)



(LXXXVII)

The action of alkali on benzanthrone can lead to 4-hydroxybenzanthrone, 4,4′-dibenzanthronyl, or violanthrone, depending on the temperature and the presence of water and an oxidizing agent or an alcohol. Thus 4-hydroxybenzanthrone is obtained in 86% yield by using anthraquinone, potassium chlorate, and 80% aqueous potassium hydroxide at about 250° in an autoclave.[39] All three reactions probably proceed by a radical mechanism (Chart 5), and it may be recalled in this connection that alkali fusion of phenol and catechol to resorcinol, which depends on the absorption of atmospheric oxygen, is fundamentally a homolytic reaction.[359, 360]

b. Production Methods. Benzanthrone, important and largely used as an intermediate, needs to be handled with care, because the dust is irritating to mucous membranes and can also produce severe dermatitis, probably allergic. An observation made in India, but apparently not elsewhere, is that some workers develop a dark blue pigmentation in the face and other exposed parts of the skin. Moisture and sunlight appear to be involved, but an investigation now in progress has not yet led to definite conclusions.[361] When the affected persons are shifted to other parts of the plant where benzanthrone is not handled, the pigmentation gradually disappears. Benzanthrone is not a carcinogen, and the minimum lethal dose (LD_{50} or dosage which kills 50% of the animals under test) is very high.

[357a] *CSD II*, pp. 962–963.

[358] H. W. Wanzlick and H. Ahrens, *Ann. Chem.* **693**, 176 (1966).

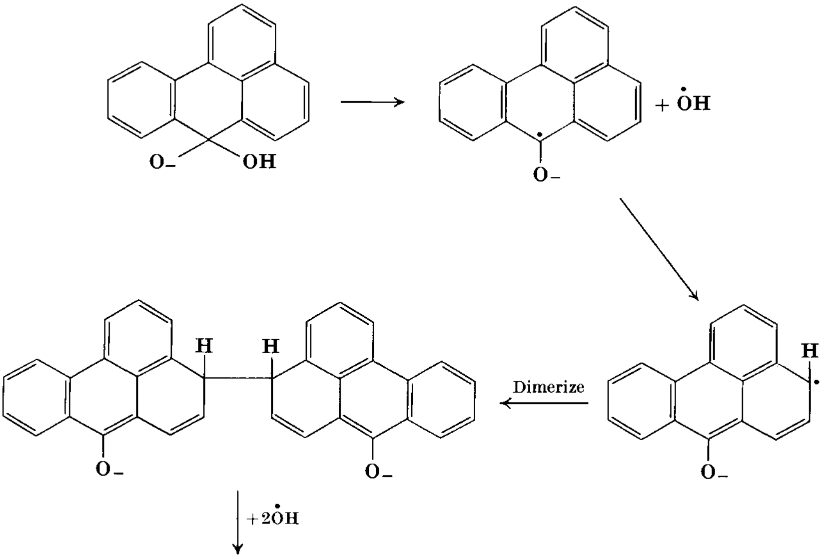
[359] J. F. Bunnett and R. E. Zahler, *Chem. Rev.* **49**, 273 (1951).

[360] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," p. 814. Cornell Univ. Press, Ithaca, New York, 1953.

[361] M. A. Martin and S. H. Zaidi, *Indian J. Ind. Med.* **14**, No. 3, 97 (1968); G. B. Singh, S. N. Sharma, and S. H. Zaidi, *Indian J. Med. Sci.* **21**, 727 (1967).

CHART 5

Mechanism of Reaction of Benzanthrone with Alkali



4,4′-Bibenzanthronyl + 2 $\dot{\mathrm{H}}$ (or H_2) + 2 OH^-

Papers and patents continue to appear on modifications in the established procedures that lead to higher yields. A convenient starting material for the production of benzanthrone is *o*-benzoylbenzoic acid; after cyclization with oleum, the strength of the acid is adjusted, and iron powder (the quality of which is important) and glycerol are added. The addition of copper sulfate to the reaction mixture has been recommended. Crude benzanthrone is suitable for the production of CI Vat Blue 20 (CI 59800); but benzanthrone purified by vacuum sublimation or solvent extraction is necessary for other dyes. Violanthrone is obtained in over 80% yield by fusion of benzanthrone with alkali, sodium acetate, and nitrate in biphenyl or 2(or 4)-hydroxybiphenyl[362]; the use of triethanolamine or triethylene glycol gives 94–97% yield.[363] Polyethylene glycols or their monoalkyl ethers of molecular weight 200–600 improve the fluidity of the fusion mass, giving a better reaction at lower temperatures

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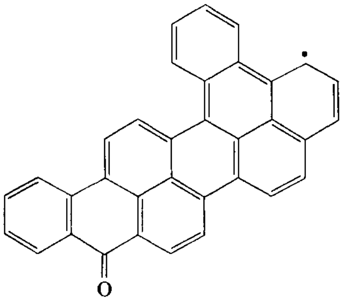
[362] S. Zemka, T. Lisik, and Zaklady Przemyslu Barwnikow Boruta, *PolP* 46,599; see also I. Reichel, E. Secosan, and D. Hentiu, *Rev. Chim.* (*Bucharest*) **9**, 80 (1958); DuP, *USP* 2,872,459.

[363] V. L. Plakidin *et al.*, and Rubezhansk Chemical Combine, *RP* 164,371.

and allowing the omission of purification.[364] 3,3′-Bibenzanthronyl can be converted to violanthrone by merely heating for 10 minutes at 380–390° in a stream of nitrogen.[365]

Improved methods for the preparation of 3,3′-bibenzanthronyl sulfide and its conversion to isoviolanthrone are described in several patents.[366]

Violanthrone B is a by-product, valueless as a dye, which accompanies violanthrone and to which the indicated structure has been assigned by Aoki.[367] It is paramagnetic, showing a strong ESR absorption. About 40% of the molecules are in a free-radical state, the free radical resulting from the detachment of a hydrogen atom from the CH_2 group.[368]



Violanthrone B

c. Bibenzanthronyls. 3,3′-Bibenzanthronyl is obtained in 85–90% yield and high purity by adding polyphosphoric acid in the usual MnO_2–H_2SO_4 method.[369]

Dehydrogenation of 4,4′-bibenzanthrenyl gives the yellow compound (LXXXVIII), which displays thermochromy involving the blue form (LXXXIX); the latter ultimately decomposes to violanthrene.[370]

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[364] C. K. Dien, W. R. Demler, and NAC, *USP* 9,446,810; see also J. E. Gordon, I. Von, and CCC, *USP* 3,418,321.

[365] Y. Nagai and K. Nagasawa, *Kogyo Kagaku Zasshi* **67**, 1977 (1964); *Bull. Chem. Soc. Japan* **39**, 1168 (1966); *JP* 21032/67.

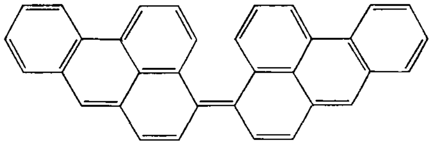
[366] G. Reuge, W. Braun, and BASF, *USP* 2,716,652; *BP* 739,250.

[367] J. Aoki, *Bull. Chem. Soc. Japan* **34**, 1817 (1961).

[368] H. Akamatu, T. Maekawa, Y. Iida, and M. Kinoshita, *Bull. Chem. Soc. Japan* **37**, 849 (1964).

[369] Y. Nagai and K. Nagasawa, *Kogyo Kagaku Zasshi* **68**, 1906 (1965); *JP* 68/07,033; *CA*, **69**, 51894 (1968); Y. Nagai, G. Nobuyuki and T. Sumio, *Kogyo Kagaku Zasshi* **71**, 383 (1968).

[370] E. Clar, G. S. Fell, C. T. Ironside, and A. Balsillie, *Tetrahedron* **10**, 26 (1960).



(LXXXVIII)

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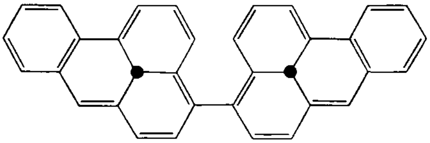
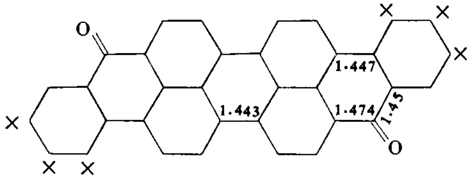


(LXXXIX)

d. Physical Properties. Violanthrone and isoviolanthrone are used as models for coal in carbonization experiments, and their crystal structures have therefore been determined.[371] They are remarkably similar. The bond lengths vary from about 1.36 to about 1.48 Å. The refinement of the structure of isoviolanthrone was carried more to completion and it was found that there are significant deviations of the molecule (the C atoms marked with a cross and the O atoms) from planarity. The formally single C—C bonds have the indicated lengths, and the others vary from 1.358 to 1.444 Å.



Isoviolanthrone

In a discussion of some general features of the processes of chemiluminescence in solution, Kurtz[372] has shown that a brilliant red chemiluminescence may be obtained from violanthrone by passing chlorine through a suspension in chloroform, then adding alkaline hydrogen peroxide, and passing chlorine again. Violanthrone loses an electron

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[371] W. Bolton and H. P. Stadler, *Acta Cryst.* **17**, 1015 (1964); W. Bolton, *ibid.* p. 1020.

[372] R. B. Kurtz, *Trans. N.Y. Acad. Sci.* [2] **16**, 399 (1953–1954).

to form a cation, which then forms a peroxide; the latter loses oxygen to form a triplet diradical.

A spectrophotometric study of changes in shade of cellulose fibers dyed with violanthrone and isoviolanthrone as the result of changes in moisture content and temperature led to the conclusion that hydrogen bonding was involved rather than aggregation of the dye molecules.[373]

e. Nontinctorial Uses. Some of the nontinctorial applications of violanthrone and isoviolanthrone are in the preparation of lubricants serviceable at about 250°[374]; dyeing of anodized aluminum[375]; catalysts in the preparation of β-cyanoethylmethyldichlorosilane[376]; and condensation polymers with Congo Red useful as semiconductors.[377] A mixture of violanthrone and coke or graphite is carbonized and heated to the graphitization temperature for nuclear fuels.[378]

f. Nitrated Violanthrone. Chromatography of a solution of nitrated violanthrone (CI Vat Green 9; CI 59850) in *o*-dichlorobenzene at 110° on alumina enabled the separation of crystalline 16-nitroviolanthrone as the main constituent. The orientation of the nitro group was proved by synthesis of the corresponding amine; an equimolar mixture of benzanthrone and 2-aminobenzanthrone was fused with alkali and the resultant mixture of violanthrone, 16-aminoviolanthrone, and 16,17-diaminoviolanthrone was separated by hot chromatography.[379] Violanthrone can be nitrated in concentrated or 100% sulfuric acid with nitric acid or sodium nitrate. Ammonium vanadate or a sulfuric acid-soluble molybdenum salt may be added.[380] Nitration of crude violanthrone (or violanthrone containing isoviolanthrone) under specific conditions to give 2.5–3.32% N, especially for the production of black vat dyes with presumably improved properties, is described in several patents.[381]

g. Aminoviolanthrone Derivatives. By the condensation of 1 mole of cyanuric chloride with 1 mole of "aminodibenzanthrone" and 1 mole of

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[373] V. G. Babkina, N. S. Dokunikhin, and N. I. Abramova, *Zh. Prikl. Khim.* **37**, 1328 (1964).

[374] E. M. Oparina *et al.*, *RP* 131,433.

[375] B. H. Kirby, W. C. Cochran, Aluminum Co. of America, and Koppers Co. *USP* 3,058,855.

[376] S. Nitzsche, P. Buchheit, and Wacker-Chemie G.m.b.H., *DBP* 1,140,577.

[377] K. Matsuda, L. T. Morin, and CCC, *USP* 3,198,767.

[378] U. K. Atomic Energy Authority, *FP* 1,401,024.

[379] S. S. Malhotra, M. K. Unni, and K. Venkataraman, *J. Sci. Ind. Res.* (*India*) **19B**, 382 (1960).

[380] M. H. Fleysher and NAC, *USP* 3,073,849.

[381] B. F. Robinson and Southern Dyestuff Corp., *USP* 2,831,871; G, *FP* 1,330,363; J. S. Milazzo, D. I. Randall, J. H. Shown, and G, *BP* 955,023; *USP* 3,127,421.

ethanolamine, a vat dye is obtained, which can probably be bound chemically to the fiber. It dyes cotton very fast blue-gray to black shades from an alkaline hydrosulfite vat. Similarly, by using diethanolamine and sulfonating the product a dye is obtained which dyes powerful greenish gray shades of good fastness properties.[382] Replacement of one chlorine in cyanuric chloride or trichloro- or tetrachloropyrimidine with aminoviolanthrone and the other chlorine atoms by ethanolamines or arylamines gives gray and black dyes.[383]

Aminoviolanthrone and -isoviolanthrone can be used as intermediates for direct cotton dyes or reactive dyes by appropriate methods.[384]

Among the numerous other patents covering derivatives of aminoviolanthrones, examples are condensation with 4-hydroxy-7,8-phthaloylcinnolines[385]; gray-blue azines by treatment with dimethyl sulfoxide and alkali[386]; complex carbazoles by condensation with dibromoacedianthrone[387]; modifications of the known oxidation or condensation methods for converting aminoviolanthrone to gray and black dyes not requiring oxidation on the fiber[388]; green dyes by condensation with appropriate stilbene derivatives.[389]

The polyamines obtained by heating di- to pentabromoviolanthrone or -isoviolanthrone with ammonia under pressure at 200° are reddish gray to black dyes.[390]

h. Indanthrene Gray 3B. Treatment of violanthrone with hydroxylamine and concentrated sulfuric acid yields a gray vat dye, Indanthrene Gray 3B (CI Vat Black 16; CI 59855).[391] Fox[392] suggested that this dye is probably 16,17-diaminoviolanthrone, but the latter has been synthesized and it dyes cotton olive green, changing to brown on treatment with hypochlorite.[379] The structure (XC) assigned by Kunz[393] is also improbable, although a scale drawing of the molecule can be made by minor adjustments in the bond lengths and bond angles of violanthrone to

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[382] M. Stäuble, K. Weber, and CIBA, *USP* 3,054,795; *BP* 891,794.

[383] CIBA, *BP* 1,012,316; 1,003,790; 991,811; 961,424; 904,997; 935,595; 897,487.

[384] G. A. Gamlen, C. Morris, D. F. Scott, H. J. Twitchett, and ICI, *BP* 950,327; J. Brassel, M. Stäuble, and CIBA, *SP* 350, 400.

[385] BASF, *BP* 719,906.

[386] CFM, *BP* 992,568.

[387] W. Zerweck, E. Schwamberger, and CFM, *DBP* 1,187,338; CIBA, *BP* 861,758.

[388] D. I. Randall, J. Taras, T. A. Martin, and G, *USP* 2,980,709; D. I. Randall, J. Taras, and G, *USP* 2,739,973; CIBA, *BP* 901,294; BASF, *FP* 1,256,463.

[389] R. S. Long, S.-M. Tsang, and CCC, *USP* 2,877,218.

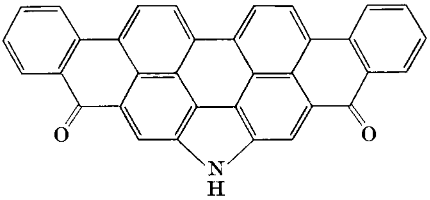
[390] G, *BP* 709,400.

[391] Cf. A. C. Robson and ICI, *BP* 585,560; BASF, *BP* 680,511.

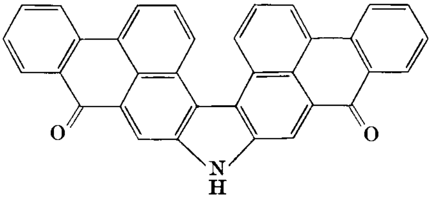
[392] M. R. Fox, *J. Soc. Dyers Colourists* **65**, 508 (1949).

[393] M. A. Kunz, *Melliand Textilber.* **33**, 58 (1952).

accommodate the pyrrole ring. The compound (XCI) was synthesized by Malhotra[394] and he was unable to cyclize it to (XC). The similar structure assigned in *CSD II*[394a] to the obsolete dye, Indanthrene Gray 3G (CI 59860), is also improbable.



(XC)



(XCI)

i. 16,17-*Dihydroxyviolanthrone and Its Ethers*

i. Preparation. Because of the great commercial importance of 16,17-dimethoxyviolanthrone (CI Vat Green 1; CI 59825), and although there are well-established procedures in technical practice, attempts continue to be made for improvements in (a) the oxidation of 4,4′-bibenzanthronyl[395] or violanthrone to 16,17-dihydroxyviolanthrone (XCII), and (b) the *O*-alkylation of (XCII). Advantages are claimed for the oxidation of violanthrone to (XCII) by potassium dichromate in dilute sulfuric acid.[396]

The ethers of (XCII) which are current commercial dyes are the dimethyl (CI Vat Green 1), diethyl (CI Vat Green 4; CI 59835), and the ethylene ether (CI Vat Blue 16; CI 71200); but numerous other and more complex ethers are mentioned in patents. An interesting example is the use of an allene, 4-chloro-1,2-butadiene, which gives a bright greenish blue dye containing the group (XCIII).[397] Bis-hydroxyalkyl ethers are obtained by using epichlorohydrin and similar alkylating agents.[398]

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[394] S. S. Malhotra, Ph.D. Thesis, University of Bombay (1955).

[394a] *CSD II*, p. 968.

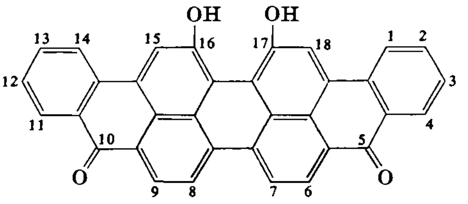
[395] R. J. Dombrowski and Allied Chemical and Dye Corp. *USP* 2,785,187; S. E. Pokhila, V. A. Yakobi, and V. L. Plakidin, *RP* 148,468; V. A. Yakobi, V. L. Plakidin, S. E. Pokhila, and P. P. Karpukhin, *Zh. Obshch. Khim.* **33**, 3369 (1963); V. L. Plakidin and V. A. Yakobi, *RP* 128,547; V. L. Plakidin, V. A. Yakobi, S. E. Pokhila, and P. P. Karpukhin, *Kinetika i Kataliz* **3**, 292 (1962).

[396] A. G. Belobrov, *Tr. Khar'kovsk. Politekhn. Inst.* **46**, 28 (1963).

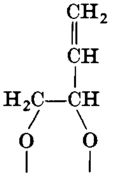
[397] P. R. Johnson and DuP, *USP* 2,662,892.

[398] H. Neresheimer, A. Ehrhardt, and IG, *DRP* 761,553. A "reactive vat dye" has been prepared by converting this product into the bromide (P. P. Karpukhin, T. A. Korotenko, and M. I. Rudkevich, *RP* 245,249).

Superior chlorine fastness is claimed for the dye from 9,9-dichlorofluorene.[399] "Improved vat dyes" of unspecified structures are obtained by condensing (XCII) with chloroacetone, 2,3-epoxybutane, etc., in the presence of 99% sulfuric acid.[400]



(XCII)



(XCIII)

Several patents deal with methods of alkylation (particularly methylation) to avoid oxidation and other side reactions and to ensure complete alkylation.[401] Methylation of (XCII) with dimethyl sulfate and potassium carbonate can be effected smoothly in a variety of solvents including nitrobenzene, *o*-nitrotoluene, acetone, and methyl ethyl ketone, although (XCII) remains largely in suspension. To prevent dehydrogenation to the diquinone dimethylaniline or formaldehyde sulfoxylate may be added. The usual treatment with sulfuric acid for "acid pasting" must be carried out carefully with the addition of boric acid to avoid demethylation. Russian workers[402] have investigated the reactions involved in converting violanthrone to the 16,17-dimethoxy derivative, and they find that 15,16,17-trimethoxy-, 15,16,17,18-tetramethoxy-, 16-hydroxy-17-methoxy-, and 5,10,16,17-tetramethoxyviolanthrone are possible by-products; the formation of the first two compounds needs to be confirmed.

In the preparation of CI Vat Blue 16 the reaction is greatly accelerated by using ethylene dibromide and triethylamine.[403]

In the dibromo derivative (CI Vat Green 2; CI 59830) of 16,17-dimethoxyviolanthrone the bromine atoms are in the 3,12-positions, as shown by the NMR spectrum of the dimethyl ether of the leuco compound (see Section III,A).

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[399] F. Max, W. Schmidt-Nickels, and G, *BP* 652,818; *USP* 2,515,723.

[400] W. Cohen and DuP, *USP* 2,888,463.

[401] I. Von and CCC, *USP* 2,781,362; CCC, *BP* 792,795.

[402] L. M. Egorova and M. M. Sergeeva, *Khim. Nauka i Prom.* **3**, 542 (1958); P. P. Karpukhin and A. G. Belobrov, *Tr. Khar'kovsk. Politekh. Inst., Ser. Khim. Tekhnol.* **6**, 93 (1959).

[403] W. J. Moran and CCC, *USP* 3,036,095.

ii. Structure, color, and semiconductor properties of ethers of 16,17-dihydroxyviolanthrone.[404] The structure and color of 16,17-dimethoxyviolanthrone were discussed in *CSD II*[404a, 405] in connection with the affinity of the leuco derivative for cellulose. The electronic absorption spectra of other 16,17-derivatives of violanthrone were subsequently examined[406] and are recorded in Table I. 16-Methoxyviolanthrone was synthesized by the method used for the synthesis of 16-aminoviolanthrone; equimolar proportions of benzanthrone and 2-methoxybenzanthrone were fused with alkali, and 16-methoxyviolanthrone separated from violanthrone and 16,17-dimethoxyviolanthrone by hot chromatography on alumina. 7,8-Dimethoxyviolanthrone was prepared by the alkali fusion of 5-methoxybenzanthrone, obtained from 5-aminobenzanthrone[407] via 5-hydroxybenzanthrone.[408] 3,12-Dimethoxyviol-

TABLE I

ELECTRONIC ABSORPTION SPECTRA OF VIOLANTHRONE DERIVATIVES[a]

Substitution in violanthrone	λ_1	ϵ_1	λ_2	ϵ_2	λ_3	ϵ_3
None	633	56,000	590	42,100	352	15,000
16-OMe	640	37,000	—	—	380	11,850
16,17-$(OMe)_2$	680	34,650	—	—	395	14,550
16,17-$(C_2H_4O_2)$	630	36,150	—	—	380	11,850
16,17-$(C_4H_8O_2)$	655	38,600	—	—	390	14,700
16,17-Me_2	607	38,000	568	29,700	405	10,000
					390	9,500
7,8-$(OMe)_2$	675	59,800	—	—	426	7,400
					390	7,800
3,12-$(OMe)_2$	645	25,000	—	—	460	6,000

[a] Solvent: *o*-chlorophenol.

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[404] K. Venkataraman, "Pointers and Pathways in Research," p. 93. Ciba of India Ltd., Bombay, 1963.

[404a] *CSD II*, p. 1293.

[405] See also M. R. Padhye, N. R. Rao, and K. Venkataraman, *Proc. Indian Acad. Sci.* **A38**, 307 (1953); C. Robinson, *Discussions Faraday Soc.* **16**, 125 (1954).

[406] P. M. Nair, T. G. Manjrekar, and M. K. Unni, *Chimia (Aarau)* **20**, 300 (1966) C. J. Sanchorawala, Ph.D. Thesis, University of Bombay (1963); see also R. A. Durie and J. S. Shannon, *Australian J. Chem.* **11**, 168 (1958).

[407] S. S. Malhotra, B. D. Tilak, and K. Venkataraman, *Proc. Indian Acad. Sci.* **A38**, 361 (1953).

[408] S. S. Malhotra, Ph.D. Thesis, University of Bombay (1955).

anthrone was prepared by the alkali fusion of 9-methoxybenzanthrone.[409] 16,17-Dimethylviolanthrone was synthesized by Hey, Nicholls, and Pritchett[410] from 2-methylbenzanthrone, both by direct alkali fusion and via 2,2′-dimethyl-3,3′-bibenzanthronyl. They found that 16,17-dimethylviolanthrone gave a deep blue vat resembling the vat of dimethoxyviolanthrone rather than the vat of violanthrone; but the shade on cotton was violet-blue, redder than violanthrone, and relatively faster to water-spotting. When 16,17-dimethylviolanthrone was submitted to prolonged heating with nitrobenzene, a product was obtained which still gave a blue vat, but dyed cotton a weak dull red shade. The product, the formation of which was favored by the presence of barium oxide, did not contain nitrogen; a structure in which the 16,17-methyl groups lost hydrogen with resultant ring closure was tentatively suggested.

If a hypothetical structure for 16,17-dimethoxyviolanthrone is considered, in which the methoxyl groups remain in the plane of the aromatic framework and the central bonds connecting the benzanthrone moieties are pure single bonds, the distance between the methoxyl oxygen atoms has to be about 1.5–1.6 Å. However, since the van der Waals radius of oxygen will need a minimum separation of about 2.8 Å between the two oxygen atoms, strong steric repulsion must exist between the methoxyl groups. As a consequence, the two oxygen atoms will be pushed out of the mean molecular plane, and the aromatic skeleton in the neighborhood of the methoxyl groups may be deformed. The net effect of these two factors on the highest occupied and lowest unoccupied π-electron levels of the molecule will normally determine the relative long-wavelength absorption of 16,17-dimethoxyviolanthrone and of violanthrone. In 16,17-dimethylviolanthrone the effect of the out-of-plane distortion of the methyl groups and the deformation of the aromatic skeleton on the π–π^* transition are indicated by the hypsochromic and hypochromic shift of $\lambda_{\max}$. Methoxyl groups have a weak auxochromic effect, as shown by the small bathochromic shifts in the absorption spectra of the 16-methoxy and 3,12-dimethoxy derivatives of violanthrone; this auxochromic effect will be diminished in the 16,17-dimethoxy compound because of the less effective conjugation of the lone pairs of the methoxyl oxygens with the aromatic π-electrons resulting from the steric repulsion. A new factor must therefore be involved in the large red shift observed in 16,17-dimethoxyviolanthrone. The repulsion between the methoxyl groups will be expected to raise the energy level

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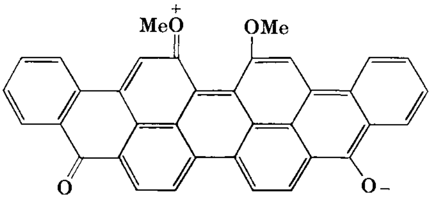
[409] P. N. Pandit, B. D. Tilak, and K. Venkataraman, *Proc. Indian Acad. Sci.* **A35**, 159 (1952).

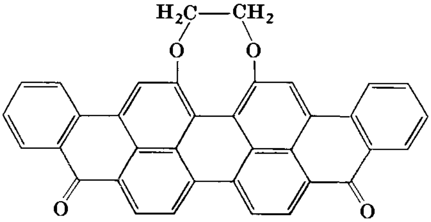
[410] D. H. Hey, R. J. Nicholls, and C. W. Pritchett, *J. Chem. Soc.* p. 97 (1944).

of the highest occupied orbital of the ground state, and this repulsion will be considerably reduced in the electron-transfer state represented by the structure (XCIV), which will make a large contribution because of its stabilization by the proximity of the two methoxyl groups and the consequent attraction of the positively charged oxygen and the available electrons of the neighboring oxygen atom. The role of such "internal solvation" in the excited state is supported by the equally strong bathochromic shift observed in the 7,8-dimethoxy derivative in which the two methoxy groups are similarly situated.



(XCIV)

Another problem which it is convenient to consider at this stage is the constitution of CI Vat Blue 16 (CI 71200) prepared by the action of ethylene dibromide or 2-chloroethyl *p*-toluenesulfonate on 16,17-dihydroxyviolanthrone. A dimeric structure was assigned to this dye in *CSD II*,[410a] but in the new *Colour Index* it is formulated as the monomeric compound (XCV) with the note that "the dimeric formula postulated for this dye is believed to be incorrect." The monomeric structure became obvious when IG work on other ethers was reported.[411] IG prepared polymethylene ethers of 16,17-dihydroxyviolanthrone in which the methylene groups were increased from 2 to 3, 4, and 6, and observed that the color changed progressively from the navy blue of the ethylene ether to green-blue-, blue-green, and dull green.



(XCV)

[410a] *CSD II*, p. 972.

[411] *FIAT* 1313, Vol. III, p. 18.

The oxygen atoms in the 16,17-positions have to be separated by a distance of the order of the van der Waals diameter, which is achieved by moving one oxygen above the plane of the aromatic framework and the other below (Fig. 1); no difficulty is then experienced in connecting them by an ethylene bridge. The monomeric structure (XCV) for the ethylene ether thus becomes sterically feasible, and is further supported by its long-wavelength absorption in comparison with the maxima of the dimethoxy and the butyleneoxy derivatives. When the ethylene bridge is inserted, it can be readily seen that the lone-pair orbitals of the oxygen atoms become very nearly parallel to the plane of the aromatic framework and are therefore largely prevented from participating in the π-electron resonance of the system. The long-wavelength absorption for the ethylene ether thus remains at very nearly the same position as that of the unsubstituted molecule; the actual values of 630 and 633 mμ for (XCV) and violanthrone further suggest that any hypsochromic shift resulting from the deformation of the aromatic skeleton is very small. As the length of the chain linking the two oxygen atoms is increased, the long-wavelength absorption becomes progressively closer to that of the 16,17-dimethoxy derivative, because the increasingly larger heterocyclic ring system will enable the carbon–oxygen bonds to come progressively closer to the conformation of the C—O bonds in 16,17-dimethoxyviolanthrone.

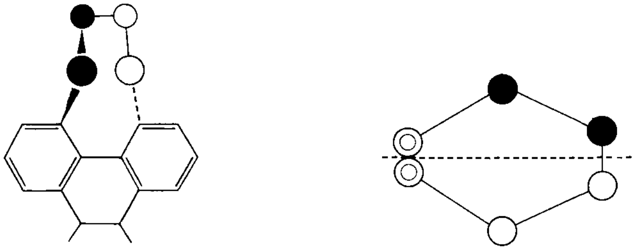


Fig. 1. Conformation of the ethylenedioxy bridge in XCV.

The monomeric structure was confirmed by the mass spectrum of the dimethyl ether of the leuco compound. The molecular ion was at *m/e* 544, and the only peak of higher mass was at 545 (14.6%), the isotopic peak of the molecular ion.[412] Doubly charged ions were abundant, as in the mass spectra of the dimethyl ethers of the leuco derivatives of other ethers of (XCII) (and of aromatic compounds in general); but the

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[412] K. G. Das, T. G. Manjrekar, and K. Venkataraman, *Indian J. Chem.* (1971) (to be published).

absence of a doubly charged ion at 544.5 (corresponding to $M + 1$) also ruled out the dimeric structure. The NMR spectra of the dimethyl ethers of the leuco derivatives of Vat Blue 16, 16,17-dimethoxy- and dimethylviolanthrone provided further support for structure (XCV). The shielding effect of the 16,17-methoxyl groups in 5,10,16,17-tetramethoxyviolanthrene was shown by the upfield shift of the 15,18-protons, which appeared at 1.27 in comparison with the 15,18-protons at 0.85 in 5,10-dimethoxy-16,17-ethylenedioxyviolanthrene. From the discussion in connection with Fig. 1, it follows that the 15,18-protons in (XCV) are not subject to the shielding influence of the ether oxygens. The 15,18-protons in 5,10-dimethoxy-16,17-dimethylviolanthrene appear at 0.78, nearly the same position as in the ethylenedioxy derivative for the same reason; the methyl groups with their large van der Waals radius are twisted out of the molecular plane and are therefore unable to exert a shielding effect on the adjacent protons.

In the course of their extensive work on organic semiconductors, Inokuchi and Akamatu[413] determined the activation energy (E) and resistivity (ρ_0) of many polycyclic aromatic compounds, and they arrived at the following generalizations: The conductivity increases with "increasing condensation of aromatic rings"; quinones are more conductive than the corresponding hydrocarbons; the pyridine ring leads to higher conductance than the benzene ring. An additional feature of their data is that although the quinones have a very much lower ρ_0 than the corresponding hydrocarbons, the difference in E is not significant; the transport of electrons from molecule to molecule appears to be facilitated by the oxygen atoms of the quinone groups.

Violanthrone and its derivatives are attractive for studying the relation between molecular structure, light absorption, and semiconductor properties, because of their availability and the fact that the resistivity values are in the range in which accurate measurements are experimentally possible. Laroia and Sinha[414] determined the activation energy (E) and resistivity (ρ_0) of violanthrone and the four derivatives listed in Table II. E normally indicates the energy required to create a free carrier. The conductivity is determined by the product of the number of free charge carriers and their mobility. An approximate idea of the mobility can be had from ρ; the lower this value the larger, roughly, is the mobility.

The change in conductivity as a function of substitution in violanthrone (Table II) reveals the influence of new factors. The activation energy rises progressively from violanthrone to the 16-methoxy and

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[413] H. Inokuchi and H. Akamatu, *Solid State Phys.* **12**, 93 (1961).

[414] K. K. Laroia and A. P. B. Sinha, private communication (1963).

16,17-dimethoxy derivatives. The value falls for 16,17-ethylenedioxyviolanthrone, but rises again for butylenedioxyviolanthrone. These changes are parallel to the shifts in the first absorption maxima of these compounds in solution; the structural changes which cause a bathochromic or hypsochromic shift in the absorption spectrum produce an increase or decrease, respectively, in ΔE—a behavior contrary to earlier observations. A bathochromic shift means that the energy gap between the ground state and excited state responsible for the optical transition has decreased, which in turn should ordinarily mean a decrease in the activation energy for semiconduction, and this has indeed been found in several series of compounds. For example, in the polyacene series increasing molecular size results in a progressive decrease in both the energy corresponding to the optical absorption and the semiconduction activation energy. Eley and Parfitt[415] have suggested that the energy gap for semiconduction should be approximately equal to the optical transition energy, on the assumption that when an electron is promoted from the highest filled level to the lowest unfilled level no further energy is required for its tunneling to the neighboring molecule. The present results indicate that substitution in the 16,17-positions of violanthrone introduces steric factors which increase the energy required for the tunneling of an excited electron to the neighboring molecule.

TABLE II

ELECTRONIC ABSORPTION SPECTRA, ACTIVATION ENERGY AND RESISTIVITY OF VIOLANTHRONE DERIVATIVES

Substitution in violanthrone	λ_{max}	E (eV)	ρ_0 (Ω cm)
None	633	0.40	6.1×10^4
16-OMe	640	0.64	2.2×10^3
16,17-$(OMe)_2$	680	0.85	5.9
16,17-$(C_2H_4O_2)$	630	0.63	1.6×10^3
16,17-$(C_4H_8O_2)$	665	0.82	2.3

j. Cyananthrene. Cyananthrene (Cyananthrone; CI 68705) is obsolete as a dye, but is of interest as a semiconductor. According to Akamatu and Inokuchi,[416] cyananthrone "has the highest conductivity so far

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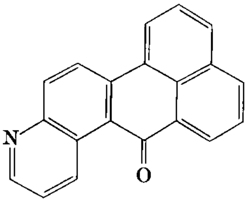
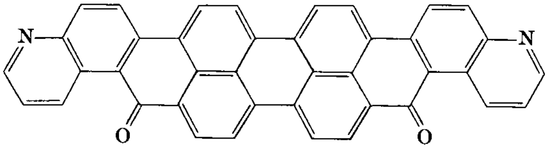
[415] D. D. Eley and G. D. Parfitt, *Trans. Faraday Soc.* **51**, 1529 (1955).

[416] H. Akamatu and H. Inokuchi, *Proc. 3rd Carbon Conf.*, 1959, p. 51.

known among the single organic compounds. Its conductivity is almost comparable to that of selenium, which is a typical inorganic semiconductor." The source from which cyananthrone was obtained has not been specified, but the structure (XCVII) is mentioned. Bally's "benzanthronequinoline"[416a] has the structure (XCVI), and cyananthrone was assigned the structure (XCVII) by analogy with the formation of violanthrone from benzanthrone.[417]



(XCVI)



(XCVII)

Bradley and Sutcliffe[418] repeated the preparation of cyananthrone with a slight modification of Bally's conditions and submitted the crude black product to a process of purification, involving extraction with trichlorobenzene and phenol and hot chromatography of the soluble fraction. A minute amount of a dye was thus isolated, which exhibited in concentrated sulfuric acid solution an absorption spectrum corresponding to an isoviolanthrone and not to a violanthrone derivative. They then concluded that cyananthrone had the isoviolanthrone structure. The presence of (XCVII) in cyananthrone was not excluded by Bradley and Sutcliffe's work, which only provided evidence of the fact that crude cyananthrone contains a substance which probably has the isoviolanthrone structure.

Unni[419] found that a sample of Cyananthrene O obtained from Farbenfabriken Bayer contained 14% of acetone-soluble substances; chromatography of a benzene solution on alumina led to 4(*N*),5-pyridinobenzanthrone, 1-azanaphthacene-6,11-dione, 2-aminoanthraquinone, and several unidentified fractions. The residual dye was a mixture of vattable (47%) and unvattable (35%) fractions, neither of which could be crystallized. Both gave similar color reactions, but the absorption spectra in sulfuric acid were different in the region beyond 770 mμ. The spectrum of the vattable portion showed an absorption maximum at 880 mμ; the spectrum of violanthrone in sulfuric acid has a peak at

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[416a] *CSD II*, p. 978.

[417] P. N. Pandit, B. D. Tilak, and K. Venkataraman, *Proc. Indian Acad. Sci.* **A32**, 39 (1950).

[418] W. Bradley and F. K. Sutcliffe, *J. Chem. Soc.* p. 2118 (1952).

[419] M. K. Unni, Ph.D. Thesis, University of Bombay (1958).

848 mμ, while isoviolanthrone shows no absorption beyond 790 mμ. The available evidence therefore indicates that cyanthrone contains the dipyridino derivatives of both violanthrone and isoviolanthrone.

k. Miscellaneous Derivatives of Violanthrone and Isoviolanthrone. Chlorination of violanthrone in *o*-dichlorobenzene at 140–145° is accelerated by the addition of sodium chloride; the tetrachloro derivative is obtained in 16 hours.[420] Halogenation, alkylation, and other chemical reactions on compounds such as violanthrone and isoviolanthrone can be carried out in a mixture of aluminum chloride and 10–13% of acetamide, dimethylformamide, urea, and their derivatives.[421] Up to five atoms of bromine can be introduced by bromination in an $AlCl_3$–NaCl melt.[422] Hexadecachloroviolanthrone can be prepared by chlorination at 100–250° and over 50 atm pressure in the presence of a Group IV metal halide.[423] *C*-Alkylation of violanthrone and isoviolanthrone gives navy blue and violet dyes.[424] Perfluoroalkylated violanthrone and dichloroisoviolanthrone are used to dye Teflon.[425] A mixture of dimethyl terephthalate (120), dimethyl violanthrone-3,12-dicarboxylate (0.026), ethylene glycol (100), and magnesium oxide (0.024), heated under reflux and further processed, gives reddish purple polyester fiber.[426] Complex vat dyes of doubtful practical value are prepared by condensing halogenated violanthrone or isoviolanthrone with aromatic amines (aminoanthraquinones, aminobrasan derivatives, etc.), and subsequent cyclization if necessary.[427]

Chloromethylation was mentioned in Section III,E, and reference may be made to further patents in this area, some of which cover the preparation of vat dyes by suitable condensations of the chloromethyl groups.[428] The pyridinium salt of bis(chloromethyl)isoviolanthrone has bactericidal, fungicidal, and insecticidal properties.[429]

[420] G. R. Genta and NAC, *USP* 2,995,552.

[421] W. Braun and BASF, *DBP* 878,647; see also A. Caliezi, W. Kern, and CIBA, *USP* 2,827,464; *BP* 807,092.

[422] G. R. Genta and G, *USP* 2,692,885; G, *BP* 708,752.

[423] S, *BeP* 665,732; see also S, *FP* 1,448,922.

[424] BASF, *BP* 694,072.

[425] Minnesota Mining and Mfg. Co., *BP* 840,725.

[426] J. E. McIntyre, E. C. Pugh, and ICI, *BP* 838,716.

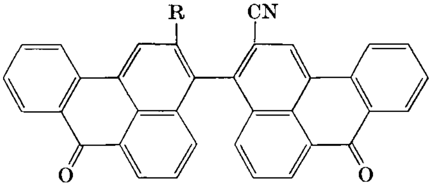
[427] P. Nawiasky, G. R. Genta, and G, *BP* 703,294; 703,296; W. Schmidt-Nickels, D. I. Randall, and G, *USP* 2,862,931; *BP* 856,805.

[428] S. Coffey, N. H. Haddock, F. Lodge, J. Wardleworth, C. Wood, and ICI, *USP* 2,544,825; 2,559,597; *BP* 613,980; 623,998; D. I. Randall and G, *USP* 2,645,646; 2,703,321; W. Clarke, G. H. Keats, R. Thornton, C. Wood, and ICI, *USP* 2,768,171; CIBA, *BeP* 619,754; P. W. B. Semmens, G. E. Penketh, and ICI, *BP* 760,019; ICI, *Neth. Appl.* 6,409,271; W. O. Jones, A. Parkinson, J. Wardleworth, and ICI, *BP* 675,863; A. Tartter, W. Federkiel, M. Rosenkranz, and BASF, *BP* 1,006,892.

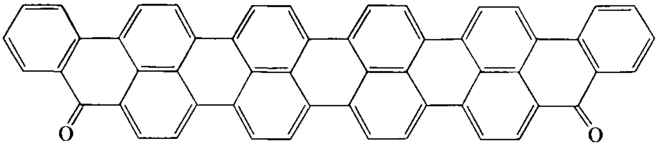
[429] D. I. Randall and G, *USP* 2,619,492; C. Marschalk, R. Ratchewski, and Francolor, *FP* 1,008,578.

The introduction of water-solubilizing groups (such as $SO_2NHCH_2CH_2$ —OSO_3Na) into violanthrone and especially isoviolanthrone is the subject of several patents (see Section III,D).

The condensation of 9-methyleneanthrone[429a] with RCH═CH—CH═CHCN (R = H, Me, or CN) yields the 3,3′-bibenzanthronyls (XCVIII), which can be cyclized with alcoholic potassium hydroxide at 120° to the corresponding violanthrones, mainly blue dyes for cotton.[430]



(XCVIII)



(XCIX)

Various benzobenzanthrones and the corresponding violanthrones and isoviolanthrones have been synthesized, but no vat dyes with useful properties were obtained.[431] The 1,12-benzoperylene analog of violanthrone can be obtained by a Diels-Alder reaction of methyleneanthrone and 1,3-cyclohexadiene, followed by alkali fusion of the bibenzanthronyl derivative thus obtained and dehydrogenation. Halogenation yields red to bordeaux dyes for cotton.[432] The quaterrylene analogs of violanthrone and isoviolanthrone, designated as violongthrone (XCIX) and isoviolongthrone, have been synthesized by Nagai.[433] They can be vatted with difficulty, but have no dyeing properties. As expected, they are considerably better semiconductors than violanthrone and isoviolanthrone. They

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[429a] *CSD II*, p. 961.

[430] J. M. Straley, R. C. Harris, and EKCo., *USP* 2,716,124; see also H. W. Schwechten, O. Bayer, and FBy, *USP* 3,047,577; *BP* 889,335.

[431] W. Bradley and F. K. Sutcliffe, *J. Chem. Soc.* p. 1247 (1952).

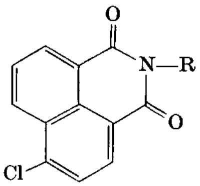
[432] J. M. Straley and EKCo, *USP* 2,659,735.

[433] Y. Nagai and K. Yamamoto, *Kogyo Kagaku Zasshi* **68**, 2257 (1965); Y. Nagai and K. Nagasawa, *J. Chem. Soc. Japan, Pure Chem. Sect.* **87**, 284 (1966).

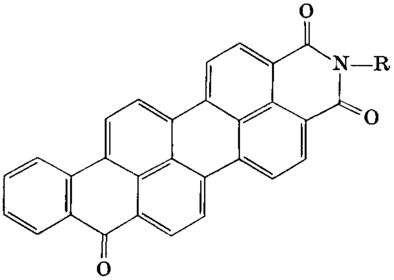
show ESR signals with spin concentrations of $7.0 \times 10^{18}/g$ and $3.5 \times 10^{18}/g$.

2. *Miscellaneous Benzanthrone Derivatives*

Benzoyleneperylene dyes (CI) have been synthesized by Gotoh and Nagai[434] by the condensation of benzanthrone with *N*-alkyl-4-chloronaphthalimides (C), but in poor yield. The *n*-propyl derivative dyed cotton a bright bluish shade.

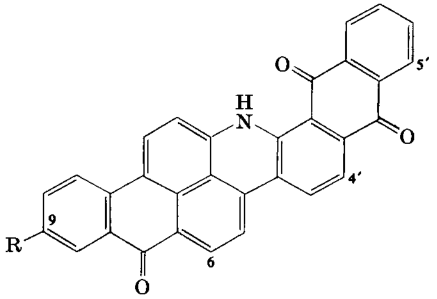


(C)



(CI)

The monoaza analogs of CI Vat Green 3 (CI 69500) from 1-azabenzanthrone and from 1-azaanthraquinone, respectively, are greenish blue and dark blue.[435]



CI Vat Green 3 (CI 69500; R = H)
CI Vat Black 25 (CI 69525; R = NH—AQ)

The importance of the dyes such as CI Vat Green 3 and CI Vat Black 25 (CI 69525), obtained by cyclization of 3-(α-anthraquinonylamino) benzanthrone and its derivatives to acridines,[435a] is shown by numerous patents. After bromination of benzanthrone in nitrobenzene to form the 3-bromo or 3,9-dibromo derivative, the product can be directly treated

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[434] N. Gotoh and Y. Nagai, *Kogyo Kagaku Zasshi* **67**, 152 (1964).

[435] M. Yokote *et al.*, *J. Chem. Soc. Japan, Ind. Chem. Sect.* **58**, 677 (1955); **57**, 52 (1954).

[435a] *CSD II*, p. 980.

with 1-aminoanthraquinone, copper oxide, and acid-binding agents to give vat dye precursors.[436] Olive green vat dyes of excellent fastness to washing are obtained by introducing sulfonamide groups (SO_2NHR, SO_2NR_2).[437] A blue-gray vat dye is obtained by condensing a mixture of mono- and dichlorobenzanthrones with 1-aminoanthraquinone in the presence of copper powder, steam-distilling, and fusing the product with methanolic potassium hydroxide at 135–140°.[438] The introduction of an α-anthraquinonylamino group in the 6-position of the benzanthrone nucleus in Vat Green 3 gives olive green to green vat dyes of excellent fastness to light and much clearer hue than dyes containing an acylamido group in the anthraquinone half.[439] 1,5-Dichloroanthraquinone can be converted to 6,11-dichlorobenzanthrone and bromination gives 3,6-dibromo-11-chlorobenzanthrone, which is useful for preparing derivatives of Vat Green 3 with AQNH, anilino, benzamido, and other groups in the 6-position.[440] The introduction of an *o*-methoxybenzamido group in the 4′-position of Vat Green 3 gives a dye suitable for dyeing military uniforms, because of the good fastness and the low infrared reflectance of the olive shades.[441] The product obtained by the condensation of the 4′-amino derivative of Vat Green 3 with 1-aminoanthraquinone-2-carbonyl chloride dyes cotton a maroon shade of excellent fastness. The dye has also very good printability. The hypsochromic shift from olive green to maroon is remarkable.[442] Annelation of 2-phenylthiazole with Vat Green 3 in the 5′,6′-positions gives a khaki dye.[443]

Successive treatment of the condensation product of 3-bromobenzanthrone and 5-aminoanthrimide with aluminum chloride in pyridine and in benzenesulfonyl chloride gives a product dyeing olive shades.[444]

Cyclization of Vat Black 25 to a carbazole can be effected by heating with aluminum chloride in urea at about 100°. Nuclear halogenation can be simultaneously carried out by adding a halogen or halogen precursor, and khaki to olive green vat dyes are thus obtained.[445]

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[436] L. Hruska and K. Brezina, *CzechP* 106,744.

[437] FBy, *USP* 2,901,479; 2,805,224; *BP* 788,433; 773,116.

[438] L. D. Lytle and CCC, *USP* 2,456,589; S. F. Torre and CCC, *USP* 3,008,962.

[439] FBy, *BP* 994,216; see also *BP* 987,372.

[440] K. Wunderlich, H. S. Bier, F. Baumann, and FBy, *USP* 3,134,781; *BP* 994,216.

[441] I. Von, A. S. Tomcufcik, W. B. Hardy, R. E. Herd, and CCC, *USP* 2,993,901; 3,004,029; 3,027,373–7; 3,030,368–9.

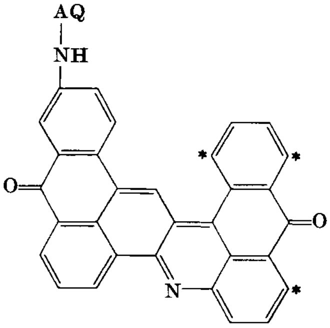
[442] E. Honold, R. Müller, and CFM, *DBP* 1,066,304.

[443] M. Scalera, H. E. Westlake, Jr., and CCC, *USP* 2,655,502.

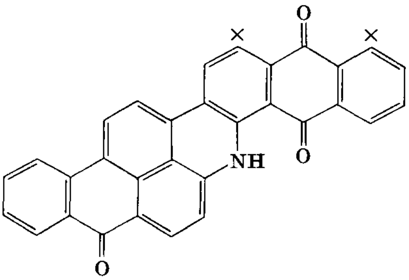
[444] F. Baumann, H. S. Bien, and FBy, *BP* 797,240.

[445] W. Braun, H. Steuerle, A. Schuhmacher, and BASF, *BP* 1,016,665; see also A. Caliezi, W. Kern, and CIBA, *USP* 2,827,464; *BP* 807,092; 809,222; CIBA, *BP* 771,748; F. Irving, A. Livingston, and ICI, *BP* 814,619; *USP* 2,863,871.

When the condensation product of 3,9-dibromobenzanthrone and 2 moles of 1-aminoanthraquinone is heated with potassium hydroxide in isobutanol, Vat Black 25 is obtained. But if the cyclization is effected by sulfuric acid or polyphosphoric acid at 50–155°, it takes a different course and a new acridine derivative (CII) is formed. The brown or blackish brown dyes of this type, in which the AQ-NH group may be in the starred positions, have excellent vat solubility, and their fastness, especially to bleaching agents, enables "them to replace the more expensive carbazole and ordinary acridine vat dyes of comparable hues."[446]



(CII)



(CIII)

When benzanthrone derivatives unsubstituted in the 4-position are treated with aminoanthraquinones and powdered potassium hydroxide in dimethyl sulfoxide at 20–25° for about 6 hours, 4-anthraquinonylaminobenzanthrones are obtained in 90% yield.[447] The isomer (CIII) of Vat Green 3, prepared from 4-aminobenzanthrone, and its derivatives in which one X is an ArCONH group have been described. They dye various shades of green. Halogenation yields bluish olive and olive green dyes.[448]

When the amide from benzanthrone-3-carboxylic acid and 1-aminoanthraquinone is heated with potassium carbonate in benzophenone at about 250°, it undergoes cyclization to (CIV), which dyes cotton violet

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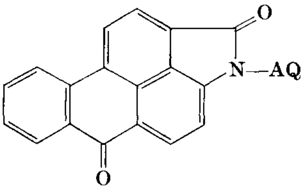
[446] J. Deinet and DuP, *USP* 3,121,719.

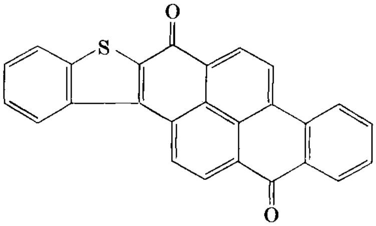
[447] W. Zerweck, E. Schwamberger, and CFM, *DBP* 1,171,441.

[448] H. S. Bien, K. Wunderlich, F. Baumann, and FBy, *BP* 987,372; W. Zerweck, E. Schwamberger, and CFM, *DBP* 1,197,182; see also IG, *DRP* 504,016; 507,344; 509,422; 662,461.

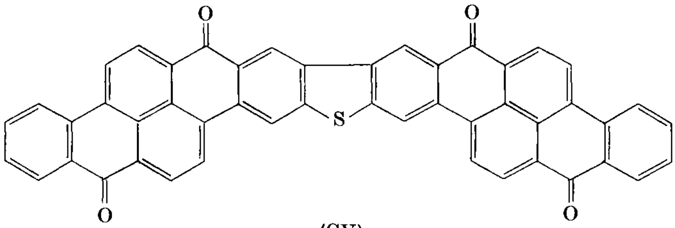
shades from an olive green vat.[449] Successive Friedel-Crafts and Scholl reactions between benzanthrone-3-carbonyl chloride and diphenylene sulfide give the bright orange dye (CV), which is also of interest as a derivative of dibenzopyrenequinone.[450] The same acid chloride by similar treatment with thionaphthene yields the chlorine-fast orange dye (CVI).



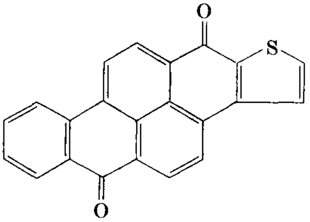
(CIV)



(CVI)



(CV)



(CVII)

Condensation of 9-bromobenzanthrone-3-carbonyl chloride with 2 moles of 1-aminoanthraquinone, followed by treatment with alcoholic potassium hydroxide at 100–200°, gives a fast gray vat dye. Further treatment with sulfuric acid or phosphoric acid or aluminum chloride–sodium chloride at about 200° results in olive green dyes.[451] The fate of the amide

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[449] W. Ruppel and BASF, *DBP* 1,156,528.

[450] W. Schmidt-Nickels and G, *USP* 2,562,872; 2,648,676; see also IG, *DRP* 741,735.

[451] F. Baumann, H. S. Bien, and FBy, *BP* 779,508; *USP* 2,846,434; FBy, *BP* 838,755.

group during drastic alkali and acid treatment and the structures of the products are obscure.[451a]

2-Ethyl-1-nitroanthraquinone can be converted to 2-acetyl-1-bromoanthraquinone, condensation of which with 3-aminobenzanthrone gives a useful yellow vat dye.[452] The condensation product of 1-aminoanthraquinone and 3-chlorobenzanthrone-9-aldehyde (from the 9-chloromethyl derivative) is a fast yellow vat dye.[453]

Condensation of a 9-methylene-10-anthrone, unsubstituted in the 1- and 2-positions, with 2-thienyl vinyl ketone, followed by cyclization using aluminum chloride and manganese dioxide gives (CVII) and its derivatives, which are yellow to orange hot-dyeing vat dyes.[454]

E. Miscellaneous Homocyclic Quinones

1. *Acedianthrones*

An X-ray structure analysis has confirmed the Clar structure for acedianthrone.[454a, 455] The bond lengths and angles in the "rather unusual five-membered rings" were measured and there was general agreement between the X-ray results and wave-mechanical calculations, except for the bond common to the two five-membered rings; the calculated length in the planar molecule was 1.44 Å, but the measured value was 1.59 Å.

Inukai and Ueda[456] found that Clar's method[457] for the preparation of bis(anthronylidene)ethane[457a] from anthrone and chloral gave good results regarding both yield and purity if sulfuric acid was used as the condensing agent instead of stannous chloride. Cyclization to acedianthrone was effected by Clar's method of boiling the intermediate with benzoyl chloride in nitrobenzene.

The condensation of an anthrone with glyoxal to form the bis(anthronylidene)ethane may be carried out in one step or in two steps via addition to form the glycol, which is then dehydrated.[458]

[451a] According to IG, *DRP* 722,868, acridines of the (CIII) type are formed.

[452] E. Klingsberg and CCC, *USP* 3,211,754.

[453] D. I. Randall and G, *USP* 2,855,409.

[454] J. M. Straley, R. C. Harris, and EKCo, *USP* 2,656,361.

[454a] *CSD II*, p. 985.

[455] P. H. Friedlander, T. H. Goodwin, and J. M. Robertson, *Acta Cryst.* **7**, 127 (1954); see also T. H. Goodwin, *J. Chem. Soc.* p. 1689 (1955).

[456] K. Inukai and A. Ueda, *J. Chem. Soc. Japan, Ind. Chem. Sect.* **53**, 175 (1950); *Rep. Govt. Chem. Ind. Res. Inst., Tokyo* **47**, 21 and 26 (1952).

[457] E. Clar, *Chem. Ber.* **72**, 2134 (1939).

[457a] *CSD II*, p. 985.

[458] D. A. W. Fairweather, J. F. McGechen, and ICI, *BP* 806,384; *USP* 2,842,561.

Bis(anthronylidene)ethane can be simultaneously oxidized and brominated to a tetrabromo derivative of the corresponding ethylene, which can be cyclized by boiling nitrobenzene to the acedianthrone. The product is a red-brown vat dye, and it is also useful as an intermediate for condensation with 1-aminoanthraquinone. The anthrimide dyes cotton bluish gray, and the corresponding carbazole dyes reddish gray.[459] The anthrimides from mono- or dibromoacedianthrone and α-aminoanthraquinones are brown vat dyes, which are nontendering. They can be carbazolized by chlorosulfonic acid or aluminum chloride.[460] The position of the bromine atoms is apparently significant, because when the dibromoacedianthrone from 2-bromo-9-anthrone is condensed with 1-aminoanthraquinone, the anthrimide and the corresponding carbazole dye cotton blue-gray.[461]

Acedianthrone can be aminated by nitration and reduction or by hydroxylamine in presence of ferrous sulfate; one or more amino groups can be introduced. The acyl derivatives are red-brown vat dyes.[462, 463] Condensation of the monoamine with 2,7-dichloroanthraquinone or 4,10-dibromoanthanthrone gives products which dye cotton reddish brown or intense dark olive brown.[463, 464]

Condensation of the dichloroacedianthrone from 1-chloro-9-anthrone with 2 moles of the aminoacridone (XLIX) or its thiaxanthone analog gives fast gray to olive green dyes.[465]

Fast red-brown prints are produced by the acedianthrone from 2-methylanthraquinone and the bromo derivatives.[466] The acedianthrone analog from 1,2-benz-9-anthrone dyes cotton a fast violet-brown.[467]

Bis(anthronylidene)ethylene, the penultimate intermediate for acedianthrone, reacts with dienophiles, yielding pigments or dye intermediates. The adduct with maleic anhydride is an olive yellow pigment.[468]

The red-violet vat dyes,[469] obtained from the condensation products of

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[459] E. Schwamberger and CFM, *BP* 726,429; *USP* 2,782,209; *DBP* 955,176.

[460] CIBA, *BP* 861,758; A. Caliezi, W. Kern, and CIBA, *SP* 347,922; cf. CFM, *BP* 690,006; 728,554.

[461] W. Zerweck, E. Schwamberger, and CFM, *DBP* 1,187,338.

[462] P. Kienzle and Fran, *FP* 1,124,539.

[463] See also K. A. J. Chamberlain and ICI, *BP* 672,905–7.

[464] A. Caliezi, W. Kern, and CIBA, *USP* 2,827,464; 2,945,866; *BP* 807,092; 858,586.

[465] K. A. J. Chamberlain, D. A. W. Fairweather, and ICI, *USP* 2,542,312; *BP* 672,908; K. A. J. Chamberlain and ICI, *USP* 2,636,034; *BP* 678,522; W. Zerweck, E. Schwamberger, and CFM, *BP* 699,149.

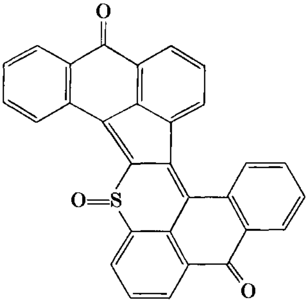
[466] A. Caliezi and CIBA, *USP* 2,918,345; *BP* 859,256.

[467] A. Caliezi and CIBA, *USP* 2,919,284; *BP* 877,487.

[468] W. Zerweck, E. Schwamberger, and CFM, *DBP* 1,187,753.

[469] H. Scheyer and IG, *DRP* 470,501.

anthrones and glyoxal by alkali fusion, are transformed into new nontendering olive and green vat dyes by treatment with sulfur, sulfur halides, or alkali sulfides in presence of aluminum chloride or sulfuric acid.[470] Thionation of bis(anthronylidene)ethylene with sulfur and sodium sulfide in alcohol at 80–105°, followed by oxidation, gives a product which dyes cotton pink from a red vat.[471] By treatment of a bis-(anthronylidene)ethylene with aluminum chloride and thionyl chloride



(CVIII)

(with or without the addition of a sulfur monochloride) at 20–25°, yellow-olive to yellow-green vat dyes are obtained.[472] Indanthrene Yellow Green GC is probably prepared in this manner[93] and is constituted as a trichloro derivative of (CVIII).

2. *Pyrene, Chrysene, and Fluoranthene Derivatives*

Reference was made in *CSD II*[472a] to pyrene, chrysene, and fluoranthene as raw materials for vat dyes. Holbro[473] has surveyed Ciba research in this area.[474] Because these polycyclic hydrocarbons were much more expensive than anthracene or anthraquinone, they could only be used for dyes showing extraordinarily valuable properties, such as great tinctorial strength, novel shades, or unusual fastness. The position today is different; pyrene and fluoranthene of 98–100% purity are available at about the same price as 99–100% anthracene.

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[470] CFM, *BP* 722,575.

[471] E. Schwamberger and CFM, *DBP* 1,270,714.

[472] E. Schwamberger and CFM, *USP* 2,645,634; *BP* 715,767; cf. Bayer.[93, p.14]

[472a] *CSD II*, p. 946.

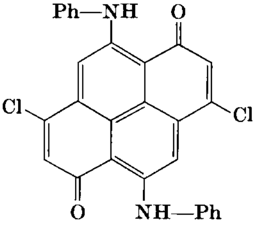
[473] T. Holbro, *J. Appl. Chem.* **3**, 1 (1953).

[474] See also Y. Abe and Y. Nagai, *Yuki Gosei Kagaku Kyokai Shi* **14**, 220 (1956); J. Arient, *Chem. Prumysl.* **9**, 310 (1953).

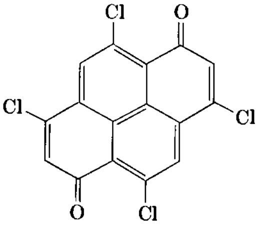
The direct cotton dye, Sirius Light Blue F3GL, of the dioxazine class and the solubilized vat dye, Anthrasol Green I3G, were mentioned in *CSD II*; the parent vat dye (CIX) is prepared by oxidizing hexachloropyrene to the tetrachloroquinone (CX), which is condensed with aniline. Indanthrene Brilliant Green H3G (CI Vat Green 24) is the analog from *m*-chloroaniline. Acylamidopyrenequinones are vat dyes. Thus bromination of pyrene-1,6-quinone in chlorosulfonic acid gives the 2-bromo and 2,7-dibromo derivatives, which can be condensed with benzamides.[475] Vat dyes whose structures are unknown are prepared by treating tetrachloropyrenes with aluminum chloride at 100° or higher temperature and then with hot oleum.[476]

1-Pyrenoline (CXI), prepared by the Skraup reaction on 1-aminopyrene, is a useful intermediate; condensation with phthalic anhydride, for instance, yields a red vat dye. The acridone (CXII) is a green dye; and it is interesting to compare its hue with the red-violet acridone (XLVIII).[473]

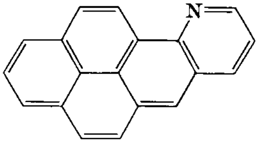
The polycyclic hydrocarbons appear to be particularly useful for vat



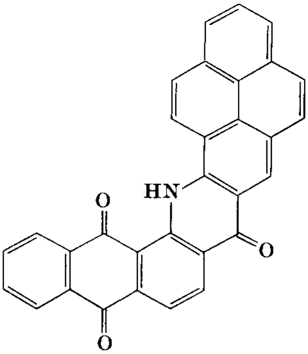
(CIX)



(CX)



(CXI)



(CXII)

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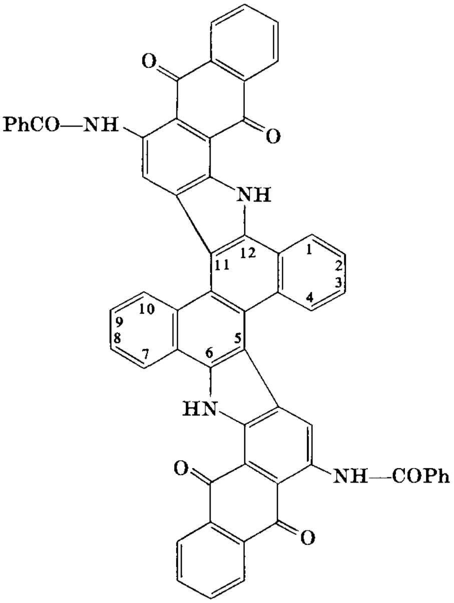
[475] J. Arient and J. Dvorak, *Chem. Prumysl* **14**, 357 (1964).

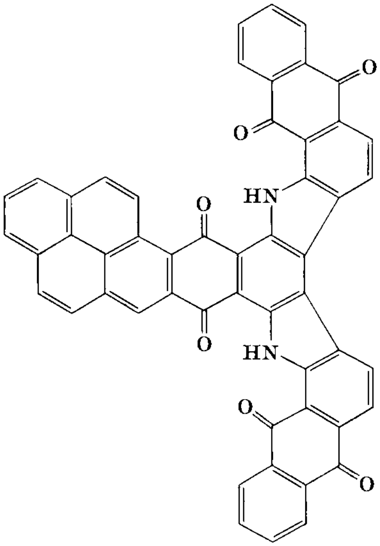
[476] H. Sieber and FH, *DBP* 951,388.

dyes and pigments containing the carbazole nucleus. The condensation product of 6,12-dibromochrysene with two molecules of 1-amino-4-benzamidoanthraquinone is a blue pigment; it can be cyclized with sulfuric acid at room temperature to the dicarbazole (CXIII), which dyes cotton very fast red-brown shades.[473, 477]

Compound (CXIV) dyes a fast olive brown; it is prepared by condensing pyrene with 3,6-dichlorphthalic anhydride, condensing the dichlorophthaloylpyrene with α-aminoanthraquinone (2 moles), and cyclizing to the dicarbazole.[473]



(CXIII)



(CXIV)

The condensation product of fluoranthene-3,8-dicarboxylic acid with 1-amino-5-benzamidoanthraquinone is a strong neutral yellow dye with very good all-around fastness.[473]

F. 1,9-HETEROCYCLIC DERIVATIVES OF ANTHRONE

1. *Flavanthrones*

The crystal structure of flavanthrone has been determined by the X-ray method, assuming the molecule to be planar.[478] The phototropy of flavanthrone has been investigated.[479]

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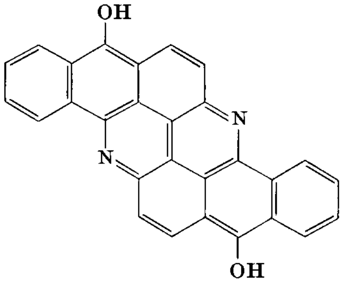
[477] See also CIBA, *SP* 218,368; 222,462–72.

[478] H. P. Stadler, *Acta Cryst.* **6**, 540 (1953).

[479] F. Feichtmayr and J. Schlag, *Melliand Textilber.* **45**, 526 (1964).

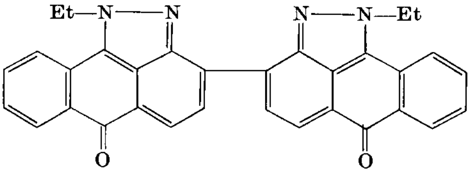


(CXV)

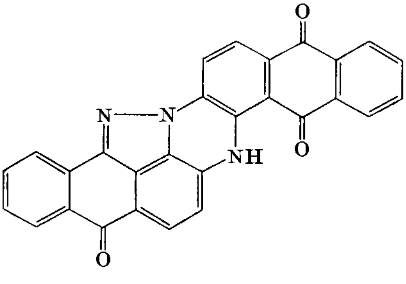
Aoki[480] considers that leucoflavanthrone has the structure (CXV)[480a] because its dibenzoate and 8,16-diazapyranthrene have nearly identical electronic absorption spectra.

2. *Pyrazolanthrone*

Cibanone Red 2B (CI Vat Red 34; CI 70330) is the *N*,*N′*-bis(alkoxyalkyl) or -(*sec*alkyl) derivative of Pyrazolanthrone Yellow,[480b] but the dye is not commercially available. Ethylation of Pyrazolanthrone



Indanthrene Rubine R



(CXVI)

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[480] J. Aoki, *Bull. Chem. Soc. Japan* **41**, 1017 (1968).

[480a] Cf. *CSD II*, p. 990.

[480b] *CSD II*, p. 993.

Yellow gives CI Vat Red 13 (Indanthrene Rubine R; CI 70320), which has the indicated structure.[481]

Acrylonitrile can be added to Pyrazolanthrone Yellow; the product (the cyanoethyl analog of CI Vat Red 13) dyes cotton an intense red.[482]

Cyclization of 2-(3-benzanthronyl)pyrazolanthrone by means of alkali to CI Vat Blue 25 (CI 70500) (Indanthrene Navy Blue R[482a]) is considered to be an ionic reaction, but the evidence is not conclusive. The accepted structure of CI Vat Blue 25 was confirmed in the course of this work.[483] The blue dye (CXVI) obtained by condensing pyrazolanthrone with 1-amino-2-bromoanthraquinone and heating the product with ethanolic potassium hydroxide has better fastness to chlorine (further improved by halogenation) than indanthrone.[484] Condensation of 4-chloronaphthalimide (in which NH may be replaced by NPh or N—C_6H_4—OMe-*p*) with pyrazolanthrone, followed by cyclization gives red-violet to red-brown dyes.[485]

Treatment of 4-, 5-, or 8-nitroanthraquinone-1-sulfonic acid with hydrazine at 70–120° gives the corresponding aminopyrazolanthrone.[486]

One mole each of pyrazolanthrone and isothiazolanthrone may be united to give a yellow dye.[487] The 3-tetrahydrofuryl analog of Vat Red 13 dyes yellower and brighter shades.[488] A process for preparing a printing paste of the isopropyl analog has been described.[489] Red vat dyes can be prepared by dimerizing pyrazolanthrone (and its *N*-alkyl derivatives) through an azo group in the 3,3′-positions.[490]

The use of 2-ethylbenzanthrone in the preparation of Vat Blue 25 gives a bluer dye, which may be halogenated.[491] 4-Phenylbenzanthrone leads to clear greenish blue dyes.[492] If the analog of Vat Blue 25 prepared

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[481] T. Maki and T. Akamatsu, *J. Chem. Soc. Japan, Ind. Chem. Sect.* **54**, 281 and 326 (1951); *Bull. Chem. Soc. Japan* **26**, 327 (1953); see also W. Bradley and K. W. Geddes, *J. Chem. Soc.* p. 1636 (1952); W. Bradley and C. S. Bruce, *ibid.* p. 1894 (1954); F. B. Stilmar, *in* Lubs[134, p.468]; contrast *FIAT* 1313, II, p. 159.

[482] W. Schmidt-Nickels, *J. Prakt. Chem.* [4] **6**, 139 (1958).

[482a] *CSD II*, p. 995.

[483] W. Bradley and K. H. Shah, *J. Chem. Soc.* p. 1902 (1959).

[484] Y. Nagai *et al.*, *Kogyo Kagaku Zasshi* **70**, 66 and 72 (1967).

[485] S. Akoyoshi and O. Tsuge, *J. Chem. Soc. Japan, Ind. Chem. Sect.* **56**, 533 (1953); **57**, 296 (1954).

[486] R. Neeff and FBy, *DBP* 1,257,149.

[487] A. Caliezi and CIBA, *BP* 880,575.

[488] W. Schmidt-Nickels, D. I. Randall, and G, *USP* 2,817,667.

[489] CIBA, *NethP* 6,400,332.

[490] W. L. Berry, W. L. Mosby, and CCC, *USP* 2,962,494.

[491] H. Schlichenmaier, H. Pohlmann, and FH, *USP* 2,882,272; 2,946,794; *DBP* 1,005,665; FH, *BP* 800,971.

[492] K. Wilke *et al.*, and FH, *BP* 766,345; *DBP* 955,085.

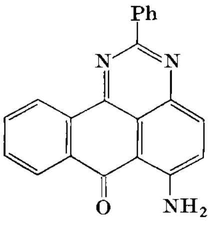
from 1-chloro-5-benzamidoanthraquinone and hydrazine is hydrolyzed, and the amino group is acylated by 1-aminoanthraquinone-2-carbonyl chloride, the product dyes cotton a bluish gray which can be built up to a strong black of very high all-round fastness.[493] The analogs of Vat Blue 25, in which the two isomeric pyrazole derivatives from 1,2-benzanthraquinone are used for the condensation with 3-bromobenzanthrone, dye cotton greenish blue; halogenation gives bluer dyes.[494]

3. *Pyrimidanthrones*

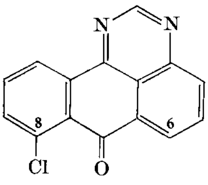
Aminoanthraquinones acylated by pyrimidanthrone carboxylic acids were mentioned in Section IV,A.

Indanthrene Yellow 7GK (CI Vat Yellow 29; CI 68400) and 4GK (CI Vat Yellow 31; CI 68405) are, respectively, the *p*-chlorobenzoyl and 2,5-dichlorobenzoyl derivatives of 6- and 8-aminopyrimidanthrone.[494a] At the time they were marketed they were of special interest as nontendering yellow dyes, but they are now of little commercial importance.

Pyrimidanthrones can be obtained in 90% yield by heating the appropriate 1-aminoanthraquinone with formamide and a small amount of ammonium vanadate in nitrobenzene. Replacing formamide by urea or cyanamide, the corresponding 2-hydroxy- and 2-aminopyrimidanthrones are produced in 89–99% yield.[495] Pyrimidanthrone derivatives can be conveniently prepared by treatment of the appropriately substituted 1-aminoanthraquinone with dimethylformamide and phosphorous oxychloride to form the *N*,*N*-dimethylformamidinium chloride ($\mathrm{AQNH{-}CH{=}\overset{+}{N}Me_2\ \overset{-}{Cl}}$), which is then submitted to the action of ammonium acetate in a solvent.[496] The yellow compound (CXVII),



(CXVII)



(CXVIII)

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[493] F. Irving, A. Livingston, and ICI, *BP* 716,558; *USP* 2,709,170.

[494] W. Eckert, W. Dauner, and FH, *DBP* 956,262.

[494a] *CSD II*, p. 996.

[495] K. Nishio, T. Kasai, and S. Tsuruoka, *Kogyo Kagaku Zasshi* **71**, 2026 (1968).

[496] H. Weidinger, H. Eilingsfeld, G. Haese, and BASF, *DBP* 1,194,867; 1,159,456; cf. BASF, *DBP* 1,132,931; 1,154,489; 1,237,122.

obtained by heating 1,4-diaminoanthraquinone with benzonitrile and *p*-toluenesulfonic acid in trichlorobenzene at 190°, represents a general type useful as intermediates, disperse dyes, and pigments; vat dyes are obtained by aroylation of the amino group.[497] Condensation of 2 moles of 8-aminopyrimidanthrone with 1 mole of 2,5-dimethoxyterephthaloyl chloride gives a strong yellow dye.[498] A bright yellow dye is obtained by condensing 4,4′-(*p*-carboxyphenyl)azobenzene with 1 mole each of 6-aminopyrimidanthrone and 1-aminoanthraquinone.[499]

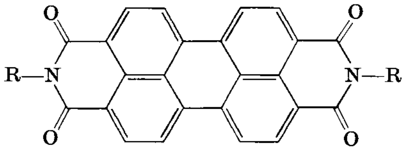
The carbazole obtained by condensing 1 mole of 1,4-diaminoanthraquinone with 2 moles of 8-chloropyrimidanthrone (CXVIII) and then cyclizing by heating with aluminum chloride dyes cotton a brown-violet with "excellent weather resistance."[500]

VII. Vat Dyes Related to the Anthraquinonoids: Derivatives of Perylene-3,4,9,10-tetracarboxylic Acid and Naphthalene-1,8-dicarboxylic and 1,4,5,8-tetracarboxylic Acids

Vat dyes prepared from perylene-3,4,9,10-tetracarboxylic acid (A) and naphthalene-1,4,5,8-tetracarboxylic acid (B) were treated as "miscellaneous dyes" in *CSD II*.[500a] Although not anthraquinonoid, they are vat dyes of the same general character and a brief review of the progress in this area is therefore included.

1. *Perylene Derivatives*

The diimide (CXIX; R = H) of (A) is marketed as a pigment (CI Pigment Brown 26; CI 71129).



(CXIX)

Since CI Vat Red 23 (CI 71130) (CXIX; R = Me) dyes a dull yellowish red, the patent claim that the N-CH_2CH_2CN analog and its halogenated

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[497] BASF, *BP* 1,061,117.

[498] D. I. Randall, N. W. Solonen, and G, *USP* 2,871,240.

[499] T. Sasa, F. Fujii, T. Aoki, and MDW, *JP* 20,249/63.

[500] H. Weidinger, H. Tarnow, J. Kranz, and BASF, *BP* 1,023,703.

[500a] *CSD II*, p. 1188.

or amino-substituted derivatives are gray vat dyes needs to be examined. The dyes are prepared by condensing (a) the diimide with acrylonitrile or (b) (A) with β-aminopropionitrile.[501]

Maki's voluminous work on vat dyes included a study of the experimental conditions for the preparation of CI Vat Red 23 and CI Vat Red 29 (CI 71140) (CXIX; R = *p*-methoxyphenyl). A recent patent describes the preparation of CI Vat Red 32 (CI 71135) (CXIX; R = *p*-chlorophenyl) by heating (A) with 2 moles of *p*-chloroaniline in an aqueous medium in presence of 1–3 moles of pyridine or 2-picoline.[502] When (A) is heated with 2-amino-4-chlorotoluene and zinc chloride at 200–210° for several hours, an almost quantitative yield of the bright yellowish scarlet dye is obtained.[503] A reddish orange pigment for nitro lacquers, PVC, and polystyrene is obtained from (A) and *p*-2-xylidine.[504] Dyes of the type (CXIX; R = *p*-hydroxyphenyl or 4-hydroxybiphenyl) dye cotton and synthetic fibers red shades of good fastness.[505] Red dyes are also obtained by condensing (A) with 4-aminoazobenzene or *o*-aminoazotoluene and zinc chloride in quinoline.[506] The condensation products of (A) and 8-aminoquinoline or its 6-methoxy derivative are red pigments.[507] Bluish red pigments of high tinctorial strength and fastness in polymers, paints, etc., are obtained by condensing perylene tetracarboxylic anhydride with melamine and its derivatives.[507a]

The hydroxamic acid and hydrazide prepared from (A) dye cotton corinth and brownish red, respectively.[508]

Compound (CXIX; R = 1-anthraquinonyl) dyes cotton bluish red from a violet vat.[509] The analog from 1,4-diamino-2-acetylanthraquinone (in which the 4-amino group reacts) dyes bordeaux; the bis-imidazole from 1,2-diaminoanthraquinone dyes violet.[506, 510] If (A) is condensed with *p*-phenylenediamine and the bis(*p*-aminophenyl)imide is further condensed with 1-aminoanthraquinone-2-carbonyl chloride, the product dyes cotton bright red.[511]

In two Russian patents 5-aminosalicylic acid, 1,5-diaminoanthra-

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[501] W. Schmidt-Nickels and G, *USP* 2,794,805.

[502] R. L. Walker and DuP, *USP* 3,340,264.

[503] FBy, *BP* 788,777; R. Knoche and FBy *DBP* 1,031,449; *USP* 2,888,460.

[504] W. B. Braun, M. Bertl, and BASF, *DBP* 1,094,897.

[505] J. Koch and CIBA, *DBP* 1,128,584; *BP* 887,971.

[506] W. B. Braun, E. Anton, and BASF, *DBP* 1,230,946; 1,213,555; see also *FP* 1,384,677.

[507] K. Nagasawa, K. Maehara, and Nippon Kayaku Co., *JP* 21,858/69.

[507a] F. Irving, D. G. Wilkinson, and ICI, *BP* 1,167,044.

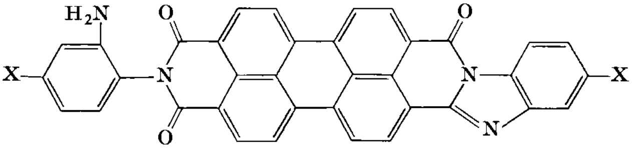
[508] E. Honold and CFM, *DBP* 1,147,702.

[509] BASF, *BP* 1,056,299.

[510] W. Braun, E. Anton, and BASF, *DBP* 1,213,554.

[511] E. Honold and CFM, *DBP* 950,801; cf. G, *USP* 2,668,815.

quinone, 3-aminobenzanthrone, etc., are condensed with (A) in quinoline in the presence of concentrated hydrochloric acid.[512] Maki and Hashimoto[513] found that by condensing (A) with an excess of *o*-phenylenediamine (or its *p*-chloro derivative) the main products were (CXX; X = H, or Cl), new, deep violet vat dyes with very good fastness properties. The bis-imidazoles were blue-violet nonvattable pigments. Since 3,4-diaminoanisole was unstable, 3-nitro-4-aminoanisole was condensed with (A) and the nitro group then reduced. The monoimidazole (CXX; X = OMe) was vattable, and dyed cotton a deep red-violet; the bis-imidazole was a nonvattable blue pigment.



(CXX)

The analog of Quinoline Yellow[513a] obtained in 33% yield by heating quinaldine with (A) dyes cotton red from a violet vat. It can be prepared in double the yield by alkali fusion of the condensation product of quinaldine and naphthalic anhydride.[514]

2. *Naphthalene Derivatives*

Arient, who has a long series of papers[515, 515a–d] on "aroyleneimidazole dyes," has also written a comprehensive review,[516] from which it is clear that recent interest is in their use as pigments and disperse dyes.[515] Cis and trans isomers of several dyes can be separated by chromatography.[515a] The electronic spectra and chemical reactivity of CI Vat Red 15, CI Vat Orange 7, and related compounds have been discussed in terms of the HMO theory.[515b]

Using 2,6- and 2,7-dichloronaphthalene-1,4,5,8-tetracarboxylic acid for the condensation with *o*-phenylenediamine, Arient has studied the

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[512] P. P. Karpukhin, M. I. Rudkevich, and E. A. Rzhetskii, *RP* 204,467; 216,874.

[513] T. Maki and H. Hashimoto, *J. Chem. Soc. Japan, Ind. Chem. Sect.* **54**, 479 (1951); *Bull. Chem. Soc. Japan* **25**, 411 (1952); **27**, 602 (1954).

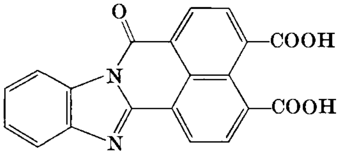
[513a] *CSD II*, p. 1197.

[514] A. E. Porai-Koshits and I. I. Chizhevskaya, *J. Gen. Chem. USSR* (*English Transl.*) **26**, 2175 (1956).

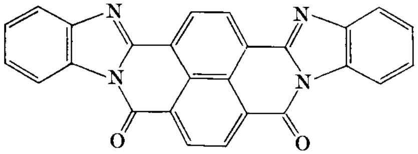
[515] J. Arient *et al.*, *J. Soc. Dyers Colourists* **85**, 246 (1969).

[515a] J. Arient *et al.*, *Collection Czech. Chem. Commun.* **24**, 111 (1959).

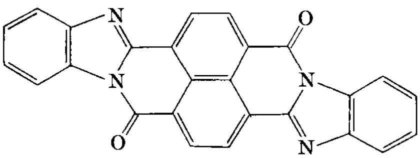
[515b] J. Arient *et al.*, *Collection Czech. Chem. Commun.* **31**, 1180 (1966).



(CXXI)



CI Vat Red 15
CI 71100



CI Vat Orange 7
CI 71105

resonance, inductive, and steric effects of the chlorine atoms on the rate and direction of cyclization.[515c] Starting from the dicarboxylic acid (CXXI) many symmetric and unsymmetric dyes were prepared by condensation with monoamines, diamines (including benzidine and other *p*-diamines, 1,2- and 2,3-diaminoanthraquinones), and triamines [tri-(*p*-aminophenyl)methanes]. The first type was applicable as disperse dyes, and the others as orange, scarlet, brown, and olive green vat dyes, dyeing fast shades from vats of moderate to strong substantivity.[515d]

The IG method[516a] for the separation of the cis and trans isomers (CI Vat Red 15 and CI Vat Orange 7) involved treatment with ethanolic potassium hydroxide. Minor modifications have been claimed in recent patents, especially for the purpose of preparing good pigments.[517]

The condensation of naphthalene-1,4,5,8-tetracarboxylic acid (B) with aromatic *o*- or *p*-diamines can be carried out in aqueous medium in presence of catalytic amounts of sulfuric acid.[518] When CI Vat Red 15 or the corresponding dye from 4-chloro-*o*-phenylenediamine is halogenated, red-brown dyes with greatly improved fastness to washing and chlorine are obtained.[519] The reddish brown dyes obtained from

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[515c] J. Arient *et al.*, *Collection Czech. Chem. Commun.* **28**, 2479 (1963).

[515d] J. Arient *et al.*, *Collection Czech. Chem. Commun.* **30**, 3718 (1965); see also L. M. Golomb, *et al.*, *J. Appl. Chem. USSR* (*English Transl.*) **36**, 1273 (1963); V. L. Plakidin, B. M. Krasovitskii *et al.*, *RP* 114,328.

[516] J. Arient, *Russ. Chem. Rev.* (*English Transl.*) **34**, 826 (1965).

[516a] *CSD II*, p. 1192.

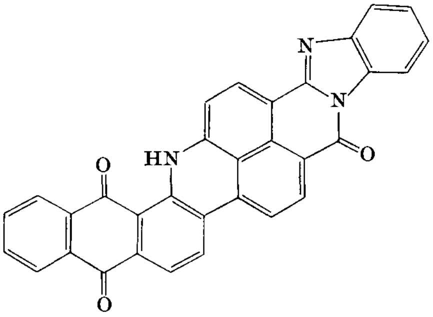
[517] J. Arient, J. Dvořák, and P. Kokes, *CzechP* 108,794; R. A. Pizzarello, J. J. De Lucia, P. L. Maguire and IC, *USP* 3,072,661; IC, *BP* 925,409.

[518] V. L. Plakidin *et al.*, *RP* 182,823.

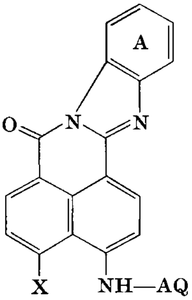
[519] G, *USP* 2,908,685; *BP* 848,768.

(B) and 1 mole each of *o*-phenylenediamine and its 4-ethoxy derivative can be prepared in one step in pyridine or acetic acid under reflux or in water in an autoclave.[520] The dyes obtained by condensing 1,2- and 2,3-diaminoanthraquinone with (B) produce fast olive shades on cotton.[521]

By starting with 4,5-dichloronaphthalene-1,8-dicarboxylic acid and carrying out the appropriate reactions with *o*-phenylenediamine and 1-aminoanthraquinone, the dye (CXXII) can be obtained, and it yields very fast yellowish green shades on cotton.[522] Analogs in which 1-aminoanthraquinone is replaced by pyrazolanthrone are blue to violet dyes.



(CXXII)



(CXXIII)

When (CXXIII), or the isomer in which X and NHAQ are interchanged, or a derivative in which ring A is substituted or AQ carries a benzamido group in the 4-position, is heated with potassium carbonate in *N*-methylpyrrolidinone or hexaethylphosphoric triamide at 150–270°, cyclization to the carbazole occurs. The products are olive green or green vat dyes.[524]

Condensation of benzanthrone-3,4-dicarboxylic acid with *o*-phenylenediamines and naphthylenediamines gives orange to gray vat dyes of very good fastness to light and washing.[525] Pigments with properties similar to those of CI Vat Orange 7 have been prepared from dichloro- and dibromopyromellitic anhydride.[526]

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[520] Toms River Chem. Corp., *BP* 1,027,134; cf. IG, *BP* 313,887.

[521] J. Arient and J. Dvořák, *CzechP* 105,501; 106,134; see also W. Eckert, O. Fuchs, and FH, *USP* 2,861,073; *BP* 854,162.

[522] H. Sieber and FH, *BP* 1,036,273; 1,079,109; *USP* 3,306,904.

[523] FH, *BeP* 643,590.

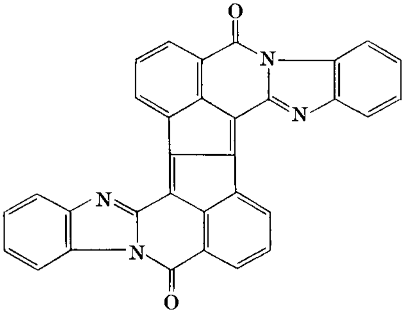
[524] FH, *BeP* 631,368.

[525] Y. Yamakazi, *Yuki Gosei Kagaku Kyokai Shi* **20**, 1028 (1962).

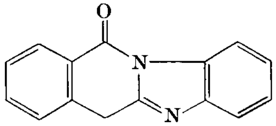
[526] B. K. Manukian, *Helv. Chim. Acta* **52**, 2143 (1969).

CI Vat Red 29, CI Vat Red 15, CI Vat Orange 7, and their derivatives dispersed in lubricating oil are useful as high-temperature greases.[527]

A few dyes containing imidazole rings, but derived from homophthalic acid, may be considered at this stage. The acedianthrone analog (CXXIV) prepared from (CXXV) by condensation with glyoxal sulfate and subsequent fusion with sodium *m*-nitrobenzenesulfonate in an aluminum chloride–sodium chloride melt is a violet vat dye of high affinity. Several related dyes have also been described.[528, 529] During the preparation of (CXXV) from homophthalic acid and *o*-phenylenediamine, 25% of the isomer is formed and is rejected.



(CXXIV)



(CXXV)

VIII. Solubilized Vat Dyes

Vat dyes in which solubilizing groups (such as COOH, SO_3H, $SO_2NHCH_2CH_2OH$) are introduced, apparently with the main object of improving vattability and penetration into the fiber, were mentioned in Section III,D. This section[529a, 530] deals with sulfuric esters of the leuco derivatives of vat dyes.

Indigosol Red Violet IRRL and Violet I5R (CI Solubilized Vat Violet 6 and 7; CI 59315 and 59321) are the sulfuric esters of the dihydro derivatives of 2,8-dimethoxy and diethoxyanthanthrone, respectively. The parent vat dyes are made especially for this purpose; but the dimethoxy compound (Spinning Violet 3BV) has also been used for the mass coloration of viscose. Dokunikhin[292] has shown that Anthrasol Brown

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[527] J. L. Zakin and Socony Mobil Oil Co., *USP* 3,126,341; 3,102,860; *BP* 965,922; 969,784.

[528] M. F. Sartori, A. Oken, and H. E. Schroeder, *J. Org. Chem.* **31**, 1498 (1966).

[529] H. E. Schroeder and DuP, *USP* 2,785,167.

[529a] Cf. *CSD II*, Chapter XXXIV.

[530] See also K. Moldaenke, "Ullmann," Vol. 11, p. 696.

IBR contains only two –O—SO_3Na groups, although the parent vat dye (CI Vat Brown 1; CI 70800) contains three anthraquinone units; but the structure proposed by him in which the outer CO groups undergo reduction is unsupported by any evidence.

The lightfastness of dyeings of solubilized vat dyes can be increased by 1–2 units (on a 5-unit scale, although the usual lightfastness scale is 1–8) by mercerization after dyeing or boiling with soap and soda ash, according to a Russian paper; the saponification of the leuco esters is thus completed and there is also the usual change in the physical state of the dye.[531] The solubilized vat dyes in the commercial range have high lightfastness when they are applied under the correct conditions, and it must be assumed that the reported results refer to a particular dye with anomalous lightfastness properties.

The method used for the preparation of Indigosol Blue IBC (CI Solubilized Vat Blue 6; CI 69826), oxidation of (CXXVI), can be applied to the synthesis of other indanthrone derivatives substituted in the 3,3′-positions by groups such as SO_2R.[532] Improvements in the oxidation procedure have also been suggested.[533]

Three solubilized vat dyes (two of which are obsolete), prepared by coupling diazotized 1-aminoanthraquinone (or 1-amino-6-chloroanthraquinone) with acetoacetanilide (or its 4-chloro- or 4-chloro-2,5-dimethoxy derivative), and then converting the pigments into the sulfuric esters of the corresponding anthrahydroquinones, are mentioned in CI (CI 60600*; 60605; 60610*) (Anthrasol Yellow IG and I3G; Anthrasol Golden Orange IGG[533a]). Indigosol Red AB (CI Solubilized Vat Red 3) is prepared by diazotizing (CXXVI) and coupling it with the *o*-anisidide (CI Azoic Coupling Component 20) of 2-hydroxy-3-naphthoic acid; it is inferior in its fastness properties to the other solubilized anthraquinonoid vat dyes.[534] Analogous dyes from 1-aminoanthraquinone will be brighter and perhaps more useful than Indigosol Red AB, but the required acid sulfate (CXXVII), of leuco-1-aminoanthraquinone is difficult to prepare, and more difficult to diazotize.[535] Treatment of (CXXVII) with cyanuric chloride gives a dye which can be applied on

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[531] S. S. Rakhlina, Z. A. Strunina, and L. P. Kozlova, *Tekstil'n. Prom.* No. 2, 56 (1962).

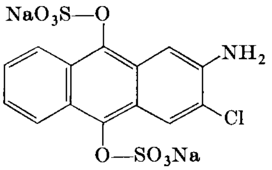
[532] CCC, *BP* 731,122; *USP* 2,712,017; W. B. Hardy, H. E. Westlake, Jr., and CCC, *USP* 2,716,653.

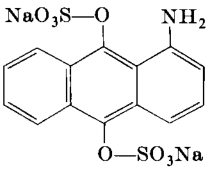
[533] W. B. Hardy, R. B. Fortenbaugh, and CCC, *USP* 2,659,727; *BP* 715,738.

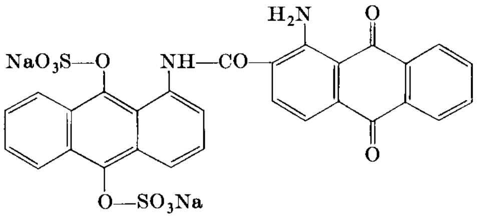
[533a] See also *CSD II*, p. 1051.

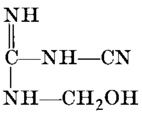
[534] H. R. Schweizer, "Künstliche Organische Farbstoffe," p. 390. Springer, Berlin, 1964.

[535] V. Ya. Fain, L. M. Golomb, and V. L. Plakidin, *J. Appl. Chem. USSR* (*English Transl.*) **34**, 1565 (1961).


(CXXVI)


(CXXVII)


(CXXVIII)


$$HN{=}C(NH{-}CN)(NH{-}CH_2OH)$$
(CXXIX)

cotton first as a reactive dye, and then developed in an acid oxidizing bath; very fast yellow shades are thus obtained.[536] Yellow dyes, applied by the normal dyeing process, are obtained by condensing (CXXVII) and its derivatives (2 moles), or 1 mole of (CXXVII) and 1 mole of a suitable amine, with cyanuric chloride.[537] Red dyes such as (CXXVIII) have good fastness to light and can be prepared by condensing 1-amino-anthraquinone-2-carbonyl chloride with (CXXVII) carrying halogen or benzamido groups in suitable positions.[538]

Acid sulfates of leuco vat dyes (e.g., from isoviolanthrone containing $SO_2NHCH_2CH_2{-}O{-}SO_3Na$ or $SO_2CH_2CH_2{-}O{-}SO_3Na$ groups) can be "fixed on cellulose in alkaline media." The dyes then become very fast to migration and solvents and are especially useful for coloring artificial leather.[539]

Reduction with zinc dust and acetic acid in *N*-methylacetamide and sulfation in the same base can be used for vat dyes, such as the diphthaloylcarbazole CI Vat Yellow 28 (CI 69000), the leuco derivatives of which are difficult to esterify.[540] Sulfuric esters of leuco vat dyes, which are difficult to prepare by the usual methods, can also be obtained in good yield by reducing the dye with sodium borohydride and dithionite in

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[536] CIBA, *BP* 999,792.

[537] DH, *BP* 961,351; 961,884–5; 962,017; 968,468; see also *BP* 930,294.

[538] DH, *BP* 952,803.

[539] CIBA, *BP* 1,012,316.

[540] FH, *BP* 916,367; see also W. Eckert, F. Meininger, G. Pfeiffer, and FH, *USP* 2,958,696; *BP* 853,264.

N-methylacetamide and then treating with sulfur trioxide in *N*-methylacetamide.[541]

Sulfuric esters of leuco vat dyes are stabilized by the addition of dicyandiamide and its derivatives, such as the methylol (CXXIX).[542] It is claimed in the patent that this effective method of stabilization is free from the disadvantages of earlier attempts, which consisted in the addition of excess alkali and/or urea, and which led to weak and spotty dyeings and prints or to products caking during storage.

The solubilized vat dye corresponding to CI Vat Red 35 (CI 68000) can be prepared by the simultaneous reduction–sulfation and cyclization of 1-(2′-naphthylamino)anthraquinone-2-carboxylic acid.[543]

A polyester-cotton fabric padded with a solution of CI Solubilized Vat Green 1 (CI 59826) and a salt which splits off acid when heated, dried at 100°, and baked for 1 minute at 200°, is dyed a level and solid green.[544] An interesting variation of the usual sulfuric ester of the leuco compound as a method of applying vat dyes after solubilization is to treat cotton yarn in a package-dyeing machine with the sodium salt of the di- or trisulfonic acid of the product of the condensation of 3,9-dibromobenzanthrone with 2 moles of 1-aminoanthraquinone at about 82°, followed by alkaline dithionite at the same temperature for 1 hour and final oxidation with perborate. Under these conditions cyclization to the acridine takes place on the fiber, and a level shade similar to a dyeing of CI Vat Black 25 (see Section VI,D,2) is obtained.[545]

It has been claimed that some vat dyes react chemically with polycaprolactam when they are melted together, forming covalent bonds.[546]

Chloroacetic acid reacts much more readily with sulfur trioxide than acetic acid, and sulfochloroacetic acid ($HO_3S—CHCl—COOH$) has been suggested as a useful reagent for solubilizing vat dyes.[547] The acid can be converted to the carbonyl chloride by phosgene or *p*-toluenesulfonyl chloride, and interaction with a leuco vat dye (prepared, for instance, by heating the dye with iron powder in pyridine until reduction is complete) then gives the sulfochloroacetate, finally isolated as the sodium salt. The special properties of the sulfochloroacetates of the leuco dyes as solubilized vat dyes in comparison with the well-established sulfuric esters have not been specified.

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[541] O. Fuchs, F. Meininger, G. Pfeiffer, and FH, *BP* 953,172.

[542] E. Kaplan, W. P. Munro, and CCC, *USP* 2,827,358.

[543] W. B. Hardy, E. M. Hardy, and CCC, *BP* 710,301–2; *USP* 2,649,452–3.

[544] FH, *BP* 1,101,836.

[545] J. Deinet and DuP, *USP* 3,238,231; 3,254,935.

[546] L. N. Mizerovskiĭ, *Khim. Volok.* No. 2, p. 24 (1968).

[547] W. Eckert, R. Kühne, and FH, *BP* 769,688; *USP* 2,765,309.

Pyridinium and quaternary ammonium salts of the chloroacetates of leuco vat dyes are claimed to have greater affinity for vegetable fibers than the sulfuric esters[548]; but this is of doubtful advantage, since the low affinity of the sulfuric esters, in comparison with the leuco dyes in alkaline solution, is a useful property for dyeing pastel shades and for padding processes.

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[548] F. Meininger, W. Eckert, R. Orthner, and FH, *DBP* 967,136.

CHAPTER IV

PHTHALOCYANINES

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I. Introduction

The last fifteen years or so have seen steady rather than spectacular progress in the phthalocyanine field in terms of technological advances, although much has been done, in spite of the inherent problems of solubility and purification, towards a better understanding of the chemistry of phthalocyanine derivatives. The most important of the many recent reviews are the monograph of Moser and Thomas,[1] containing an extensive bibliography (to 1961) of phthalocyanine compounds, and a complementary survey by Lever[2] covering the fundamental chemistry of phthalocyanines. The developments and advances in phthalocyanine technology have also been usefully summarized.[3]

Production of phthalocyanine pigments (α- and β-copper phthalocyanine blues and polyhalogenated greens) in the United States in 1966 amounted to approximately 12 million pounds out of a total pigment production of 51 million pounds. The corresponding quantities for phthalocyanine dyestuffs production were approximately 2 million pounds out of a total of 220 million pounds.[4] These figures very roughly represent something of the order of one-fifth of the total world production, although the ratio of pigment to dyestuff manufacture is not necessarily constant.

The above statistics serve to show the still dominating influence of the pigment consumer on phthalocyanine manufacture. Phthalocyanine pigments will be fully considered in the chapter on pigments although, because of their importance, certain aspects of the manufacture and technology of copper phthalocyanine and some of its derivatives will be dealt with in this chapter, even though the work may be oriented towards pigment requirements. A considerable proportion of the non-pigment usage is now accounted for by the phthalocyanine fiber-reactive dyes, which will be described in the chapter on reactive dyes. The other remaining technically important outlets for phthalocyanines (e.g., direct, ingrain, and solvent-soluble dyes) will be dealt with in this chapter as part of a complete survey of recent advances in the chemistry and properties of metal-free, copper, and other metal phthalocyanines.

II. Copper Phthalocyanine

A. MANUFACTURE

Although the two original methods of manufacture, viz., (1) the phthalic anhydride–urea (Wyler–Riley[5]) process and (2) the phthalonitrile process (as described, for example, by IG[6,7]), are still the only

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[1] F. H. Moser and A. L. Thomas, "Phthalocyanine Compounds." Reinhold, New York, 1963.

[2] A. B. P. Lever, *Advan. Inorg. Chem. Radiochem.* **7**, 27 (1965).

[3] R. E. Brouillard. *Am. Ink Maker* **35**, 36 (1957); G. Booth, *Chimia* (*Aarau*) **19**, 201 (1965).

[4] Production and Sales, U.S. Tariff Commission, 1966.

[5] M. Wyler and ICI, *BP* 464,126; A. Riley and ICI, *BP* 476,243.

[6] BIOS 960.

[7] FIAT 1313, Vol. III.

technically important alternatives, a tremendous amount of effort has been expended throughout the world on modification and refinement of these two processes. Details of precise conditions used are not disclosed by manufacturers and the patent literature is the only guide to current trends, which are summarized below.

1. *Phthalic Anhydride–Urea Process*

Standard conditions for this process involve heating a mixture of phthalic anhydride (4 moles), urea (~16 moles), cuprous chloride (1 mole), and a catalytic amount of ammonium molybdate in a high-boiling solvent such as kerosene, nitrobenzene, or trichlorobenzene. The solvent is recovered by distillation either directly from the reaction or after the product has been filtered off and the crude copper phthalocyanine is further treated as demanded by the requirements of the consumer. If acid-pasting is proposed, then the tetrasulfate may be formed by the addition of the required quantity of sulfuric acid to the reaction mass,[8] or the copper phthalocyanine may be separated from the reaction mass after dissolution in excess sulfuric acid.[9]

Although the introduction of the solvent into the process is normally considered desirable to give a workable reaction mass, recent claims have been made for advantageously dispensing with it, either by operating in a suitable heated mill[10] or using a continuous melt process. The latter can be achieved by passing a thin layer of the premixed reactants along a screw rotating within a cylinder heated at reaction temperature (200–220°)[11] or alternatively using preformed granular copper phthalocyanine as a heel, rotating in a cylinder at 180° and feeding the reactants.[12] A modified bake process can also be operated by heating on stainless steel trays in the presence of a comparatively small amount of solvent (e.g., 10–60% nitrobenzene on total charge).[13]

Claims have been made for the beneficial effects of a wide variety of additives to the urea/solvent process. The inclusion of ammonium chloride (0.4 to 1.5 moles/mole of phthalic anhydride) gives a small improvement in the yield (90% vs. 85%) of copper phthalocyanine, although a much greater increase is observed with other metal phthalocyanines[14] (see Section IV,B). The addition of an equimolar amount of

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[8] G. Barnhart and DuP, *USP* 2,602,800.

[9] CCC, *BP* 1,107,527.

[10] A. P. Hopmeier, E. N. Blackstead, and Sun. Chem. Corp., *USP* 3,280,142

[11] E. F. Klenke and DuP, *USP* 2,964,532.

[12] D. E. Mack and Hercules Powder Co., *USP* 3,188,318.

[13] CIBA, *BP* 909,375.

[14] M. H. Fleysher and Allied Chem. Corp., *USP* 3,074,958.

SO_3 to the reaction (particularly in the form of Sulfan) is also said to give an improved yield,[15] as is operation of the process in the presence of 8 to 15% (based on the weight of the high-boiling solvent used) of a lower-boiling solvent, such as monochlorobenzene or mixed xylenes.[16]

Cuprous chloride and ammonium molybdate remain the best sources of copper and catalyst, respectively, in spite of considerable investigation of alternatives.[17, 18]

2. *Phthalonitrile Process*

IG[6, 7] operated two different processes based on phthalonitrile—a pyridine solvent process and a bake process—the latter having the advantage of operation on a continuous basis. Very little significant advance has been made over these processes, which are still attractive alternatives to the phthalic anhydride–urea process, given a favorable price for phthalonitrile.

In the solvent process, the organic base may be replaced by an inorganic base such as sodium hydroxide or calcium oxide,[19] but Sherwin-Williams[20] has shown how sensitive the reaction is to solvent, temperature, and source of copper and claims an improved process using an ammonia/cupric acetate complex for reaction with phthalonitrile in nitrobenzene in the presence of anhydrous ammonia. One advantage claimed for his last process is the elimination of the chlorinated copper phthalocyanine formed when copper halides are used, although this can apparently also be achieved by operating a copper chloride–nitrobenzene reaction under mild conditions in the presence of a catalyst. Preferred catalysts are compounds of molybdenum, titanium, or iron, which reduce the reaction time and temperature from 10–12 hours at 220° to 10–20 minutes at 170°.[21]

The latest nonsolvent process to be disclosed involves reaction of vaporized phthalonitrile at elevated temperatures (~300°) with finely divided copper chloride formed as a suspension in nitrogen as an inert carrier. This is claimed to produce pigmentary copper phthalocyanine

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[15] H. Gerson, W. E. Bachman, and Allied Chem. Corp., *USP* 3,300,512; *BP* 1,116,409.

[16] M. Dudnikov and CCC, *USP* 2,657,213.

[17] V. F. Borodkin and K. V. Usacheva, *Izv. Vysshikh Uchebn. Zavedenii, Khim. i Khim. Tekhnol.* **3**, 142 (1958); *CA* **53**, 4295 (1959).

[18] F. H. Moser and Standard Ultramarine, *USP* 2,469,663.

[19] R. Stocker, A. Bucher, and CIBA, *USP* 2,276,598; *BP* 538,957.

[20] Sherwin-Williams Co., *BP* 640,576.

[21] G. Schulz, R. Polster, F. J. Frank, G. Wellenreuther, and BASF, *FP* 1,484,927; 1,515,285.

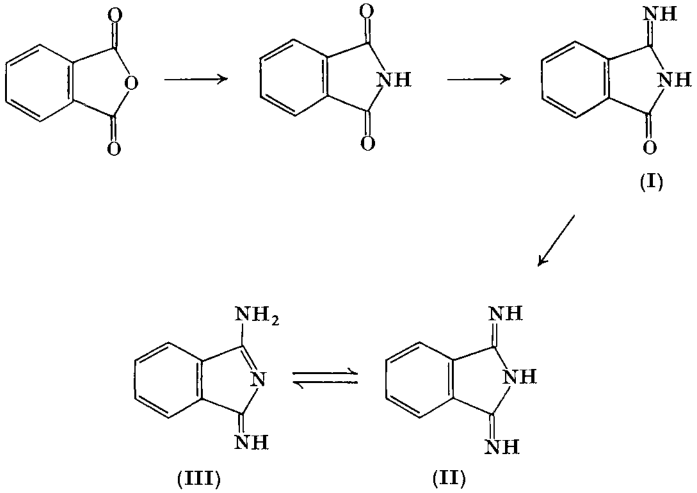
(β) directly, without the necessity for further particle-size reduction, an essential further stage in all previous processes.[22]

Most of the above processes, particularly when operated at elevated temperatures, tend to produce a proportion of nuclear chlorinated product when copper chlorides are used as metal sources. Kujoshi[22a] has studied the kinetics of the phthalonitrile process and attempted to devise a method for producing chlorine-free product efficiently.

B. MECHANISM OF FORMATION

The formation of the phthalocyanine macrocycle in the phthalic anhydride–urea process involves the probable initial reaction sequence given in Chart 1. The urea supplies only three atoms of nitrogen per molecule of phthalic anhydride, even though the process is usually operated using about four molecules of urea per molecule of phthalic anhydride. The urea may react in the form of a decomposition product and the function of the excess urea may be to provide further decomposition product(s), for example, ammonia (a known major by-product), to assist and stabilize the reaction. By ^{14}C-labeling experiments, it has been proved that the urea does not supply its carbon to the macrocycle[23] and that copper phthalocyanine and by-product phthalimide prepared

CHART 1



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[22] H. F. Bartolo, J. H. Braun, C. H. Winter, and DuP, *USP* 3,230,231.

[22a] H. Kujoshi, *J. Japan. Soc. Col. Mater.* **39**, 129 (1966).

[23] S. N. Brumfield, V. W. Foltz, C. M. McGhee, and A. L. Thomas, *J. Org. Chem.* **27**, 2266 (1962).

from phthalic anhydride with ^{14}C in the C-7 position are both radioactive, whereas the evolved CO_2 is not.[24]

Although 1-keto-3-iminoisoindoline (I) was isolated in the initial work on the phthalic anhydride–urea process, it was not until many years later (1949) that 1-amino-3-iminoisoindolenine [(III), tautomeric with diiminoisoindoline (II)] was isolated. This led to the production of the Phthalogen dyestuffs, the use of which demonstrates how readily the diiminoisoindoline units form a tetrameric macrocycle (see the chapter on Phthalogens).

The mechanism involved in the phthalonitrile process is less certain. Preparation of phthalocyanines from phthalic acid diamide or *o*-cyanobenzamide presumably involves dehydration as a first step. Although phthalonitrile can potentially form intermediate metal complexes (*N*- or π-bonded) more readily than phthalic anhydride, these would be considerably different from those derived from (III) and the fact that certain nontransition metals appear to form phthalocyanines readily from phthalonitrile is difficult to understand. The form of the copper in terms of oxidation state and ligands associated is certainly important on an empirical basis and leads one to suppose that a ligand-exchange reaction is initially involved. The mechanism of the formation of metal-free phthalocyanine from phthalonitrile (Section III) may also be relevant.

C. Polymorphic Forms

Two forms of copper phthalocyanine are well established and commercially important: the metastable polymorph (redder, α-form) obtained by reprecipitation of the crude pigment from concentrated sulfuric acid (acid-pasting) or by "salt-milling" with an inorganic salt which is subsequently washed out, and the stable polymorph (greener, β-form), which is formed initially in most processes and may be obtained directly from the reaction, provided that no finishing operation is required (see the chapter on pigments).

At least four other forms have been authenticated. A γ-form is obtained by slurrying copper phthalocyanine, prepared in solvent medium, with 60% aqueous sulfuric acid.[25] A so-called R-form, claimed to be redder and stronger than the α-form, is prepared by fusion of a mixture containing phthalonitrile, urea, and cupric chloride with intense agitation under conditions of high shear.[26] Two other forms are both, un-

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[24] S. N. Brumfield, B. C. Mays, and A. L. Thomas, *J. Org. Chem.* **29**, 2484 (1964).

[25] J. W. Eastes and CCC, *USP* 2,770,629.

[26] F. L. Pfeiffer and CCC, *USP* 3,051,721.

fortunately, designated δ, and a suggested differentiation is that the δB-form is obtained by treating the α-form with benzene in aqueous sulfuric acid[27] and the δK-form by milling crude copper phthalocyanine in the presence of sodium chloride, sulfuric acid, and urea.[28] The patents claiming the newer polymorphs give details of the X-ray diffraction spectra which distinguish them from the earlier α- and β-forms.[29]

III. Metal-Free Phthalocyanine

A. MANUFACTURE

The early manufacturing process based on the ready demetallization of disodium phthalocyanine is still operated. The latter is prepared by heating phthalonitrile with the sodium derivative of a high-boiling (e.g., amyl) alcohol in an excess of the alcohol and demetallization effected by treatment of the isolated disodium phthalocyanine with methanol.[6,30] The overall yield is about 70%.

Although metal-free phthalocyanine is probably less important commercially (and manufacture in the United States has apparently ceased[1]) following the advent of improved pigmentary forms of β-copper phthalocyanine, modified processes continue to be patented. Improved yields are claimed when the alcohol (e.g., benzyl alcohol) is diluted with an inert solvent (e.g., decalin or trichlorobenzene).[31] As alternatives to sodium alcoholates for reaction with phthalonitrile there may be used (yields in parentheses) calcium oxide (40–50%),[7,32] sodium hydride and an alcohol (80%),[33] sodium tetrakis(amyloxy)borate (81%),[34] or sodium sulfide in an alkoxyethanol (84%).[35]

Apart from the above variations in the so-called indirect method (i.e., involving demetallization), some advances have been made with the direct method. The latter description covers preparation by heating phthalonitrile with a basic compound such as ammonia or a tertiary amine,[30] a process which usually results in a comparatively low yield of impure product. Specific bases giving improved yields (80%) are piperidine and cyclohexylamine, and the results have been correlated to

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[27] B. P. Brand and ICI, *BP* 912,526; *USP* 3,150,150.

[28] Kemisk Vaerk Koge, *BP* 981,364; *USP* 3,160,635.

[29] R. H. Wiswall and CCC. *USP* 2,486,351.

[30] I. M. Heilbron, F. Irving, R. P. Linstead, J. F. Thorpe, and ICI, *BP* 410,814.

[31] CIBA, *BP* 708,039.

[32] R. A. Brooks and DuP, *USP* 2,681,348.

[33] CIBA, *BP* 712,455.

[34] G. Hess and M. Maurer, *Ann. Chem.* **658**, 21 (1962).

[35] E. Stocker, A. Pugin, and Gy, *USP* 3,060,189; *BP* 952,775.

dissociation constants.[36] An attractive process recently described simply involves heating phthalonitrile with hydrogen under pressure (200°/150 atm), preferably in a solvent such as dioxane.[37]

Preparation of metal-free phthalocyanine from phthalic anhydride rather than phthalonitrile is not as readily effected but has been achieved by using either a stoichiometric amount of antimony[38] or catalytic quantities of titanium tetrachloride and monoethanolamine.[39]

B. PROPERTIES

Phthalocyanine is less chemically stable than its copper complex; for example, a solution in concentrated sulfuric acid is 50% decomposed in 20 hours at room temperature. It has been suggested that this decomposition proceeds through a protonated species ($H_2PcH_4^{4+}$) which is readily hydrolyzed through loss of conjugation in the macrocycle. It may be relevant that copper phthalocyanine forms an isolatable disulfate, whereas metal-free phthalocyanine forms a monosulfate under the same conditions.[40, 41] The stability in sulfuric acid, for acid-pasting purposes, is improved by operating under nitrogen[42] and, although this is claimed to be due to the absence of oxygen, the elimination of atmospheric moisture may also be a contributory factor.

Metal-free phthalocyanine can be used to form metal derivatives on a preparative basis (see Section IV) and formation of an alkali metal or related quaternary ammonium salt has been exploited as a means of temporary solubilization of the pigment (in, e.g., ethylene glycol monoethyl ether or pyridine) in order to reprecipitate, by decomposition, on cellulosic fibers as a dyeing process.[43]

A similar dyeing process has been described which uses the solvent-soluble reaction product (said to be an oxide; see Section VI) obtained on treatment of metal-free phthalocyanine with 30–50% nitric acid.[44]

Like copper phthalocyanine, metal-free phthalocyanine exists in several polymorphic forms. When prepared by the usual indirect method described earlier it is obtained mainly in the α-form, with small amounts of the so-called β- and γ-forms. Although these three forms are distinguishable by their X-ray diffraction patterns, there is some doubt

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[36] W. L. Rintelman and DuP, *USP* 2,485,167; 2,485,168.

[37] H. Mueller and BASF, *BP* 998,255; *USP* 3,297,712; *DAS* 1,234,342.

[38] F. F. Ehrich and DuP, *USP* 2,820,796.

[39] H. Yagi, T. Hori, and NSK, *JP* 6127/55; *CA* **51**, 16558 (1957).

[40] Y. Bansho, T. Sekiguchi, and M. Yamashita, *Kogyo Kagaku Zasshi* **65**, 2023 (1962); *CA* **58**, 12705 (1963).

[41] B. D. Berezin, *Zh. Fiz. Khim.* **35**, 2494 (1961); *CA* **58**, 9275 (1963).

[42] R. R. Merner and DuP, *USP* 2,917,518.

[43] C. J. Pederson and du Pont, *USP* 2,741,531; 2,741,534.

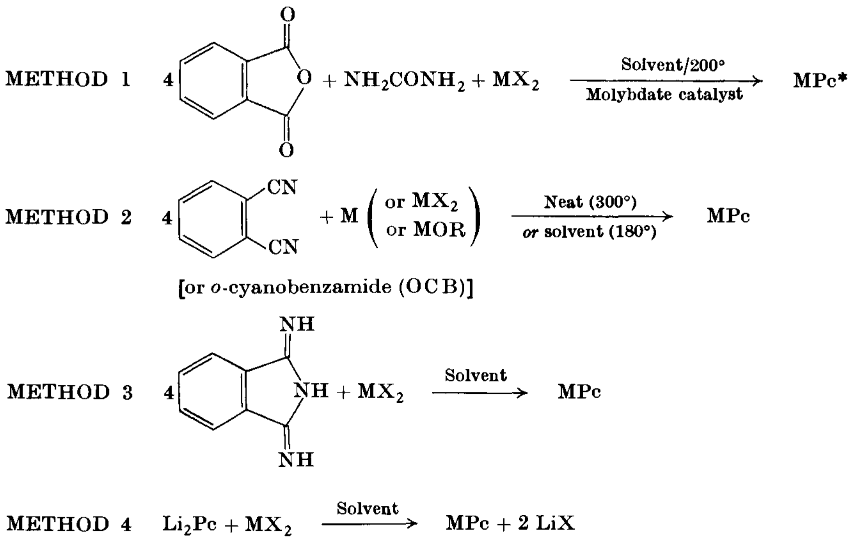
[44] Kogyogyuzutsuin, *JP* 11, 349/66; *Derwent Japan* **5**, No. 26 (1966).

whether the γ-form is merely a less crystalline form of the α-polymorph. In order to obtain the greener β-form the transformation to the α-form during working up operations can be prevented by grinding with specific water-soluble substrata in the presence of an organic solvent.[45, 46] An improved method consists of treatment of an alkali metal phthalocyanine with benzyl alcohol and ammonium sulfate at 180°.[47] A new polymorph designated X-form and having increased photosensitivity has recently been described; it is obtained by subjecting the other polymorphs to specific milling processes.[48]

IV. Phthalocyanines of Other Metals

The phthalic anhydride–urea process (Method 1) or the phthalonitrile process (Method 2) described earlier for copper phthalocyanine can often be used for the preparation of other phthalocyanine complexes. Two other important preparative methods are also used starting from either diiminoisoindoline (Method 3) or the phthalocyanine macrocycle containing replaceable central atoms (e.g., H, Li, or Ca) (Method 4). These four methods are summarized in Chart 2.

CHART 2



* Pc represents the phthalocyanine anion $C_{32}H_{16}N_8^{2-}$ or (in the case of substituted derivatives) anions containing appropriately less hydrogen.

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[45] CIBA, *BP* 687,387.

[46] BASF, *DBP* 950,799; *CA* **53**, 3721 (1959).

[47] CIBA, *BP* 708,040.

[48] J. F. Byrne, P. F. Kurz, and Xerox Corp., *USP* 3,357,989; *BP* 1,116,554.

Many literature references to the preparation and properties of phthalocyanine complexes have been previously collected[1,2] and only selected references are given in Tables I[49–58] and II, which represent up-to-date summaries designed to lead the reader directly to details of preparation of the known products.

TABLE I

PREPARATION AND PROPERTIES OF PHTHALOCYANINES OF THE NONTRANSITION ELEMENTS

Group	*Complex*	*Method*	*Properties*	*References*
IA	$\mathrm{Li_2Pc}$	2 (LiOAm)	Sol. in acetone and alcohols hydrolyzed with $\mathrm{H_2O}$	49
	$\mathrm{Na_2Pc}$	2 (NaOAm)	Demetallized with MeOH or mineral acid	50
	$\mathrm{K_2Pc}$	2 (KOAm)		50
IIA	BePc	2 (etched Be)	Hygroscopic	50
	MgPc	2 (Mg)	(Hydrate)	50
	CaPc	2 (CaO)	—	7, 50
	BaPc	2 (BaO)	—	50
IIB	ZnPc	2 (Zn)	—	50
		1 ($\mathrm{Zn/TiCl_4}$)	—	51
	CdPc	2 (Cd)	—	50
	HgPc	4 ($\mathrm{HgCl_2 + Li_2Pc}$)	—	49
IIIB	AlClPc	2 ($\mathrm{AlCl_3}$)	Hydrolyses to Al(OH)Pc	50, 52
	GaClPc	2 ($\mathrm{GaCl_3}$)	(From *o*-cyanobenzamide)	53
	InClPc	2 ($\mathrm{InCl_3}$)	(From *o*-cyanobenzamide)	53
IVB	$\mathrm{SiCl_2Pc}$	2 ($\mathrm{SiCl_4}$)	Hydrolyses to $\mathrm{Si(OH)_2Pc}$	54
		3 ($\mathrm{SiCl_4}$)	—	55
	$\mathrm{GeCl_2Pc}$	2 ($\mathrm{GeCl_4}$)	—	56
	SnPc	2 (Sn)	—	50, 57
	$\mathrm{SnCl_2Pc}$	2 ($\mathrm{SnCl_2}$)	—	50, 57
	PbPc	2 (PbO)	—	50, 57
VB	AsClPc	4 ($\mathrm{AsCl_3/DMF}$)	—	58
	$\mathrm{Sb_2Pc}$	2 (Sb)	Structure uncertain	49
	SbClPc	4 ($\mathrm{SbCl_3 + H_2Pc}$)	—	49

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[49] P. A. Barrett, D. A. Frye, and R. P. Linstead, *J. Chem. Soc.* p. 1157 (1938).

[50] P. A. Barrett, C. E. Dent, and R. P. Linstead, *J. Chem. Soc.* p. 1719 (1936).

[51] M. Shinabe *et al.* and NSK, *JP* 842/54; *CA* **49**, 11019 (1955).

[52] J. E. Owen and M. E. Kenney, *Inorg. Chem.* **1**, 331 (1962).

[53] D. Colaitis, *Bull. Soc. Chim. France* p. 23 (1962).

[54] R. D. Joyner and M. E. Kenney, *Inorg. Chem.* **1**, 236 (1962); *USP* 3,094, 536.

[55] M. K. Lowery, A. J. Starshak, J. N. Esposito, P. C. Krueger, and M. E. Kenney, *Inorg. Chem.* **4**, 128 (1965).

[56] R. D. Joyner and M. E. Kenney, *J. Am. Chem. Soc.* **82**, 5790 (1960); *USP* 3,094,535.

[57] W. J. Kroenke and M. E. Kenney, *Inorg. Chem.* **3**, 251 (1964).

[58] H. A. Rutter and J. D. McQueen, *J. Inorg. & Nucl. Chem.* **12**, 361 (1960).

A. THE NONTRANSITION ELEMENTS

It can be seen from Table I that the original methods of the Linstead school still predominate and even the latter additions (i.e., Ga, In, Si, Ge, and As phthalocyanines) are prepared by essentially similar techniques. Preparation from phthalonitrile (Method 2) is widely applicable, although it seems that, for no obvious reason, preparation from *o*-cyanobenzamide gives higher yields in some cases (e.g., $[SiCl_2Pc]$[55]).

The most interesting derivatives of the above series are obtained by reaction of the halogeno, or derived hydroxy, derivatives of the Group IIIB and Group IVB elements. Aryloxy and alkyloxy derivatives having

$$MCl_{1\text{ or }2}Pc \rightarrow M(OH)_{1\text{ or }2}Pc \xrightarrow{ROH} M(OR)_{1\text{ or }2}Pc \qquad (1)$$

considerably modified physical properties are readily obtained. An outstanding example is the benzene-soluble $Si(OC_{18}H_{37})_2Pc$, which has a melting point of 152° without decomposition.[59] An important development arising out of the work on silicon derivatives is the preparation of highly stable siloxane polymers containing an almost straight backbone linked through the central silicon atoms.[59a]

B. THE TRANSITION ELEMENTS

Table II summarizes[14, 49, 50, 58, 60–79], with key references to details, the most recent information on the preparation of transition metal phthalocyanines. Due to many additions over the last few years the only notable gap in the table is now in respect to a complex of tungsten, due presumably to the polymeric and consequently unreactive nature of tungsten halides. It must, however, be added that considerable difficulty is anticipated in the purification and further characterization of phthalocyanines of the rare earth elements and the heavy metals.[76, 80]

As with aluminum, silicon, and tin (Table I), substitution about the central atom has been demonstrated with chromium,[66] manganese,[81] and iron.[2] But here, unlike the examples in the non-transition series, the compounds thus available are due principally to changes in coordination number and oxidation state of the central atom. In view of this it is perhaps surprising that more examples have not been encountered; one would expect CoPc, RuPc, and complexes of the other Group VIIIA and Group VIIIB metals to form series of five- or six-coordinate derivatives. In this connection it should be noted that great care is clearly required in

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[59] P. C. Krueger and M. E. Kenney, *J. Org. Chem.* **28**, 3379 (1963).

[59a] *Chem. Eng. News* **40**, 41 (1962).

TABLE II

Preparation and Properties of Phthalocyanines of the Transition Elements

Group	*Complex*	*Method*	*Properties*	*References*
IVA	TiClPc	4 ($TiCl_3$)	Oxidized to TiOPc	60
	$TiCl_2Pc$	2 ($TiCl_3$)	Hydrolyzed to TiOPc	61
	TiOPc	From chloro	Probably polymeric	60, 61
	$Zr(OH)_2Pc$	2 ($ZrCl_4$)	May alternatively be formualted $(MOPc)_n$.hydrate	62
	$Hf(OH)_2Pc$	2 ($HfCl_4$)		62
VA	VOPc	2 (V_2O_5)		50, 63
	$NbCl_x(OH)_yPc$	2 ($NbCl_3 + NbCl_5$)	Mixed product, partially hydrolyzed	64
	$TaCl_x(OH)_yPc$	2 ($TaCl_5$)	Mixed product, partially hydrolyzed	64
VIA	CrPc	2 [$Cr(CO)_6$]	Oxidized to Cr(OH)Pc	65
	Cr(OH)Pc	2 [$Cr(OCOCH_3)_3$]		66
	MoOPc	2 (MoO_2Cl_2/DMF)	(Low yield of characterizable product)	67
VIIA	MnPc	2 (Mn)	Demetallized with H_2SO_4, readily oxidized and absorbs O_2	50, 58
	MnOPc	From MnPc	Polymeric	68
	$(ReClPc)_2.2PhNH_2$	2(K[$ReOCl_4$] + OCB)	Complex oxide product broken down with aniline	68a
VIII	FePc	2 (Fe + OCB)	Further coordinates with bases are CN^-	50
		2 [$Fe(CO)_5$]	—	65
	FeClPc	From FePc	—	49
	RuPc	2 ($RuCl_3$ + OCB)	—	69
	$Os(SO_4)Pc$	2 (OsO_4)	Product from H_2SO_4; probably polymeric Os(IV)	70
	CoPc	4 (Co)	—	50
		1 ($CoCl_2$)	—	14
	$Rh(HSO_4)Pc$	2 ($RhCl_3$)	Product ppt. from H_2SO_4	71
	$Ir(HSO_4)Pc$	2 ($IrCl_3$)	Some chlorination of Pc ring	72
	NiPc	1 ($NiCl_2$)	—	73
	PdPc	4 ($PdCl_2$)	—	49
	PtPc	2 ($PtCl_2$)	—	50

TABLE II (*continued*)

Group	*Complex*	*Method*	*Properties*	*References*
IB	CuPc	1 and 2	(see Section II,A)	
	AgPc	4 ($AgNO_3$)	Ag(I) or Ag(II)?	49
	AuPc	3 (AuBr)	Thought to be Au(II)	74
Lanthanides	MPc	2 (MCl_3 + OCB)	M = Eu, Gd, Yb; solvent-soluble	75
		2 [$M(OCOCH_3)_3$]	M = Pr, Nd, Er, Lu; uncharacterized mixtures	76
Actinides	$ThCl_2Pc$	2 ($ThCl_4$)	Product not characterized	77
	UO_2Pc	4 [$UO_2(NO_3)_2$/DMF]	—	78
		2 (UO_2Cl_2/DMF)	—	79

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[60] R. Taube, *Z. Chem.* **3**, 194 (1963).

[61] B. P. Block and E. G. Meloni, *Inorg. Chem.* **4**, 111 (1965).

[62] V. E. Plyushchev, L. P. Shkloner, and I. A. Rozdin, *Zh. Neorgan. Khim.* **9**, 125 (1964); *CA* **60**, 8879 (1964); see also P. Mühl, *Z. Chem.* **1**, 352 (1967).

[63] J. M. Assour, J. Goldmacher, and S. E. Harrison, *J. Chem. Phys.* **43**, 159 (1965).

[64] J. C. Burbach and Union Carbide, *USP* 3,137,703; see also Y. A. Buslaev, A. A. Kuznetsova, and L. F. Goryachova, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **3**, 170 (1967).

[65] E. G. Meloni, L. R. Ocone, and B. P. Block, *Inorg. Chem.* **6**, 424 (1967).

[66] J. A. Elvidge and A. B. P. Lever, *J. Chem. Soc.* p. 1257 (1961).

[67] H. A. O. Hill and M. M. Norgett, *J. Chem. Soc., A* p. 1476 (1966).

[68] J. A. Elvidge and A. B. P. Lever, *Proc. Chem. Soc.* p. 195 (1959).

[68a] H. Przywarska-Boniecka, *Roczniki Chem.* **40**, 1627 (1966); *CA* **66**, 72008 (1967).

[69] P. C. Krueger and M. E. Kenney, *J. Inorg. & Nucl. Chem.* **25**, 303 (1963).

[70] B. D. Berezin and N. I. Sosnikova, *Dokl. Akad. Nauk SSSR* **146**, 604 (1962); *CA* **58**, 13410 (1963).

[71] B. D. Berezin, *Dokl. Akad. Nauk SSSR* **150**, 1039 (1963); *CA* **59**, 7148 (1963).

[72] B. D. Berezin and G. V. Sennikova, *Dokl. Akad. Nauk SSSR* **159**, 117 (1964); *CA* **62**, 3637 (1965).

[73] N. A. Ebert and H. O. Gottlieb, *J. Am. Chem. Soc.* **74**, 2806 (1952).

[74] A. MacCragh and W. S. Koski, *J. Am. Chem. Soc.* **87**, 2497 (1965).

[75] M. G. Gurevich and K. N. Solovev, *Dokl. Akad. Nauk Belorussk. SSR* **5**, 291 (1961); *CA* **57**, 15948 (1962).

[76] I. S. Kirin, P. N. Moskalev, and Y. A. Makashev. *Zh. Neorg. Khim.* **10**, 1951 (1965); *CA* **63**, 13449 (1965).

[77] L. Wolf and H. J. Jahn. *J. Prakt. Chem.* [4] **1**, 257 (1955).

[78] N. A. Frigerio and U.S. Atomic Energy Commission, *USP* 3,027,319.

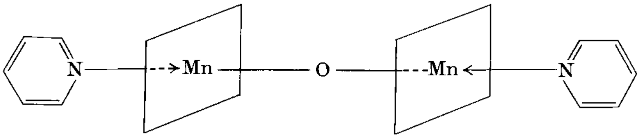
[79] J. E. Bloor, J. Schlabitz, C. C. Walden, and A. Demerdache, *Can. J. Chem.* **42**, 2201 (1964).

[80] S. Kirin, P. N. Moskalev, and V. Y. Mishin, *Zh. Obshch. Khim.* **37**, 280 (1967).

[81] G. Engelsma, A. Yamamoto, E. Markham, and M. Calvin, *J. Phys. Chem.* **66**, 2517 (1962).

the characterization of such complexes. Phthalocyanine derivatives of ruthenium, osmium, and iridium have recently been obtained as adducts with phthalonitrile. The phthalonitrile is surprisingly firmly bound if it is only present as a solvate, as suggested.[82]

Variation of the oxidation state by reversible absorption of oxygen, as with MnPc,[68] is of particular importance through its possible relevance to biological oxidative processes. The pyridine complex of the oxide of MnPc, originally thought to be Mn^{IV}OPyPc, has been shown by X-ray structural determination to have an oxygen-bridged formulation represented by (IV).[83] A recent review[84] on the mechanism of formation of this complex postulates a Mn(OH)pyPc intermediate requiring a final dehydration stage. Even though this clearly calls for further study, and a rapid multistage reaction may be taking place, there is no evidence to contradict an initial step involving the oxygen acting as a π-bonded ligand, thus maintaining the analogy with Griffith's proposed mechanism[84a] for the formation of oxygenated heme. The ability of FePc to form an unstable oxygen complex and of $FePc(4\text{-}SO_3H)_4$ to absorb oxygen[84b] may be related to the behavior of MnPc so that the mechanism involved when FePc is used as a catalyst (see Section VI) may derive from a study of the more stable MnPc complexes. One might speculate also on the possibility of CO and NO behaving as diatomic molecules related to oxygen in the formation of complexes with metal phthalocyanines (cf. behavior of iron porphyrin complexes). Very recent work[85] has, in fact, shown that the β-forms of iron(II), chromium(II), manganese(II), and cobalt(II) (but not nickel, copper, or vanadyl) phthalocyanines absorb one molecule of nitric oxide reversibly.



(IV)

Further discussion on the preparation of metal phthalocyanines will be limited to a brief consideration of the manufacture of iron, cobalt, and

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[82] I. M. Keen and B. W. Malerbi, *J. Inorg. & Nucl. Chem.* **27**, 1311 (1965).

[83] L. H. Vogt, A. Zalkin, and D. H. Templeton, *Inorg. Chem.* **6**, 1725 (1967)

[84] A. Yamamoto, L. K. Philips, and M. Calvin, *Inorg. Chem.* **7**, 847 (1968).

[84a] J. S. Griffiths, *Proc. Roy. Soc.* **A235**, 23 (1956).

[84b] D. Vonderschmitt, K. Bernauer, and S. Fallab, *Helv. Chim. Acta* **48**, 951 (1965).

[85] C. Ercolani and C. Neri, *J. Chem. Soc., A* p. 1715 (1967); *ibid.* p. 2123 (1968).

nickel phthalocyanines, the only complexes other than copper currently of potential technical importance. Advances since the original phthalic anhydride–urea process[5] consist mainly in the addition of agents to the reaction mixture to improve the yield. In this category there may be mentioned the use of ammonium chloride in the manufacture of CoPc[14] and the use of sodium ethane sulfonate, trisodium phosphate, or sodium sulfate in the manufacture of NiPc.[86] The only novel modification to the phthalonitrile process is the use of cobalt or nickel hydroxide with trichlorobenzene in the presence of quinoline, which is claimed to give high yields of especially pure products.[87]

In considering the role of the complex-forming additives in the synthesis of iron phthalocyanine from phthalimide it has been concluded that the reaction proceeds in a series of condensation/reduction steps and that excessive amounts of catalyst may inhibit the reaction.[88] No comments on mechanism other than those made on the mechanism of formation of CuPc can be added, but it is interesting to note that NiPc has recently been prepared from diiminoisoindoline via the stepwise formation of four identifiable metal complex intermediates.[89]

V. Nuclear-Substituted Metal Phthalocyanines

A. HALOGENO DERIVATIVES

A great deal of effort has been expended in recent years on improvements in the halogenation of copper phthalocyanine. This is all directed towards the derived green pigments. (See also Chapter VI on pigments.)

1. *Chlorination*

The standard manufacturing procedure for fully chlorinated CuPc is still based on the use of a molten eutectic mixture of aluminum chloride and sodium chloride (see *CSD II*, p. 1132). Modifications to this process include the use of aluminum chloride melts in conjunction with sulfur trioxide or chlorosulfonic acid,[90] sulfur dichloride,[91] pyrosulfuryl chloride (prepared by heating together chlorosulfonic acid and thionyl chloride),[92] and combinations of sulfur dioxide and chlorine[93] or sulfuryl chloride

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[86] R. E. Brouillard and Gy, *USP* 2,647,127; 2,647,128; 2,673,854.

[87] P. Urban and Universal Oil Products, *USP* 3,140,292; *BP* 1,062,602.

[88] A. P. Rudenko and H. P. Dobroselskaya, *Zh. Obshch. Khim.* **30**, 3077 (1960); **31**, 3667 (1961); **32**, 531 (1962).

[89] T. J. Hurley, M. A. Robinson, and S. I. Trotz, *Inorg. Chem.* **6**, 389 (1967).

[90] A. Caliezi, W. Kern, T. Holbro, and CIBA *USP* 2,862,929; *BP* 821,629.

[91] F. F. Ehrich and DuP, *USP* 2,833,784.

[92] J. D. Stewart, K. G. Hargreaves, and Gy, *BP* 926,978.

[93] D. I. Randall, J. Taras, and G, *USP* 2,873,279; *BP* 818,831.

and sulfur monochloride[94] as indirect chlorinating agents for CuPc. The $AlCl_3/SO_2$ melt is said to be desirably more fluid and its use has extended to the partial chlorination of CoPc for the preparation of vat dyes.[95]

Alternative inorganic solvents for the halogenation of phthalocyanines, such as chlorosulfonic acid or sulfuric acid, are usually considered less satisfactory in view of the undesirable side reactions (viz., oxidation and/or sulfonation) taking place under the vigorous conditions necessary. Chlorination of CuPc in chlorosulfonic acid with sulfur monochloride and iodine monochloride as catalysts is, however, claimed to be effected at relatively low temperature (<100°)[96] and the introduction into CuPc of up to two chlorine atoms (product for stabilized blue pigment) can be readily achieved at low temperature in oleum.[97] The use of $TiCl_4$ or $SiCl_4$ as solvents for halogenation has recently been claimed.[98]

Organic solvents, such as carbon tetrachloride, nitrobenzene, or chlorinated benzenes, are not usually regarded as satisfactory[99] because of the limited solubility of the substrate even under pressure. Novel solvents used include perchlorocyclopentene and perchloroindan,[100] organic sulfonic acids (e.g., mixed isomers of toluenesulfonic acid),[101] and a combination of trichlorobenzene with an abrasive material such as ground sodium chloride.[102] The use of molten phthalic anhydride has been resuscitated by chlorination in the presence of a molybdenum catalyst ($MoCl_5$ or MoO_3) and preforming, then subsequently recovering for reuse, dichlorophthalic anhydride.[103]

Chlorination of CuPc at 200° in a vertical bed fluidized with nitrogen has been described.[104] X-Ray diffraction patterns for CuPc derivatives with varying chlorine content (mainly 4, 8, and 16 atoms per molecule) have been studied, and the degree of polymorphism involved has been related to the inhibition of crystal growth when the chlorine content is higher than eight atoms per molecule.[105]

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[94] A. Hamilton, J. D. Stewart and Gy, *USP* 3,320,276; *BP* 925,379.

[95] D. I. Randall, J. Taras, and G, *USP* 3,009,919; *BP* 867,035.

[96] H. Holtzman, E. Simon, and Ansbacher-Siegle, *USP* 2,662,085.

[97] G. Geiger and S, *USP* 3,030,379; *BP* 878,753.

[98] S, *BP* 1,032,012.

[99] V. F. Borodkin and K. V. Usacheva, *J. Appl. Chem. USSR* (*English Transl.*) **29**, 1487 (1956).

[100] FBy, *BP* 736,436.

[101] H. Holtzman, E. Simon, and Ansbacher-Siegle, *USP* 2,793,214.

[102] G. R. Genta and Allied Chem. Corp., *USP* 2,995,552.

[103] R. M. Ferrill and Hercules Inc., *BP* 1,068,590; *DAS* 1,271,860.

[104] G. Barnhart, R. W. Grimble, and DuP, *USP* 2,586,598.

[105] M. Shigemitsu, *Bull. Chem. Soc. Japan* **32**, 607 (1959); *CA* **54**, 7728 (1960).

Methods of chlorination of metal-free and other metal phthalocyanines are often disclosed in those patents essentially directed at CuPc, but an improved process specifically for metal-free polychloro phthalocyanine (a product of limited technical importance) uses a combination of sulfur dioxide and chlorine, a reaction medium of trichlorobenzene, and antimony trisulfide as catalyst.[106]

2. *Bromination*

Although it has long been known that brominated products were desirably yellower in shade than the corresponding chlorinated products[107] (see Table III), it was not until 1959 that a mixed bromochloro copper phthalocyanine was introduced commercially.[108] The technical difficulties were mainly in achieving the optimum conditions for controlled simultaneous bromination and chlorination. Complete bromination (i.e., introduction of 15 to 16 Br atoms) is extremely difficult and the yellowest product readily obtained contains about 11 to 12 atoms of bromine and 3 to 4 atoms of chlorine per molecule.

TABLE III

REFLECTANCE SPECTRA (MAIN ABSORPTION MAXIMA) OF SOME PHTHALOCYANINES

Pc	β-CuPc	α-CuPc	H_2Pc	$CuPcCl_{15}$	H_2PcCl_{15}	$CuPcBr_6Cl_8$	$CuPcBr_8Cl_6$	$CuPcBr_{15}$
(mμ)	480	482	484	495	498	501	504	510

Recently patented processes are mainly based on the use of aluminum chloride melts. The main alternatives are the use of elemental bromine, in conjunction with chlorine or alternative chlorinating agents under highly specific conditions,[109–111] or the use of sodium bromide in the eutectic as a bromine generator.[94, 112–114] The latter is attractive because of the high efficiency of conversion, liberation of bromine, and bromination taking place preferentially to chlorination when chlorine is passed into a bromide-containing melt. A possible disadvantage, however, is

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[106] G, *BP* 809,498.

[107] A. L. Fox and DuP, *USP* 2,247,752.

[108] E. A. Wich, *Am. Ink Maker* **37**, 26 (1959); *Am. Dyestuff Reptr.* **48**, 42 (1959).

[109] R. Fazackerley, A. Kershaw, and ICI, *BP* 850,232; 932,943.

[110] V. A. Giambalvo, W. L. Berry, and CCC, *USP* 3,332,961.

[111] G. Geiger, A. Geiger, and S, *FP* 1,283,566.

[112] G, *BP* 933,242.

[113] R. Fazackerley, A. Kershaw, and ICI, *BP* 925,266.

[114] L. Waerth, G. Chabrier, and Fran, *FP* 1,263,272.

that the quantity of sodium bromide necessary to achieve relatively highly brominated products leads to undesirable thickening of the melt and consequent higher aluminum chloride usage. Chlorosulfonic acid has been used as a thinning agent in melts.[115] When bromine and chlorine are used together, bromine monochloride may be the effective agent. The use of bromine and thionyl chloride as the mixed halogenating agent has also been described, with pyrosulfuryl chloride as the reaction medium.[116]

The orientation of halogenation is said to be important, the bromine being preferentially introduced into the α-positions to attain maximum yellowness of shade. This is achieved by successive additions of bromine and chlorine to an aluminum chloride/sulfur trioxide melt.[110] The shades of the mixed bromochloro products obtained by this procedure are given in Table III, in terms of absorption maxima of reflectance spectra, and compared with other phthalocyanines.

3. *Synthesis from Chloro or Bromo Phthalic Derivatives*

The use of partially chlorinated copper phthalocyanine (containing about one chlorine per molecule) is technically the most important way of stabilizing the α-form pigment (see Chapter VI). Manufacture is conveniently carried out by the introduction of the appropriate quantity of 4-chlorophthalic anhydride into the phthalic anhydride–urea process or, alternatively, operating the phthalonitrile process in a solvent such as nitrobenzene with cupric chloride and a tertiary aromatic base in such a way that simultaneous partial chlorination is effected to the desired degree.[117, 118]

Tetra- and octahalogeno copper phthalocyanines can be made from the appropriate halogenated phthalic anhydrides but the products are of limited technical importance, even though the copper phthalocyanine derived from equimolar quantities of monochloro and dichloro (mixed isomers) phthalic anhydrides (i.e., $CuPcCl_6$) has been described as a color match for Peacock Blue (dominant wavelength 485 mμ; cf. Table III).[119] Products derived from 4-bromo-, 4,5-dibromo-, and tetrabromophthalic anhydrides containing from 1 to 16 bromine atoms have been compared for shade and other physical properties.[120]

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[115] CIBA, *BP* 910,137.

[116] FBy, *BP* 949,714.

[117] J. Jackson and DuP, *USP* 2,933,505.

[118] R. Polster, R. Schroedel, D. von Pigenot and BASF, *BP* 1,073,348.

[119] Interchemical Corp., *BP* 717,783.

[120] Y. Bansho, S. Suzuki, T. Sekiguchi, and I. Saito, *Kogyo Kagaku Zasshi* **65**, 2027 (1962); *CA* **58**, 12705 (1963).

Of much greater potential importance is the synthesis of fully halogenated copper phthalocyanines from tetrahalophthalic anhydrides. Although many of the process modifications described earlier for phthalocyanine manufacture are also claimed to be efficacious in the production of hexadecachloro copper phthalocyanine, and specific catalysts such as ammonium hexafluorotitanate[121] and other titanium and zirconium compounds[122] are claimed to give improvements, it is usually recognized that the use of tetrachlorophthalic anhydride results in low yields of impure products. The undesirable dullness introduced by demetallization and/or retention of catalyst residues cannot readily be removed and products obtained by halogenation are generally superior.[123] Synthesis from tetrahalophthalonitrile (cupric chloride/urea/nitrobenzene) has recently been claimed to give products of good quality in high yield.[124]

4. *Fluorophthalocyanines*

Direct fluorination of copper phthalocyanine or exchange reactions with polychloro copper phthalocyanine and HF are not readily effected (see CSD II, p. 1133). Novel products are obtained on treating compounds such as copper phthalocyanine tetra-4-carboxylic acid with a mixture of sulfur tetrafluoride and hydrogen fluoride. The carboxylic acid groups are converted into CF_3 groups and fluorine is introduced into the benzene rings; the surprising property of such products, e.g., $CuPcF_4(CF_3)_4$, is their solubility in organic solvents such as acetone.[125] The recent availability of tetrafluorophthalonitrile has led to its use in the synthesis of the derived copper hexadecafluorophthalocyanine[126] but no doubt the product (described as royal blue) suffers from the same defects mentioned in Section V,A,3.

B. SULFONIC ACIDS AND THEIR FUNCTIONAL DERIVATIVES

1. *Sulfonic Acids*

Simple sulfonic acids, $CuPc(SO_3H)_n$ where $n = 2$, 3, or 4, e.g., Direct Blues 86 and 87 (CI), are of decreasing importance due to the advent of improved direct dyes (see, e.g., Section V,B,3) and of reactive dyes (see

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[121] Interchemical Corp., *BP* 892,735.

[122] E. B. Newton, H. J. Kehe, and B. F. Goodrich Co., *USP* 2,824,107; 2,824,108.

[123] V. F. Borodkin, Y. G. Erykalov, and K. V. Usucheva, *Zh. Prikl. Khim.* **29**, 1606 (1956); *CA* **51**, 2760 (1957).

[124] Gy, *BP* 1,013,370; *FP* 1,389,808.

[125] V. Weinmayr and DuP, *USP* 3,006,921.

[126] D. E. M. Wotton and Imperial Smelting Corp., *BP* 1,037,657.

the chapter on reactive dyes). No significant advances have been made over the original methods of oleum sulfonation of copper phthalocyanine, which can be controlled to give a range of simple derivatives with the sulfonic acid mainly entering in the 3-(α-)position, or the use of 4-sulfophthalic acid, to synthesize the isomeric series. The disulfonic acid can be synthesized directly from phthalonitrile (4 moles) by baking at 200° with copper sulfate (1 mole) in the presence of sodium hydrogen sulfate (8 moles). This is a somewhat surprising result since neither phthalonitrile nor copper phthalocyanine is appreciably sulfonated on heating with an alkali hydrogen sulfate.[127]

New outlets for sulfonated copper phthalocyanines include use as additives for improvement of solar evaporation (10 ppm gives a 29% increase in rate),[128] use as anions to form glycol-soluble salts of Victoria Pure Blue BO or other basic dyes for ballpoint pen inks,[129] and use as textile dyes by application in conjunction with an aminoplast, e.g., urea–formaldehyde resins, followed by a curing process.[130]

Cobalt phthalocyanine is partially sulfonated (to contain 15 to 40% of the monosulfonic acid) in 10% oleum under mild conditions to give the vat dyestuff Indanthrene Brilliant Blue 4G (CI Vat Blue 29).[131] For discussion of the derived leuco compound see Section VI. The disulfonic acid of cobalt phthalocyanine, which is claimed to be best prepared by sulfonation in an inert atmosphere (conc. H_2SO_4, 8 hours at 120° or 26% oleum, 18 hours at 20 to 30°; under CO_2),[132] is used as an oxidation catalyst in the sweetening of gasoline.[133] Cobalt phthalocyanine tetra-4-sulfonic acid has been prepared by Fukada from the ammonium salt of 4-sulfophthalic acid by the urea process[134] and the same worker has prepared analogously the tetrasulfonic acids of nickel,[135] iron,[136] chromium,[137] manganese,[138] and zinc[138] phthalocyanines. In the preparation of similar tetrasulfonic acids using metal-free phthalocyanine tetra-4-sulfonic acid[139] as a ligand in aqueous solution, the rate-

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[127] E. F. Klenke and DuP, *USP* 3,041,347.

[128] B. S. Wildi, W. B. Tuemmler, and Monsanto, *USP* 3,099,630.

[129] C. Q. Miller, W. W. Ranson, and DuP, *USP* 2,950,285; 2,950,286.

[130] CIBA, *BP* 957,231; *FP* 1,313,698.

[131] F. Baumann, B. Bienert, and FBy, *USP* 2,613,128; *BP* 704,310.

[132] M. H. Fleysher, W. B. Richards, and Allied Chem. Corp., *USP* 3,091,618.

[133] Universal Oil Products, *BP* 849,998.

[134] N. Fukada, *Nippon Kagaku Zasshi* **75**, 1141 (1954); *CA* **51**, 12729 (1957).

[135] N. Fukada, *Nippon Kagaku Zasshi* **75**, 586 (1954); *CA* **51**, 11154 (1957).

[136] N. Fukada, *Nippon Kagaku Zasshi* **76**, 1378 (1955); *CA* **51**, 17945 (1957).

[137] N. Fukada, *Nippon Kagaku Zasshi* **77**, 1421 (1956).

[138] N. Fukada, *Nippon Kagaku Zasshi* **79**, 396 and 980 (1958); *CA* **54**, 4612 (1960).

[139] K. Bernauer and S. Fallab, *Helv. Chim. Acta* **44**, 1287 (1961).

determining step is the N—H dissociation which is catalyzed by species like $MeOH^+$.[140]

The visible spectra of phthalocyanine sulfonic acids and their implications are discussed in Section VII.

2. *Sulfonyl Halides*

Phthalocyanine sulfonyl chlorides are most important intermediates for the production of sulfonamides (Section V,B,3), sulfonic esters (Section V,B,3) and various reduction products (Section V,C). The group is introduced by treatment of the phthalocyanine with chlorosulfonic acid at elevated temperature (120–140°), the product being essentially 3-substituted and containing from one to four SO_2Cl groups depending upon the conditions (time and temperature of reaction) chosen. The reaction is more specific than sulfonation, in which a little 4-sulfonation occurs. Some sulfonic acid is present in the reaction mixture in equilibrium with the sulfonyl chloride and for complete conversion to the latter the presence of an ancillary agent such as PCl_5, PCl_3, or thionyl chloride is required. These chlorinating agents are usually added at the end of the reaction to shift the equilibrium, but even when they are employed it is still difficult to obtain pure sulfonyl chlorides due to their ease of hydrolysis.

4-Substituted sulfonyl chlorides can only be obtained from the corresponding sulfonic acids by reaction with chlorosulfonic acid or a chlorinating agent such as PCl_5 in a solvent (e.g., nitrobenzene).

Copper phthalocyanine readily protonates to give a species of almost unlimited solubility in chlorosulfonic acid[141] and is quite stable under the above reaction conditions but, although phthalocyanines of many other metals are often disclosed in patents as being chlorosulfonated under similar conditions, some metal phthalocyanines, for example, iron phthalocyanine, are much less stable and require special conditions.

Although sulfonyl fluorides can be obtained by exchange reactions of the sulfonyl chloride with an alkali metal fluoride, the products are inevitably mixtures of the type $CuPc(SO_3H)_x(SO_2F)_y$ and competing hydrolysis makes it difficult to attain y values of $\geqslant 1$.

3. *Sulfonamides and Sulfonic Acid Esters*

The use of $-SO_2NH-$ or $-SO_2NR-$ ($R =$ alkyl or aryl group) as bridging groups between a phthalocyanine, particularly copper phthalocyanine, and some other grouping the introduction of which modifies the physical or chemical properties is of prime importance. It is, in fact, by far the

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[140] I. Schiller and K. Bernauer, *Helv. Chim. Acta* **46**, 3002 (1963).

[141] B. D. Berezin, *Zh. Prikl. Khim.* **36**, 1181 (1963); *CA* **59**, 10809 (1963).

most versatile and well-used device for ringing peripheral changes in order to extend the use of the chromophore outside the pigment field.

a. Solvent-Soluble Dyes. Sulfonamides derived from simple amines like cyclohexylamine have found outlets for many years due to their solvent solubility. Improved products, used, for example, in the ballpoint pen inks, resins, waxes, lacquers, plastic compositions, and spin-dyed cellulose acetate, have been produced through the use of more sophisticated amines such as γ-methoxypropylamine,[142] γ-isobutoxypropylamine,[143] lauryloxypropylamine,[144] *tert*-dodecyl triethylenetetramine,[145] and ethylene glycol-*O*-ethyl-*O*′-(γ-aminopropyl) diether.[146] The products all give bright blue or turquoise shades; some modification in shade can be effected by simultaneous introduction of another chromophore, as for example through the use of 4-amino-2′-nitrodiphenylamine-4′-sulfonic acid-*N*:γ-isopropoxypropylamide to give a solvent-soluble green dye.[147]

Another way of introducing oleophilic groups is by salt formation. Phthalocyanine sulfonic acid sulfonamides form stable salts with 1-dodecyl-2-iminoimidazolidine[148] or γ-(2′-ethylhexoxy)propylamine,[149] and basic sulfonamides of the type $\text{CuPc}(\text{SO}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_{2-3}$[150] form glycol-soluble salts with monooctyl phthalate.[151]

b. Introduction of Functional Groups. Reduction of sulfonyl chlorides leading to products with $-\text{SO}_2-$ or –S– links will be discussed in Section V,C but the $-\text{SO}_2\text{N(R)}-$ link is still the most important in consideration of the preparation of phthalocyanine derivatives capable of further reaction. In the case of pendant groups containing reactive hydrogens, amino groups predominate, their introduction being achieved by reaction of the sulfonyl chloride with one end of a diamine such as an alkylene diamine, phenylene diamine, or phenylene diamine sulfonic acid.[152] Such phthalocyanine intermediates are of particular importance in the reactive dye field for attachment of the reactive groups by acylation (see the chapter on reactive dyes), but are also used to prepare fast dyeings by

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[142] C. Zickendraht, E. J. Koller, and CIBA, *USP* 2,897,207; *BP* 865,679.

[143] A. Tartter, A. Schoellig, H. Otterbach, O. Stichnoth, and BASF, *BP* 868,913.

[144] CIBA, *BP* 943,133.

[145] Gy, *BP* 947,935.

[146] Gy, *BP* 989,459.

[147] CIBA, *BP* 1,039,116; 1,120,418.

[148] Gy, *BP* 967,894.

[149] M. Groll, K. Triebeneck, W. Theuber, and FBy, *BP* 1,059,457; *USP* 3,365,463.

[150] FBy, *BP* 784,843.

[151] FBy, *BP* 803,525.

[152] BASF, *BP* 827,568.

further reaction on the fiber (particularly cellulosics) with agents such as epoxides,[153] isocyanates,[154] and acryloyl compounds.[155] Hydroxyalkyl groups, particularly in phthalocyanine sulfonhydroxyethylamides, can also be cross-linked on the fiber by reaction with polymethylol compounds.[156]

Pendant tertiary amino groups are important through their ability to either form water-soluble salts or be further alkylated to form cationic dyes, e.g., $CuPc(SO_2NHCH_2CH_2CH_2N^+Me_3)_{2-3}$.[150] An alternative method of preparation of products such as $CuPc(SO_2NHCH_2CH_2NEt_2)_3$ consists of alkylation of the sodium derivative of the primary sulfonamide with 1-diethylamino-2-chloroethane.[157] The ability of phthalocyanine sulfonamides to form water-soluble sodium derivatives allows acylation with, for example, cyanuric chloride,[158] to be carried out and has also been utilized by Hoechst in a dyeing process in which the insoluble secondary sulfonamide, e.g., $CuPc(SO_2NHPh)_3$, is precipitated within the fiber.[159]

The introduction of pendant metallizable groups leads to chrome dyes of some technical importance. As alternatives to the early use of aminosalicylic acids[7] for this purpose, aminoalkylaminosalicylic acids[160] or dihydroxybenzenecarboxylic acids (e.g., β-resorcylic acid)[161] may be used, the latter series forming stable esters.

Treatment of textiles with resins, as in the application of crease-resist finishes, can be adapted by using dyes modified to contain groups capable of interaction with the resin, with beneficial results in fastness following the cross-linking thus achieved. Methylol groups for this purpose are readily introduced by formaldehyde treatment into water-soluble phthalocyanine dyes containing sulfonamide,[162] sulfonhydrazide,[163] aminotriazinyl,[164, 165] or glyoxaldiurein residues. The latter, containing

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[153] CIBA, *FP* 1,210,142

[154] FBy, *BP* 886,013.

[155] G. Luetzel, W. Rohland, A. Tartter, G. Barts, W. Dietrich, W. Federkiel, R. Mueller, and BASF, *DAS* 1,155,088; *BP* 923,162.

[156] E. Enders, O. Bayer, K.-H. Gehringer, and FBy, *DAS* 1,143,482.

[157] FBy, *BP* 807,224.

[158] FBy, *BP* 879,578.

[159] FH, *BP* 1,060,233.

[160] FBy, *BP* 785,629.

[161] DH, *BP* 768,444; 868,682.

[162] A. Tartter, W. Braun, J. Eisele, G. Krehbiel, G. Lange, R. Mueller, H. Weissauer, and BASF, *DAS* 1,156,530; *BP* 895,029.

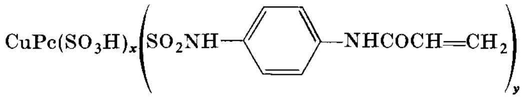
[163] H. Distler, K. Merkel, R. Mueller, A. Tartter, H. Weissauer, H. V. Werner, and BASF, *DAS* 1,099,986; *BP* 899,899.

[164] P. F. Clark, H. T. Howard, and ICI, *BP* 904,227.

[165] A. Tartter, W. Braun, H. Weissauer, and BASF, *DAS* 1,160,127 (*BP* 942,569); *DAS* 1,151,613 (*BP* 908,301).

a "built-in" resin system, can be introduced through either a sulfonamide[162] or a sulfonic acid ester[166] linkage.

The principle of cross-linked copolymers containing combined dyes has been extended to the use of vinyl-containing dyes. A preformed copolymer contained in a suitable emulsion can be applied to textiles as an alternative to the use of pigment-binder systems with the advantage of improved rubbing fastness.[167] For example,



may be copolymerized with butyl acrylate, methyl methacrylate, and *N*-methylmethacrylamide in a suitable mixture of solvents and the resulting product applied in a printing mixture.[168]

c. Other Water-Soluble Dyes. Direct dyes for cellulosic textiles and paper of general formula $CuPc(SO_3H)_x(SO_2NHR)_y$ are an improvement over sulfonated products since x, y, and R can be varied according to specific requirements, having very marked effects on such properties as affinity and substantivity. Apparent improvements in strength through x and y variations are usually dependent on aggregation and other physical effects during and after dyeing. A product with $R = H$, $x = 0.5$ to 0.9 and $y = 2.1$ to 2.5, with $x + y = 3$ (the values, as in all such cases, representing statistical averages of mixed products) has recently been found outstandingly suitable for paper.[169] The dyes with R = cyclohexyl, $x = 1$ or 2, and $y = 2$ are of some additional interest since they can be prepared from the tri- or tetrasulfonamides by partial hydrolysis with concentrated sulfuric acid.[170]

The use of anionic phthalocyanine dyes on noncellulosic fibers, particularly wool and synthetic polyamides, presents problems (weak and uneven dyeings) in spite of much work on the variation of the x, y, and R parameters in the above general formula. Geigy has claimed the use of phthalocyanines containing sulfated hydroxyalkylsulfonamides (e.g., $R = CH_2CH_2OSO_3H$) specifically for improved results on wool.[171]

[166] DH, *BP* 970,442.

[167] K. Gulbins and W. Schwindt, *J. Soc. Dyers Colourists* 81, 579 (1965).

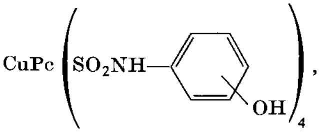
[168] H. Wilhelm, G. Louis, G. Lange, H. Weidinger, D. Mahling, and BASF, *DAS* 1,139,092; *BP* 946,182.

[169] BASF, *BP* 1,046,520.

[170] ACNA, *BP* 1,010,570.

[171] Gy, *BP* 876,691; 975,981.

The corresponding thiosulfates ($R = CH_2CH_2SSO_3H$)[172] can also be used for wool, particularly Wool Fast Turquoise Blue SW (Inthion Brilliant Blue 5GL) [$CuPc(3\text{-}SO_2NHCH_2CH_2SSO_3H)_3$], although since this reacts with the cysteine in the fiber[173] it may not be comparable with the other types. Hydroxyaryl derivatives, e.g.,



can also be sulfated to give dyes for wool.[174] The use of modified water-soluble phthalocyanine dyes for wool may still require the use of special dyeing methods with the incorporation of auxiliaries to achieve optimum results.[175, 176]

The introduction of a nitro-dye chromophore by reaction of copper phthalocyanine sulfonyl chloride with 4-amino-4′-nitrodiphenylamine-2′-sulfonic acid, gives green dyes for leather and paper.[177] Pendant mercapto groups can be introduced, giving dyes for use as sulfur colors or, alternatively, which are capable of reaction on the fiber via reaction of the sulfonyl chloride with aminophenylthiosulfates or diaminodiphenyl disulfides.[177a]

C. Other Derivatives Containing Directly Linked Sulfur

1. *Reduction of Phthalocyanine Sulfonyl Chlorides*

Identified reduction products contain sulfinic acid ($-SO_2H$) or thiol ($-SH$) residues and are obtained by methods conventionally applied to aromatic sulfonyl chlorides, although the products almost inevitably also contain some coproduced sulfonic acid groups.

Preparation of phthalocyanine sulfinic acids using sulfite or bisulfite as the reducing agent has been described[178, 179]; this method is, however,

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[172] W. Schultheis, K. Schimmelschnidt, H. Hoffmann, E. Baier, and FH, *DAS* 1,163,473; *BP* 949,956.

[173] F. Osterloh, *Melliand Textilber.* **44**, 57 (1963).

[174] FBy, *BP* 1,046,059.

[175] CIBA, *BP* 795,946; 860,908; 889,585.

[176] Gy, *BP* 948,685.

[177] BASF, *BP* 749,349.

[177a] W. J. Bryan, T. E. Lesslie, G. A. Geselbracht, and Martin-Marietta Corp., *USP* 3,325,511; 3,334,116.

[178] FH, *DAS* 1,236,107; *BP* 1,060,086.

[179] D. Razavi and CN, *FP* 1,418,196; *BP* 1,064,637.

said to lead to excessive hydrolysis with consequent limitation to the introduction of a maximum of one sulfinic acid residue. Hydrazine under slightly alkaline conditions (pH 8) is claimed to be a superior reducing agent and can lead [Eq. (2)] to phthalocyanines containing two sulfinic acid residues.[180]

$$\mathrm{CuPc(SO_3H)(SO_2Cl)_3} \xrightarrow[\mathrm{pH\,8}]{\mathrm{N_2H_4}} \mathrm{CuPc(SO_3Na)_2(SO_2Na)_2} \tag{2}$$

This reduction takes place under such mild conditions that it must be questioned whether methods [163, 181] for the production of sulfonhydrazides are free from reductive side reactions.

When excess NaHS or Na_2S is used as the reducing agent under mild conditions products of the type $CuPc(SO_2Na)_2(SO_2SNa)_2$ are obtained from copper phthalocyanine 3- or 4-tetrasulfonyl chlorides.[182, 183]

The phthalocyanine sulfonic sulfinic acids obtained as above may be used as dyes[179] but are more important as intermediates. The sulfinic acid group can be alkylated with, for example, ethylene oxide,[178] or reacted with ammonium thiocyanate, thiourea, or a thiosulfate to give thiocyano or polysulfide derivatives for use as sulfur colors.[184] Reaction of $CuPc(4\text{-}SO_2Cl)_4$ to give $CuPc(4\text{-}SCN)_4$ by this route would be a very attractive alternative to the original method based on $CuPc(4\text{-}NH_2)_4$.[185]

Mercaptophthalocyanines are obtained by reduction of the chlorosulfonyl group with zinc/acid[186] or iron/acid.[187] They can be used as a basis for sulfur colors or, like sulfinic acids, as intermediates. Alkylation of the mercapto groups can be achieved with ethylene dichloride, ethylene oxide,[188] epibromohydrin,[189] or chloroacetic acid.[190] As sulfur colors, the mercapto derivatives tend to produce grayish green to blue shades when applied from sulfide baths. Improved products are claimed when the reduction of the chlorosulfonyl group is carried out in the

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[180] G. A. Gamlen, P. W. Hickmott, and ICI, *BP* 960,643.

[181] G, *BP* 613,782.

[182] G. E. Geselbracht, W. J. Bryan, and Martin-Marietta Corp., *USP* 3,338,918.

[183] D. Razavi and CN, *FP* 1,413,126; *BP* 1,119,961.

[184] G. E. Geselbracht, W. J. Bryan, W. S. Griffith, and Martin-Marietta Corp., *USP* 3,361,758; 3,378,568.

[185] N. H. Haddock and ICI, *BP* 541,146.

[186] N. H. Haddock and ICI, *BP* 544,953; *USP* 2,342,663.

[187] R. L. Mayhew and G, *USP* 2,484,300; *BP* 654,507.

[188] D. Taber and American Aniline Products, *USP* 3,152,108; 3,152,109; 3,287,348.

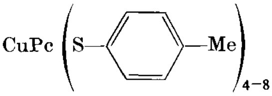
[189] D. Taber, E. E. Renfrew, H. W. Pons, and American Aniline Products, *USP* 3,152,110.

[190] BASF, *BP* 713,865.

presence of thiourea[191] or by further treatment of the mercapto derivatives with elemental sulfur.[192] Sulfur dyes, which by their behavior may contain mercapto groups, can be obtained directly by the inclusion of sulfur in the phthalonitrile process, particularly in the case of cobalt phthalocyanine.[193]

2. *Thioethers*

Reaction of polyhalogeno phthalocyanines with mercaptans or thiophenols gives the corresponding thioethers.[194] Products of the type



thus obtained are green, solvent-soluble (e.g., in benzene) and can be used for the mass coloration of synthetic polyamides.[195] The same type of arylmercapto derivative can be sulfonated to give green direct dyes,[196] or alternatively chlorosulfonated[197] or chloromethylated[198] to give intermediates towards modified solvent-soluble dyes.

3. *Sulfones*

Friedel-Crafts reactions using either a phthalocyanine sulfonyl chloride as the sulfonylating reagent or a phthalocyanine as the substrate for reaction with a simple sulfonyl halide are difficult to perform, partly because of the low solubility of the phthalocyanine reactant. Mono-(phenylsulfonyl) cobalt phthalocyanine, a vat dye with improved fastness to chlorine, can be produced, with some simultaneous chlorination also taking place, by reaction of cobalt phthalocyanine with $PhSO_2Cl$ ($SbCl_3$ catalyst).[199]

D. SUBSTITUTED ALKYL DERIVATIVES

1. *Chloromethyl Compounds and Their Derivatives*

Chloromethyl phthalocyanines are by far the most important class under this heading. They are next in importance to sulfonyl chlorides as

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[191] F. Schmidt and VEB Farben Wolfen, *BP* 992,381.

[192] CFM, *BP* 784,353.

[193] BASF, *BP* 707,710.

[194] S, *BP* 588,231; *USP* 2,456,274.

[195] S, *BP* 860,628; *USP* 3,023,186.

[196] S, *BP* 629,488.

[197] S, *BP* 1,029,433.

[198] T. A. Martin, D. I. Randall, and G, *USP* 2,795,584.

[199] T. A. Martin and G, *USP* 2,953,574.

versatile intermediates for the production of a wide range of products through reaction of the chlorine atom. By analogy with sulfonyl chlorides they can be reacted with amines, phenols, and other compounds containing reactive H atoms with the advantage that simultaneous hydrolysis is less of a problem, but with the disadvantage that the final derived products are almost always duller, and thus less attractive, than comparable derivatives of sulfonyl chlorides.

The original method for the chloromethylation of phthalocyanines based on reaction with *sym*-dichlorodimethyl ether or paraformaldehyde in an aluminum chloride melt[200] has been extended to derivatives containing, for example, arylthio, aryloxy, or aryl residues.[201] Alternative processes involve reaction of paraform with the phthalocyanine dissolved in a mixture of sulfuric and chlorosulfonic acids,[202] or reaction of dichlorodimethyl ether with a sulfuric acid solution.[202a] From one to eight groups, or mixtures corresponding to these numbers, can be introduced according to the conditions used, but normally from two to four groups are adequate for subsequent attainment of the required solubility, etc.

Cationic compounds derived from chloromethylated copper phthalocyanine (so-called "onium" derivatives) are important as ingrain dyes, typified by Alcian Blue 8GX (CI 74240) (see *CSD II*, p. 1140). As an alternative to the original method of quaternization with a tertiary amine it may be advantageous in certain cases to react with a secondary amine and subsequently alkylate with, for example, dimethyl sulfate,[203] or an alkylene oxide.[204] Where the derivative is an isothiouronium compound the products are of additional interest for the coloration of polyacrylonitrile.[205] Modified onium derivatives are obtained when quaternization is effected with *N*,*N*-dimethylaminoacetic acid, giving zwitterions of the type $\mathrm{CuPc[CH_2{-}N^+(Me)_2CH_2COO^-]}_n$ which are advantageously applied to cellulosic materials under alkaline conditions.[206]

Appropriate variation of the *N*-substituents in this series of quaternaries leads to modified properties. Where one of the substituents is a hydroxyalkyl group, as in $\mathrm{CuPc[CH_2N^+Me_2(C_2H_4OH)]_3}$, which can be obtained by reacting the dimethylaminomethylene compound with

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[200] N. H. Haddock, C. Wood, and ICI, *BP* 586,340; *USP* 2,435,307.

[201] N. H. Haddock, F. H. Slinger, C. Wood, and ICI, *BP* 686,391; *USP* 2,542,327–8.

[202] BASF, DBP 843,726; *BP* 689,153.

[202a] P. Drenchko and G, *USP* 3,252,992; *BP* 1,023,411.

[203] N. H. Haddock and ICI, *BP* 770,784.

[204] FH, *DAS* 1,220,065; *BP* 1,050,885.

[205] B. N. Parsons and ICI, *BP* 1,081,391.

[206] A. Tartter, A. Blum, and BASF, *DAS* 1,154,789; *BP* 928,413.

ethylene oxide, the products are especially suitable either for dyeing or printing cellulosic material or for use in pastes for ballpoint pens.[207] Improved water solubility results from the use of *N*,*N*-dimethylhydrazine as quaternizing agent[208] and where the products are used as temporarily soluble dyes by decomposition with alkali on the fiber, quaternaries derived from ω-chloro-*N*-methylphthalimide are said to be advantageous.[209]

Although tertiary amine derivatives can be prepared by alkylation of $CuPc(CH_2NH_2)_n$, with, for example, formaldehyde,[209, 210] they are usually prepared by interaction of chloromethyl compounds and secondary amines. The use of higher alkylamines such as diisobutylamine[211] or heterocyclic amines such as hexamethyleneimine or pyridine[212] results in solvent-soluble products. Diethanolamine derivatives such as $CuPc[CH_2N(CH_2CH_2OH)_2]_{3-4}$ can be esterified with either acetic anhydride,[213] giving solvent-soluble products, or sulfuric acid,[214] giving water-soluble products. Again by analogy with chlorosulfonyl compounds, the chloromethyl derivative can be reacted with difunctional amines such as γ-dimethylamino propylamine to give basic dyes.[150]

Other outlets for the tertiary amine derivatives include their use as pigment stabilizers [215–217] and the dyeing of paper with simple salts, e.g., $CuPc(CH_2NEt_2 \cdot HCl)_3$.[218] Products which are of polymeric nature, for addition to pigments in order to improve their resistance to flocculation, can also be obtained by reacting chlormethylated copper phthalocyanine with primary amines, such as isopropylamine.[219]

Other products obtained from chloromethylated copper phthalocyanines include $CuPc(CH_2SH)_n$ by reaction with sulfide,[220] $CuPc(CH_2SSO_3H)_n$ by reaction with thiosulfate,[221] and substituted benzyl derivatives by Friedel-Crafts reaction. This latter provides an alternative

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[207] FH, *BP* 1,050,886; 1,108,057.

[208] Allied Chem. Corp., *BP* 987,049.

[209] G. Rösch, H. Klappert, and FBy, *DAS* 1,114,964; *BP* 877,894.

[210] FBy, *BP* 724,212.

[211] D. I. Randall, T. A. Martin, and G, *USP* 2,547,972.

[212] A. Tartter and BASF, *DAS* 1,097,596.

[213] H. T. Howard, C. D. Marrable, and ICI, *BP* 883,807.

[214] A. Tartter and BASF, *DAS* 1,061,009; *BP* 848,782.

[215] A. Schoellig, R. Schroedel, H.-J. Sasse, and BASF, *DAS* 1,239,270; *BP* 949,739.

[216] G. Barron, W. Black, A. Topham, and ICI, *BP* 972,805.

[217] W. Black, J. Mitchell, A. Topham, and ICI, *BP* 1,082,945.

[218] J. F. Harris, C. D. Marrable, and ICI, *BP* 844,338.

[219] J. Mitchell, A. Topham, and ICI, *BP* 1,082,967; 1,113,060.

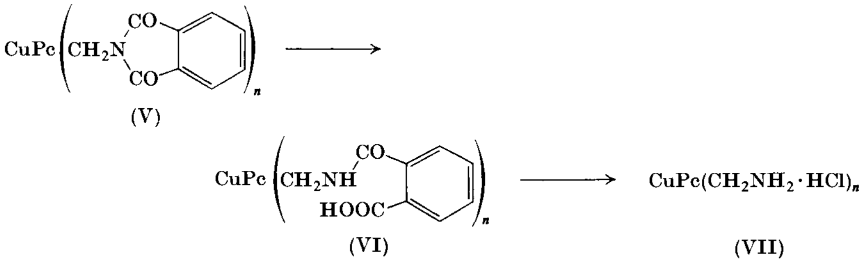
[220] FH, *BP* 733,471.

[221] V. D. Poole and ICI, *BP* 955,004.

means of introducing pendant functional groups by the use of suitable agents, e.g., dodecylbenzene (solvent-soluble product),[222] methyl phenyl thioether (for subsequent ternarization),[223] phenols,[224] or *m*-aminophenol (for subsequent acylation).[225] Water-soluble dyes are obtained by oleum sulfonation of chloromethylphthalocyanines[226] or, alternatively, halomethylation with bis(chloromethyl) ether can be effected in the presence of oleum.[227]

2. *Amidomethylation*

Although formaldehyde reacts with a sulfuric acid solution of copper phthalocyanine with the introduction of one or two hydroxymethyl groups,[228] it is reaction with *N*-methylol compounds (i.e., amides or imides and formaldehyde) that leads to the more important series of substituted aminomethyl derivatives. Copper phthalocyanine reacts with a mixture of phthalimide and paraformaldehyde[229] (or preformed ω-hydroxy-*N*-methylphthalimide[230]) in sulfuric acid medium with formation of phthalimidomethyl derivatives (V). An alternative synthesis involves reaction with ω-chloro-*N*-methylphthalimide in an aluminum chloride melt.[230] These derivatives may be partially hydrolyzed with alkali to give the carboxylic acid derivatives (VI) which in turn are further hydrolyzed to the aminomethyl compounds (VII) on treatment with acid. The free bases of (VII) are unstable but may be further reacted (e.g., alkylated or acylated) under controlled conditions.



(V)

(VI)

(VII)

[222] D. I. Randall, T. A. Martin, and G, *USP* 2,859,219.

[223] BASF, *BP* 809,224.

[224] W. O. Jones and ICI, *BP* 691,905.

[225] A. Tartter and BASF, *DAS* 1,192,351; *BP* 853,364.

[226] A. Tartter and BASF, *DAS* 1,131,830.

[227] G, *BP* 1,043,074.

[228] CIBA, *BP* 893,165.

[229] H. T. Lacey and CCC, *USP* 2,761,868; *BP* 695,523.

[230] FBy, *BP* 717,137.

The polar group contained in (VI) can be utilized by incorporating the products in pigments to improve flocculation properties[231] or by forming salts with quaternary ammonium cations, such as hexadecylbenzyldimethylammonium, which are oil and spirit soluble.[232] When 4-sulfophthalimide is used in place of phthalimide in the above process water-soluble products result which can be used as temporarily solubilized dyes by application in the presence of hydrazine.[233] Application of the amidomethylation reaction to cobalt phthalocyanine, using either phthalimide or acetamide, leads to vat dyes of increased affinity.[234] Extension of the reaction to the use of chloroacetamide (in the presence of P_2O_5) gives products of the type $CuPc(CH_2NHCOCH_2Cl)_n$, the chlorine of which may be further reacted by quaternization, etc.[235]

3. *Other Alkyl Derivatives*

There are very few other examples of direct alkylation of phthalocyanines. Reaction of copper phthalocyanine with *n*-heptyl iodide gives a tetrasubstituted product which is fluorinated and dissolved on treatment with $C_6F_{12}O$ solvent.[236] If products are not available through chloromethylation or amidomethylation reactions they must generally be synthesized from the appropriately substituted phthalonitrile or phthalic anhydride, as with, for example, tetramethyl and octamethyl copper phthalocyanines.[237]

E. AMINE DERIVATIVES

Copper tetra(4-amino)phthalocyanine is a well-established intermediate prepared by reduction of the corresponding nitro compound. Some of the manufacturing improvements referred to earlier (see, e.g., ref. 11) in respect to copper phthalocyanine are also claimed to be applicable to the synthesis of copper tetra(4-nitro) phthalocyanine from 4-nitrophthalimide. Preparation of sulfur dyes from aminophthalocyanines has already been referred to (Section V,C,1). More recent work in this field has been directed towards the use of further-substituted aminophthalocyanines. Chlorosulfonation and subsequent reduction with iron/acid leads to greenish gray sulfur dyes[238] and a through process

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[231] CCC, *BP* 746,704.

[232] H. T. Lacey, G. R. Waitkins, and CCC, *USP* 2,823,205.

[233] N. H. Haddock and ICI, *BP* 914,249.

[234] G, *BP* 779,324; 781,749.

[235] A. Tartter and BASF, *DAS* 1,029,965; *BP* 806,175.

[236] Minnesota Mining and Manufacturing Co., *BP* 840,725.

[237] D. Colaitis, *Compt. Rend.* **250**, 328 (1960).

[238] CFM, *BP* 792,018; 816,656.

based on $CuPc(NO_2)_4$ can be operated by introducing sulfur at the chlorosulfonation stage.[239] The products of reaction between copper phthalocyanine and hydroxylamine in chlorosulfonic acid in the presence of ammonium molybdate appear similar to those obtained from $CuPc(NH_2)_4$.[240] Direct amination is presumably involved using alternative conditions to the earlier method of reacting hydroxylamine in an aluminum chloride melt.[241] There is a close analogy here with the alternative reaction media for the chloromethylation reaction (Section V,D,1). Further refinements to the hydroxylamine amination reaction have recently been described by Japanese workers.[242]

Although patented in the reactive dye field, acylamine derivatives are of little importance. Diazo derivatives are only important in the production of sulfur colors, although an interesting novel application is their use of polymerization initiators whereby the chromophore is incorporated into the polymer.[243]

F. AZOPHTHALOCYANINES

The azo and phthalocyanine chromophores can be linked in a variety of ways and the resulting products have some importance, particularly in the green shade range. As with previously discussed elaborations about the phthalocyanine nucleus, the sulfonamide linkage is the most often used. The preferred method of preparation is reaction of a chlorosulfonyl phthalocyanine with an amine-containing coupling component, such as an aminonaphthol or aminoarylpyrazolone; the resulting product may then be coupled with a suitable diazo component to form direct or reactive dyes (see chapter on reactive dyes). Green dyes result from the use of 1-aminophenyl-3-methyl-5-pyrazolones[244] and brown to violet dyes from the use of J-acid, which forms the coupling component (VIII).[245] These phthalocyanine-containing coupling components, e.g., (IX), are also important in the azoic field for the production of green shades on the fiber.[246]

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[239] CFM, *BP* 816,657.

[240] CFM, *BP* 761,287.

[241] BASF, *BP* 680,511.

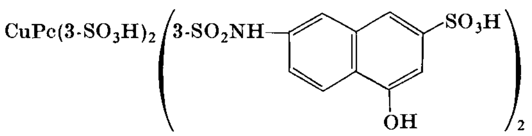
[242] NSK, *JP* 16632/64; *JP* 20078/64; *JP* 7030/68.

[243] Dainichiseika Color and Chem., *BeP* 685,224; 637,190; *BP* 1,065,961.

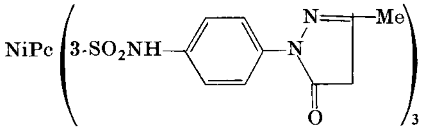
[244] FBy, *BP* 830,920.

[245] J. Reichel, R. Palea, and I. Iorga, *Bull. Stiint. Tech. Inst., Politehn. Timisoara* **6**, 53 (1961); *CA* **58**, 1564 (1963).

[246] FBy, *BP* 811,221; 811,222; 844,419.

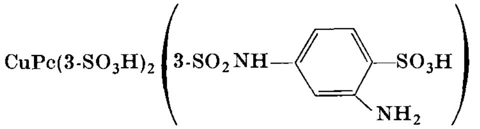


(VIII)



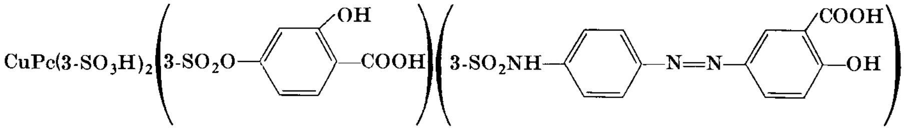
(IX)

The alternative of using amino-containing phthalocyanines such as

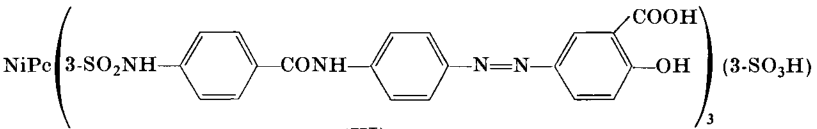


as diazo components[247] is less attractive due to possible complications in their diazotization.

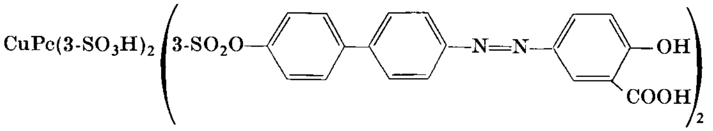
Aminoazo dyes can also be reacted with chlorosulfonyl phthalocyanines; the most important types here. e.g. (X)[248] and (XI)[249] contain metallizable groups for mordanting. Certain hydroxyazo dyes give analogous esters such as (XII).[250]



(X)



(XI)



(XII)

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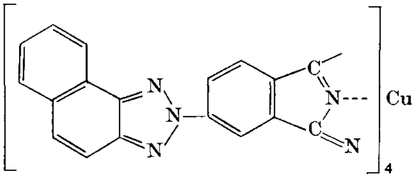
[247] H.-G. Harke, G. Oertel, H. Holtschnidt, and FBy, *BP* 1,112,875.

[248] DH, *BP* 763,343; 779,489.

[249] Gy, *FP* 1,421,156.

[250] H. B. Gottlieb and DuP, *USP* 2,801,997.

It is difficult to obtain satisfactory azo phthalocyanine pigments via chlorosulfonyl reactions due to simultaneous sulfonic acid formation. Two alternatives are to use methylene-bridged coupling components, such as $CuPc(CH_2NHCOCH_2COCH_3)_4$[251] or to synthesize the macrocycle from azo-substituted phthalic acids. When the amino azo compound 4-aminophthalic acid → β-naphthylamine is used, simultaneous triazole formation takes place to give the green pigment represented by (XIII).[252]



(XIII)

G. OTHERS

The main group of phthalocyanines not previously covered under earlier headings are those derived directly from alternatively substituted phthalic compounds. Hetero substituents are also included here for convenience.

Trimellitic acid can be used, if necessary in conjunction with phthalic acid, to produce phthalocyanine carboxylic acids or amides, formation of the latter being difficult to avoid in the urea process.[11, 253] It has recently been discovered that carboxyphthalocyanines are useful for the mass coloration of polyesters and polyamides by actually carrying out the polymerization in the presence of the colorant.[254]

Suitably oriented tetracyano or tetracarboxy aryl compounds give polymeric products when phthalocyanine synthesis is applied.[1] Pyromellitic derivatives are most usually exploited because of their availability. Pyromellitic dianhydride (XIV) gives blue-green to black copper derivatives which are difficult to analyze and characterize.[255] Molecular weights of up to 4000 are indicated, together with a suggestion that chainlike arrangements rather than graphitelike sheets are produced.[256] Green products have also been obtained which are alkali-soluble and must therefore still contain terminal carboxylic acid

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[251] G. Rosch, K.-H. Gehringer, and FBy, *DAS* 1,109,288; *BP* 858,070; *USP* 2,882,267.

[252] A. Pugin, E. Keller, and Gy, *DAS* 1,058,178; *BP* 791,359.

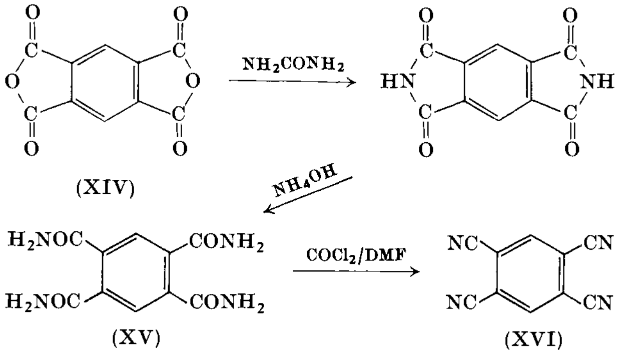
[253] F. F. Ehrich and DuP, *USP* 2,805,957.

[254] ICI, *BeP* 706,634–5.

[255] C. S. Marvel and J. H. Rassweiler, *J. Am. Chem. Soc.* **80**, 1197 (1958).

[256] W. C. Drinkard and J. C. Bailar, *J. Am. Chem. Soc.* **81**, 4795 (1959).

groups.[257] The use of 1,2,4,5-tetracyanobenzene [pyromellitonitrile; (XVI)], which can be obtained from (XIV) via the diamide (XV) by dehydration (Chart 4) with either thionyl chloride/dimethylformamide[258] or phosgene/dimethylformamide,[259] may well lead to different polymer types. Bluish black pigments can be obtained which are thought to have a honeycomb structure[259] and the metal-free phthalocyanine derived from (XVI) is described as a sheet polymer for use as a high-temperature lubricant which actually coordinates with metal bearings, etc.[260] Russian workers in their search for semiconductor materials have shown that the above polymeric types have enhanced electroconductivity compared with phthalocyanine monomers.[261]



o-Dicarboxyphenyl-phosphonous (XVII)[253] and -phosphonic (XVIII)[262] acids have been used to synthesize copper phthalocyanine derivatives for use as flocculation-resistant pigments and alkali-soluble cotton dyes, respectively. The copper phthalocyanine derived from diphenylsulfone-3,4-dicarboxylic acid (XIX) has been used as an intermediate for chrome dyes.[263]

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[257] Bergwerksverband zur Verwertung von Schutzrechten der Kohlentechnik, *BP* 801,488.

[258] E. A. Lawton and D. D. McRitchie, *J. Org. Chem.* **24**, 26 (1959).

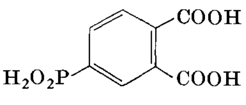
[259] W. B. Tuemmler and Monsanto, *USP* 3,245,965; *BP* 883,552.

[260] E. A. Lawton, C. M. Allen, S. Cosgrove, and Battelle Memorial Institute, *USP* 3,023,164.

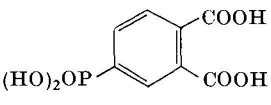
[261] A. A. Berlin, L. G. Cherkashina, E. I. Balabanov, E. L. Frankevich, and Y. G. Aseev, *Vysokomolekul. Soedin* **4**, 376 (1962); **6**, 832 (1964); **8**, 627 (1966); *CA* **57**, 16620 (1962); **61**, 5797 (1964); **65**, 10685 (1966).

[262] H. Z. Lecher, R. A. Greenwood, and CCC, *USP* 2,834,804.

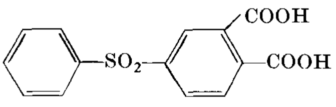
[263] FBy, *BP* 713,397.



(XVII)

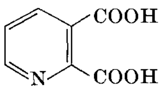


(XVIII)

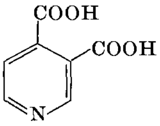


(XIX)

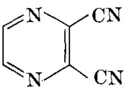
Azaphthalocyanines have been prepared from pyridine-2,3-dicarboxylic acid [quinolinic acid; (XX)],[264] pyridine-3,4-dicarboxylic acid [cinchomeronic acid; (XXI)],[265] 2,3-dicyanopyridine, and 2,3-dicyanopyrazine (XXII)[266] and their properties studied. Commercially, inclusion of a small proportion of quinolinic acid in the preparation of copper (chloro) phthalocyanine is claimed to give improved pigments.[267] The azaphthalocyanines can be quaternized by alkylation to give temporarily solubilized dyes.[268]



(XX)



(XXI)



(XXII)

VI. Oxidation and Reduction Reactions

The chemistry of the oxidation and reduction of phthalocyanine derivatives is worth considering if only because the reaction products are often of uncertain constitution. In spite of this, such products, as will be seen, can have interesting applications, particularly when the reaction is readily reversible. The action of selected oxidizing and reducing agents has been used most ingeniously for the identification of the many types of phthalocyanine dye.[269]

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[264] M. Yakote and F. Shibamiya, *J. Chem. Soc. Japan, Ind. Chem. Sect.* **61**, 994 (1958); **62**, 224 and 720 (1959).

[265] M. Yakote, F. Shibamiya, and S. Tokairin, *J. Chem. Soc. Japan, Ind. Chem. Sect.* **67**, 166 (1964).

[266] M. J. Danzig, C. Y. Liang, and E. Passaglia, *J. Am. Chem. Soc.* **85**, 668 (1963).

[267] G. Zwahlen, M. Grelat, and CIBA, *USP* 3,366,641; *BP* 1,015,699.

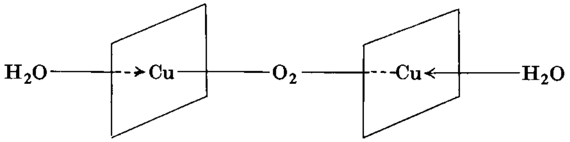
[268] G. Rösch, K.-H. Gehringer, H. Klappert, and FBy, *DAS* 1,101,664.

[269] H. Wagner and J. Pflug, *Melliand Textilber.* **44**, 281 (1963).

Oxygen-bridged molecules and π-bonded oxygen complexes have already been discussed in Section IV,B and it may be that these types can also be produced by the action of oxidizing agents other than elementary oxygen.

Oxidizing agents such as nitric acid, permanganate, or ceric sulfate, especially when reacted with solutions of phthalocyanines, disrupt the macrocycle with formation of phthalimide or related degradation products. Elvidge[270] has found that dichromate behaves specifically and has devised a method for the titration of metal phthalocyanine with 0.01N dichromate to determine the oxidation state of the chelated metal. This method is applicable to many metal derivatives but not to platinum phthalocyanine, which is exceptionally resistant to oxidation. Because of the variation in effect with different oxidizing agents it has been suggested[271] that a solution of copper phthalocyanine in sulfuric acid can be used as a selective test for oxidizing agents.

Japanese workers have recently shown that controlled nitric acid oxidation in an organic solvent gives a range of products some of which can be reversibly reduced to pigments on the fiber.[44, 272] It is suggested[273] that the purple product obtained from reaction of CuPc with nitric acid at 0° has the structure (XXIII), thus relating copper to iron and manga-



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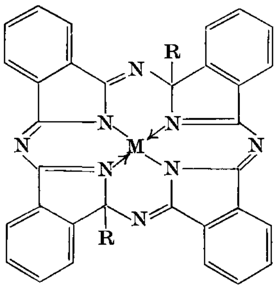
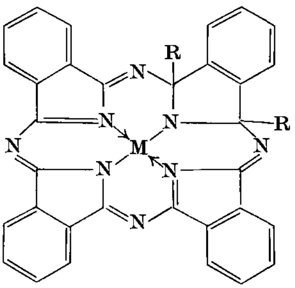


(XXIV)



(XXV)

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[270] J. A. Elvidge, *J. Chem. Soc.* p. 869 (1961).

[271] P. Cerny, *Chem. Zvesti* **9**, 94 (1955); *CA* **49**, 13819 (1955).

[272] Kogyogyuzutsuin, *JP* 4216/68; *Derwent Japan.* **7**, No. 7 (1968).

[273] T. Sekiguchi, E. Yamazaki, and Y. Bansho, *J. Chem. Soc. Japan, Ind. Chem. Sect.* **70**, 503 (1967).

nese (Section IV,B). Cobalt phthalocyanine can give rise to a similar product[274] but also possibly as many as four other oxidation products.[275] These last have indefinite constitutions but must be related to the cyclotetraisoindolenines first described many years ago. Nitric acid produces hydroxyl substituents (XXIV or XXV; R = OH), and bromine in methanol leads to bromo and methoxyl derivatives (XXIV or XXV; R = OMe or Br).[276] This type of product can also be obtained by oxidation with dichloramine-T or N-bromosuccinimide,[277] hypochlorites or peroxides (giving XXIV or XXV; R = OCOR).[278, 279]

Reversible reduction, as distinct from hydrogenation, involves addition of electrons to the inner ring and/or the central metal atom. The best way to represent the products of such reductions, particularly with respect to the location of the charge on the nitrogen atoms, remains somewhat problematical. The pseudo-leuco compound derived from Indanthren Brilliant Blue 4G[131] by vatting with hydrosulfite has been represented as the anion (XXVI),[280] but clearly other resonance forms or differently charged species are possible. The possibility also exists of a change in oxidation state of the cobalt. Reduction of copper phthalocyanine with metallic potassium in liquid ammonia probably gives the Cu(0) anion (XXVII),[281] although it has been pointed out that the Cu(II) anion (XXVIII) is a possible alternative.[282] Analogous possibilities also apply to cobalt phthalocyanine (XXVI) and vice versa.

Borodkin[283] formulated a reduced lithium phthalocyanine compound as (XXIX) [i.e., invoking yet a further alternative of carbanions; compare formulas (XXIV and XXV; R = Li)]. Taube[284] and co-workers have confirmed this constitution as $Li_4Pc \cdot 8THF$ and more logically consider the additional electrons to be located in the lowest antibonding π-orbital of the phthalocyanine. This is important when it comes to the

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[274] T. Sekiguchi, M. Akiya, and Y. Bansho, *J. Chem. Soc. Japan, Ind. Chem. Sect.* **70**, 508 (1967).

[275] T. Sekiguchi, M. Murakami, and Y. Bansho, *J. Chem. Soc. Japan, Ind. Chem. Sect.* **70**, 514 (1967).

[276] F. Baumann, B. Bienert, G. Rosch, H. Vollmann, and W. Wolf, *Angew. Chem.* **68**, 133 (1956).

[277] D. I. Randall, A. Wowk, and G, *USP* 2,914,537–8.

[278] C. J. Pederson and DuP, *USP* 2,662,895–7.

[279] C. J. Pederson, *J. Org. Chem.* **22**, 127 (1957).

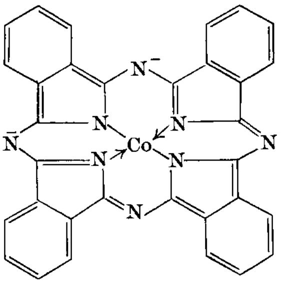
[280] F. Gund, *J. Soc. Dyers Colourists* **69**, 671 (1953).

[281] G. W. Watt and J. W. Dawes, *J. Inorg. & Nucl. Chem.* **14**, 32 (1960).

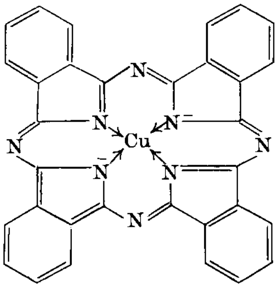
[282] W. A. Alexander and P. L. Pauson, *J. Inorg. & Nucl. Chem.* **17**, 186 (1961).

[283] V. F. Borodkin, *Izv. Vysshikh Uchebn. Zavedenii, Khim. i Khim. Tekhnol.* **2**, 424 (1959); *CA* **54**, 13667 (1960).

[284] R. Taube and P. Meyer, *Angew. Chem. Intern. Ed. Engl.* **5**, 972 (1966).



(XXVI)



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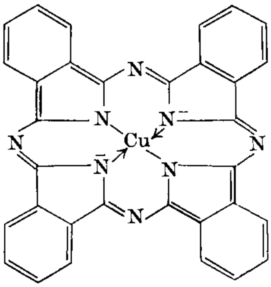
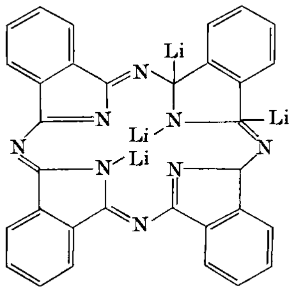


(XXVIII)



(XXIX)

consideration of reduced lithium derivatives of phthalocyanines of transition metals, where a wide range of oxidation states of the central metal atom can be exemplified. Using a solution of dilithiobenzophenone in tetrahydrofuran as reducing agent, Eq. (3) applies in a stepwise manner,

$$[\text{MPc}] \xrightarrow{+n^-} [\text{MPc}]^{n-} \tag{3}$$

where, for example, M = Mn,[285] Cr,[286] or Fe.[287] Stabilization of low oxidation states is thus achieved with isolation of crystalline zero-valent complexes.

Iron phthalocyanine is reduced by refluxing in isopropanol but no metal hydride species could be detected.[288] Hydride shifts are also absent in the PMR spectra of sulfide- or hydrazine-reduced CoPc-$(4\text{-}SO_3H)_4$.[289] It still remains an attractive possibility therefore that

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[285] R. Taube and H. Munke, *Angew. Chem. Intern. Ed. Engl.* **2**, 477 (1963).

[286] R. Taube and K. Lunkenheimer, *Z. Naturforsch.* **19b**, 653 (1964).

[287] R. Taube and H. Drevs, *Angew. Chem. Intern. Ed. Engl.* **6**, 358 (1967).

[288] H. B. Charman, *Nature* **201**, 1021 (1964).

[289] D. H. Busch, J. H. Weber, D. H. Williams, and N. J. Rose, *J. Am. Chem. Soc.* **86**, 5161 (1964).

hydrides (and possibly alkyls) of the transition metals might be stabilized by complexing with a phthalocyanine ligand.

In the dyestuffs field, light-induced reversible one-electron reduction of copper phthalocyanine derivatives takes place surprisingly readily in the presence of certain donors such as amines[290] and there is clearly much further scope for study of the chemistry of the reactive photochemically excited state.

VII. Spectra and Physicochemical Properties

Lever[2] has very adequately summarized the literature on (a) absorption and reflectance spectra, (b) fluorescence spectra, (c) electron spin resonance spectra, (d) nuclear magnetic resonance spectra, (e) infrared spectra, (f) magnetic susceptibility, and (g) electrical properties of phthalocyanines. This ever-growing accumulation of information will inevitably lead to a better understanding of the structure and properties of this important chemical class. It cannot be overemphasized, however, that the purity of the compound under study is of critical importance and that there is considerable difficulty in determining this accurately. It is not proposed to consider the above seven sections of physical properties in any detail here, but a brief consideration of ESR spectra serves to illustrate this point about purity.

ESR measurements are of considerable importance because of their relevance to the relative energies of the transition metal *d* orbitals, thus providing information on the nature of the bonding involved, and to the presence of radicals in, for example, oxidation–reduction processes.[291] Early work in this field was confused by the detection of resonance signals in metal-free and in many diamagnetic (i.e., spin-paired) metal phthalocyanines. Kholmogorov[292] concluded that these signals were not associated with the structure itself, or with α or β modifications, but were attributable either to impurities or conditions which lead to the appearance of unpaired electrons in the crystal. This view has been supported by the suggestion[293] that adsorbed oxygen impurities, either in the bulk or on the surface of the crystal, are responsible. The important point here is that the comparatively crude purification techniques available, such as recrystallization from sulfuric acid or washing with organic solvents, only gradually decrease the intensity of this radical resonance; and furthermore sublimation of the sample generally intensifies the signal. This means, of course, that this type of impurity, and possibly others,

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[290] G. Eigenmann, *Helv. Chim. Acta* **46**, 298 and 855 (1963).

[291] L. D. Rollmann and R. T. Iwamato, *J. Am. Chem. Soc.* **90**, 1455 (1968).

[292] V. E. Kholmogorov, *Opt. Spectry.* (*USSR*) (*English Transl.*) **14**, 158 (1963).

[293] J. M. Assour and S. E. Harrison, *J. Phys. Chem.* **68**, 872 (1964).

are likely to be present in most samples upon which physical measurements have been determined and that the results may be affected in consequence. ESR spectra may therefore be a worthwhile quality criterion for phthalocyanines for which pure samples are critical.

In the dyestuffs field, a valuable contribution towards an appreciation of the causes of phototropy and aggregation has derived from a study of the absorption spectra of various copper phthalocyanine sulfonic acids. Phototropy is due to a light-induced reversible one-electron reduction of the complex (supported by ESR spectra) and can be related to the degree of aggregation.[294] The 4-substituted sulfonic acids are shown to be much more highly aggregated than the 3-isomers and this is ascribed to the reduced physical hindrance to stacking. The effect is so marked with $CuPc(4\text{-}SO_3H)_4$ that although water-soluble this product has practically no substantivity for cellulose.[295]

VIII. Prospects

The development of phthalocyanine chemistry is strongly influenced by technological requirements. Originally, dyestuffs technology was the dominating influence; the entry into newer areas such as semiconductivity,[296] high-temperature lubrication,[297] specialized polymers, and catalysis has led to closer studies of both the chemistry and the physical properties. This trend will certainly continue within such new fields with even further impetus when any commercial exploitation is achieved. Reference to patents in the first three of the above four areas has already been made. In the field of catalysis, most recent work is concentrated on oxidation and autoxidation[1, 298] with patents covering the catalytic oxidation of mercaptans in petroleum distillates.[87, 299]

An attempt has been made in earlier sections of this chapter to highlight two important regions of phthalocyanine chemistry in which advances would lead to considerable progress in both dyestuff and nondyestuff fields. First, only limited work has been done aimed specifically at the effect of extraplanar ligands and changes in oxidation state of transition metal phthalocyanines.[300] A fuller understanding of these

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[294] G. Eigenmann and F. Kern, *Textil-Rundschau* **16**, 167 (1961); G. Eigenmann, *Helv. Chim. Acta* **46**, 298 (1963).

[295] J. Wegmann, *Melliand Textilber.* **48**, 59 (1967); **49**, 687 (1968).

[296] C. J. Hoffmann, *Quart. Rev.* (*London*) **18**, 113 (1964).

[297] H. H. Krause, S. L. Cosgrove, and C. M. Allen, *J. Chem. Eng. Data* **6**, 112 (1961).

[298] H. Kropf, *Ann. Chem.* **637**, 73, 93, and 111 (1960); B. D. Berezin and A. V. Loshchilova, *Kinetika i Kataliz* **8**, 592 (1967); *CA* **67**, 76585 (1967).

[299] Universal Oil Products, *BP* 991,711; 1,108,973.

[300] J. H. Weber and D. H. Busch, *Inorg. Chem.* **4**, 472 (1965).

overlapping factors should not only produce interesting new metal complexes, but could lead to important ramifications with respect to the chemistry of related natural products and biological processes. A new approach might come from an extension of ligand-exchange reactions to include the use of alternative metal derivatives, such as carbonyls, as starting materials, as has recently been applied with certain porphyrins.[301]

The second point concerns solvent solubility. Following from the previous limited discussion of physical properties, it is clear that the more ready production of characterizable solvent-soluble phthalocyanines is important, if only as a means of purification by milder techniques, e.g., chromatography, rather than sublimation. Technical coloration processes should also benefit.

Most of the present dyestuff and pigment technology is based on copper phthalocyanine and its substitution products. Alternative metal phthalocyanines are not considered to be attractive pigments,[1,302] but even if their defects cannot be overcome by, e.g., improved processing techniques, they still should not be dismissed as similarly useless in the dyestuffs field, especially when taking into account the point made earlier about further substitution on the central atom. This approach and the possibility of alternative related macrocycles being exploited probably have the highest potential in the perpetual search for more hyposochromic products based on porphyrin-type macrocycles.

The discussion in this chapter has been deliberately limited to tetrabenztetraazaporphins, but other related porphins should at least be mentioned. The most significant advances have come from the work of Linstead's school on azaporphins[303] (although these have limited interest as dyestuffs[304]) and extensive work on other metalloporphyrins, recently summarized by Falk.[305] Much of the stimulus for the latter comes, of course, from natural product work, particularly in the vitamin B_{12} field.[306] Although it has been suggested earlier that information derived from a study of phthalocyanine chemistry might be applicable to natural products, it is not impossible that, with all the current advances, the reverse might also apply.

[301] M. Tsutsui, M. Ichikawa, F. Vohwinkel, and K. Susuki, *J. Am. Chem. Soc.* **88**, 854 (1966); E. B. Fleischer and N. Sadasivan, *Chem. Commun.* p. 159 (1967); *J. Inorg. & Nucl. Chem.* **30**, 591 (1968).

[302] Lubs, pp. 594–596.

[303] J. A. Elvidge, *Chem. Soc. (London), Spec. Publ.* **4**, 28 (1956).

[304] H. France, W. O. Jones, and ICI, *BP* 686,395; 689,387–9; W. F. Beech, H. France, N. H. Haddock, H. T. Howard, A. Parkinson, J. C. Woods, and ICI, *BP* 749,692; 750,240.

[305] J. E. Falk, "Porphyrins and Metalloporphyrins." Elsevier, Amsterdam, 1964.

[306] R. L. N. Harris, A. W. Johnson, and I. T. Kay, *Quart. Rev. (London)* **20**, 211 (1966).

CHAPTER V

PHTHALOGEN DYESTUFFS

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LEVERKUSEN, WEST GERMANY

I. Introduction

Starting in 1951, Farbenfabriken Bayer AG (=FBy) of Germany placed on the market under the group name of Phthalogen a number of dyestuff developers allowing the coloration of textiles *by synthesis of heavy metal phthalocyanines on the fiber*—preferably on cotton and regenerated celluloses. Since then, these "Phthalogen" dyestuffs have increasingly been finding worldwide application for the production of very fast, and in some cases exceptionally brilliant blue and green shades.

The good fastness properties of the copper, nickel, and cobalt phthalocyanines produced with Phthalogens on the fiber are due to the dyeings only consisting of unsubstituted, or, in a preplanned manner—especially for controlling the color shade—substituted, metal phthalocyanines. In contrast thereto, all dyeings achievable on the fiber with the previously known water-soluble phthalocyanine dyestuffs[1] consist of *substituted*

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[1] See *CSD II*, p. 1134; Ullmann, Vol. 13, p. 714.

metal phthalocyanines whose (mostly 2 to 4) substituents are *unavoidably* necessitated by the different methods in which their permanent or only temporary solubility in water was caused. These substituents, such as sulfonic acid or sulfonamide, substituted methyl, or disulfide groups, always have a negative influence on the fastness properties of the dyeing.

The progressive development of the Phthalogen range[2, 2a] also rendered it possible to achieve, besides the brilliant blue to green shades, a wider range of shades including dark navy blue and black and to open up for the Phthalogens applications in the fast dyeing of yarns and more recently also for the dyeing of polyamide fibers.

The difficulties of dye synthesis on the fiber can be readily recognized by the fact that of all methods proposed in the course of many decades *only two* have been accepted; however, these two have been successfully employed to a great extent: (1) the more than 100-year-old method of production of aniline black (in the fiber-protecting variants) from aniline derivatives and aminodiphenylamine by oxidation on the fiber; and (2) the production of water-insoluble azo dyestuffs from diazonium compounds of aromatic amines by coupling with naphthols, especially those of the Naphthol AS range.

These two methods of synthesis meet the essential requirements for a synthesis on the fiber, in which the latter has to serve as a little corrosion-resistant reaction vessel:

(a) It must be possible to carry out the synthesis in a predominantly aqueous medium without any pressure, which means at temperatures around 100°.

(b) The reaction velocity of the dye formation must, just as the dye yield on the fiber, be as high as possible.

(c) The synthesis components and also the auxiliaries and the by-products, if any, must not to any appreciable extent damage the fiber.

This results in the discrepancy that the components should show, on the one hand, as great a reactivity as possible, but also, on the other, sufficient stability towards the dyeing media, especially water.

In the synthesis of azo dyes, which are also frequently produced on a large commercial scale at temperatures of about 0° to 10°, it was possible to solve the problem mentioned partly by keeping the dyebaths cool, and partly by reversible chemical stabilization of the diazo components.

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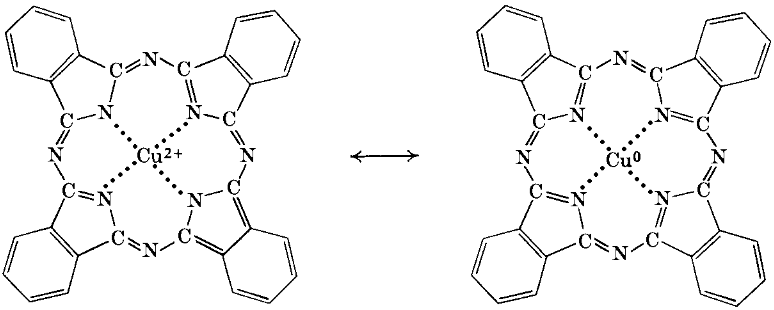
[2] F. Baumann, B. Bienert, G. Rösch, H. Vollmann, and W. Wolf, *Angew. Chem.* **68**, 133 (1956).

[2a] W. Wolf, E. Degener, and S. Petersen, *Angew. Chem.* **72**, 963 (1960).

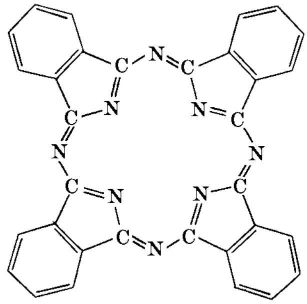
How it became possible to produce on the fiber metal phthalocyanines, for the commercial production of which in most cases temperatures of 200° and higher are employed, will be explained in the following sections.

II. The Two Structure Types of Phthalogen Dyestuff Developers and the Routes to Their Discovery

To make it easier to understand the following description, it is advisable first to give a short explanation of our present-day ideas regarding the structure of the metal(II) phthalocyanines. We consider the latter, for example CuPc (Pc = phthalocyanine), in the light of the theory of mesomerism, *as a resonance system* between the limiting forms (I) and (II).



(I) CuPc (II)



(III) DehydroPc

Structural formula (I) contains divalent copper and an *asymmetric* bond distribution in the ring system (including the benzene nuclei), as considered by the past-master of phthalocyanine chemistry, R. P. Linstead.[3]

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[3] In accordance with formula (I). It shows the same bond distribution as it had been postulated by William Küster for the analogously composed porphin dyes of the blood and of chlorophyll [*Hoppe-Seylers Z. Physiol. Chem.* **82**, 469 (1912)].

The structural formula (II), however, contains zero-valent copper and an entirely symmetric bond distribution in the ring system, as was already considered possible 25 years ago by Endermann.[4] The 16-membered internal ring of (II), which consists of a sequence of eight –C=N– groups, is planar and may be considered a quasi-aromatic system.

The metal-free ring system (III) [rationally to be designated "cyclotetra(iminoisoindolenine)"] was called "*dehydrophthalocyanine*" by Patterson and Capell[5] and included in their "ring index" as a ring system, although the compound was still unknown at the time.[5] In the following we shall also use this designation for (III) (written in abbreviated form: *DehydroPc*). About 15 years ago we were able for the first time to produce DehydroPc, although only with a purity of about 90%, and still containing about 10% metal-free phthalocyanine (=H_2Pc). For its production, see Section II,C and Baumann *et al.*[6]

DehydroPc (III) is obtained in the form of lemon yellow needle-shaped prisms which show the same crystal habit as the simultaneously present green-blue needles of H_2Pc. The almost equally difficult solubility of the two compounds has so far entirely prevented the production of pure (III). While (III) dissolves readily, with a slightly yellow coloration, at room temperature in methanol after the addition of some concentrated hydrochloric acid, it is rather rapidly split hydrolytically with brightening of the solution until finally phthalimide is separated. When heated with dimethylaniline with an addition of hydroquinone, (III) is gradually reduced to the blue H_2Pc.

A. Derivation of the Phthalogen Structures from Dehydrophthalocyanine (DehydroPc)

Considered more closely, the formula (III) of DehydroPc proves, however, to be a key structure for the chemistry of all Phthalogen dyestuffs.

(1) In coordinately hexavalent metal complexes, for example of copper, nickel, cobalt, and iron, the strongly basic DehydroPc is capable of functioning as a coordinately tetrabonded complex ligand enclosing the metal in the form of a ring. The structural formula (IV) shows the ring system (=III) in perspective view and indicates that the *metal* in such complexes carries *two further ligands L and L′* in coordinate linkage, the direction of these two bonding forces being perpendicular to the plane of

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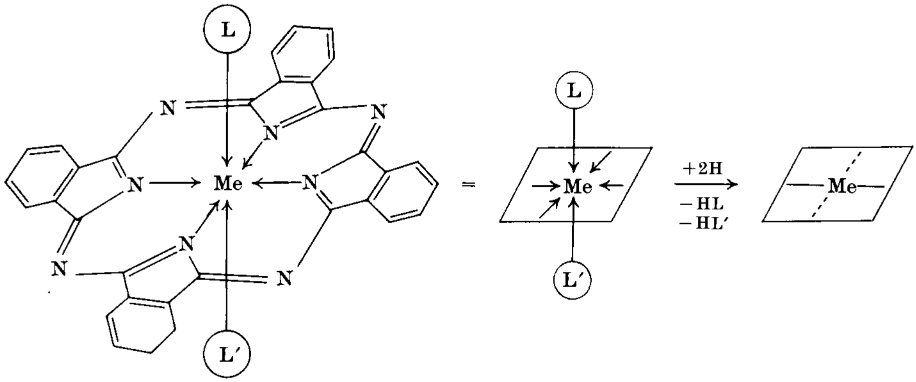
[4] F. Endermann, *Z. Physik. Chem., Abt. A*, **190**, 129 (1942).

[5] A. M. Patterson and L. T. Capell, "The Ring Index," 2nd ed., No. RRI 7541, p. 1196. 1960.

[6] See Baumann *et al.*[2, p. 138].



(IV) (IVa) (V)

the ring system (upwards and downwards). The ring system itself is thus no longer considered perfectly planar, but slightly bent fourfold (at the four nitrogen atoms which combine two isoindolenine rings), alternately upwards and downwards.

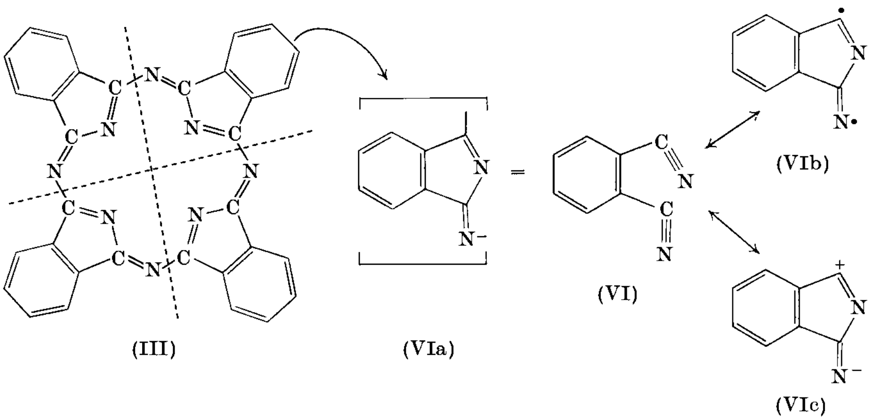
The structural formula (IVa) is only a simplified representation of the structure (IV) *showing the general structural principle of Group 1 of the Phthalogen dyestuffs,* described in the following section.

The transition from (IVa) (=IV) to the metal(II) phthalocyanine (V), as formulated above, shows that for this purpose only *two reduction equivalents* are necessary and that in this case 1 mole each of HL and HL′ are split off.

The *ligands L and L′* may have both acidic and basic character. We know well-defined complexes of the general structure (IV) in which L *and* L′ are chlorine or bromine, a methoxy or amino group, as well as such complexes in which one of the ligands is acidic and the second basic. Also, in certain cases, ligands *can be exchanged* with other ligands —depending on the kind of central metal atom and ligands. The ligands have hardly any influence on the natural color of the complexes. The natural color is substantially determined by the kind of metal atom, and so is the stability with respect to heat and hydrolyzing agents. If pure (primarily MePc-free) complexes of the structure type (IV) are brushed on paper and tested for their color, the natural colors of the cobalt complexes are strongly yellow and orange-yellow to brown-yellow; of the iron complexes, yellow-brown to olive; of the nickel complexes, a washed-out brownish red; and of the copper complexes, a washed-out yellowish gray. The stability properties mentioned also decrease in about the same sequence.

In all cases, however, the ligands determine the solubility properties of the complexes and thus (but not *only* thus) their suitability as Phthalogen dyestuffs.

(2) As the dotted separating lines in formula (III), as repeated below, show, DehydroPc consists of four equal, divalent 3-iminoisoindolenine radicals. Such a "block" of structure (VIa) is, however, nothing else but a highly reactive mesomeric limiting form of the phthalonitrile (VI).



It is virtually of no importance here whether this reactive form is formulated as a dipole (VIc)[7] or as a diradical (VIb). In any case, only a very short-lived reactive form, which tends towards stabilization with a high-energy gradient, is involved here.

In the presence of acidic and, especially, of alkaline catalysts, this stabilization tendency of the phthalonitrile favors either the formation of polymerization products or of monomeric, relatively stable addition products:

(a) The synthesis of metal-free Pc from phthalonitrile by heating with sodium methylate in amyl alcohol, which in the ultimate analysis appears to be a "cyclotetramerization" accompanied by a reduction with absorption of two hydrogen atoms, has long been known.

(b) The knowledge that polar compounds of the general structure H^+—R^- can be added to phthalonitrile to form 1-substituted 3-iminoisoindolenines of structure (VII) is of more recent date and is primarily based on results of research work done in the laboratories of Farbenfabriken Bayer.

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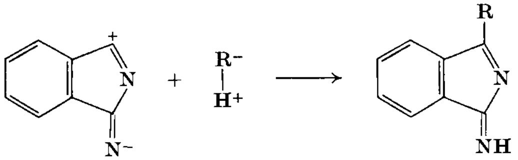
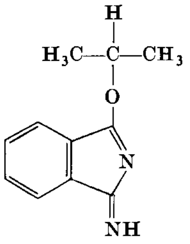
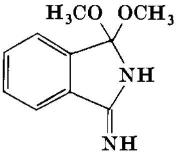
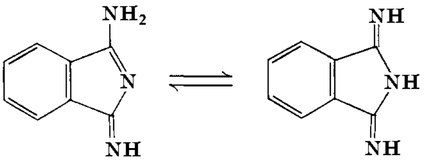
[7] An opinion advocated long ago by N. H. Haddock [see *J. Soc. Dyers Colourists* **61**, 70 (1945)].


(VIc) (VII)

The addition products of low alcohols (C_1–C_3), which are formed in the presence of the corresponding sodium alcoholates, as well as the addition products with ammonia, primary, and secondary amines, are of special interest. Phthalonitrile gives with isopropanol, for example, the 1-isopropoxy-3-iminoisoindolenine (VIII), with methanol the 1,1-dimethoxyisoindolene (IX), and with liquid ammonia (at temperatures around 100° under pressure) the 1-amino-3-iminoisoindolenine (Xa), which is tautomeric with 1,3-diiminoisoindolene (Xb).[8] Such reactions are described in more detail in Section C,2. It should, however, be mentioned here that the tautomer pair (Xa)–(Xb) is the most important product of the Phthalogen dyestuff range.

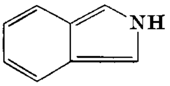

(VIII)

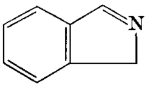

(IX)

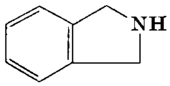

(Xa) (Xb)

It is advisable to subdivide the Phthalogen dyestuffs into three groups, which in the following section will be characterized more closely as groups 1, 2, and 2a. (See Table I.)

[8] The names of compounds (VI) to (X) described here are derived from the parent ring systems A = isoindole, B = isoindolenine, and C = isoindolene (=dihydroisoindole).


A

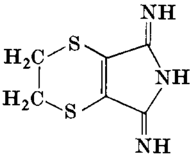

B


C

The two structural isomers A and B have so far been unknown in isolated form. The formulas A, B, and C show the isoindole skeleton as recommended by IUPAC. We do not use this in the text because, in connection with phthalocyanine formulas, the symmetric representation of the N-containing five-membered ring appears to be more advisable.

Group 1 comprises besides the metal–DehydroPc complexes (with Cu, Ni, or Co as the central metal atom), a novel, deeply green-blue $Co^{III}Pc$ complex which can be easily developed without any addition of a reducing agent. Regarding their structure, all Phthalogen dyestuffs of this group are very closely related to the metal phthalocyanines. The three first-mentioned representatives of this group no longer require for their development anything other than a reducing agent.

Group 2 only comprises *metal-free* 1,3-diiminoisoindolenes: the unsubstituted product of formula (X) as well as its 5-phenyl and 5-methyl derivatives. Some commercial types of this group contain besides (X) varying quantities of the analogously constituted sulfur-containing 1,3-diimino-4,7-dithia-4,5,6,7-tetrahydroisoindolene (XI), which will be described in more detail in Section C,4. All Phthalogen dyestuffs of Group 2 *must* be applied to the fiber *together* with the correct quantity of a heavy metal donor. Soluble heavy metal complexes especially suitable for this purpose are the commercial products Phthalogen K and Phthalogen Ni (see Section III).



(XI)

To simplify the use of the Phthalogen types of Group 2 and to exclude dosing mistakes, the Phthalogen range also contains ready-formulated mixtures of 1,3-diiminoisoindolenes *with* (under economic conditions) optimum quantities of the metal donors Phthalogen K or Ni. Such mixtures are characterized in the trade names of the appropriate Phthalogen dyestuffs by the suffix *M* in the last place. *Subgroup 2a* of the Phthalogen dyestuffs (see Table I) comprises exclusively such mixtures.

The following sections (B and C) deal with the Phthalogen Groups 1 and 2 in chronological sequence of their discovery, as far as possible in accordance with the application dates of patents granted. This simultaneously results in a brief history of discovery.

B. PHTHALOGEN DYESTUFFS OF GROUP 1 (DEHYDROPC–METAL COMPLEXES)

In the course of work for determining the best operating conditions for the production of CoPc by the phthalic anhydride urea fusion process[9] with cobalt chloride, with an addition of ammonium molybdate as a catalyst[9a] and of some nitrobenzene for suppressing foam formation,[10] which means by the well-known process for the production of heavy metal phthalocyanines, Baumann and Bienert observed that besides the CoPc expected, substantial quantities of well-crystallized, strongly orange-yellow to yellow cobalt complexes were formed which were easily soluble in various solvents and which had so far been unknown.[11] It was furthermore observed that these cobalt complexes on heating to elevated temperatures, but also after addition of relatively strong reducing agents at room temperature, are converted into CoPc.[12] The introduction of the patent specification according to Baumann and Bienert[12, p.2, lines 15–54] contains the following passage: "The special importance of the new process for technology consists in that it allows the production of cobalt phthalocyanine on a stratum and in particular on the fiber." Also, the practical examples 8 and 9 of this patent specification illustrate methods for applying and developing these cobalt phthalocyanine developers on cotton as they have later proved advisable for most Phthalogen dyestuffs.

In more detailed investigations, it was recognized that by the above-described process,[11] dependent on temperature *differences* of 30–50°, two different well-defined cobalt complexes of the same kind, but with greatly different solubility properties, are obtained.

At temperatures around 160–175°, there is at first formed, besides CoPc, a complex which is free from chlorine, crystallizes in relatively large orange-yellow rhombs, and is easily soluble in glacial acetic acid, but insoluble in alcoholic sodium hydroxide solution. Today we ascribe to this complex the *structure* (XII) *of an amido–diiminoisoindolino–DehydroPc–cobalt complex.*

At elevated temperatures of the production melt, up to the boiling point of nitrobenzene, (XII) gradually converts itself into the chloro complex (XIII), while the quantity of the still available CoPc also greatly decreases. The CoPc can be caused to disappear entirely by adding a small quantity of ammonium nitrate, chloro–diiminoisoindolino–DehydroPc–cobalt complex (XIII) being obtained[13] in yields around

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[9] M. Wyler and ICI, *BP* 464,126; 464,673 (concerning increasing the yield by adding boric acid).

[9a] A. Riley and ICI, *BP* 476,243 (concerning high yield increase by adding ammonium molybdate).

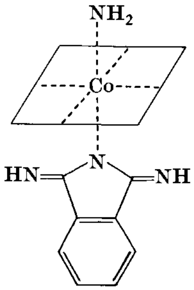
[10] ACNA, *FP* 877,464; 888,479.

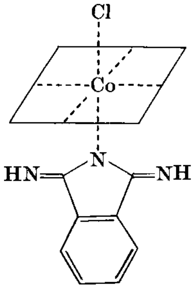
[11] F. Baumann, B. Bienert, and FBy, *DBP* 839,939.

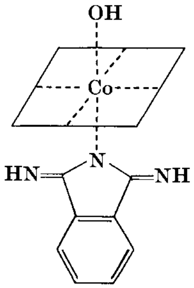
[12] F. Baumann, B. Bienert, and FBy, *DBP* 861,300 (claim 2 of this patent especially protects the production of CoPc on the fiber in the presence of reducing agents).

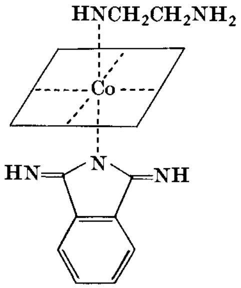
[13] F. Baumann, B. Bienert, H. Vollmann, and FBy, *DP* 855,710.

90% of the theory and in virtually pure form. The chlorine atom required for the conversion of (XII) into (XIII) originates from the cobalt chloride used and is still present in the reaction mixture in the first reaction phase —when (XII) is formed—in the form of ammonium chloride.


(XII)


(XIII)


(XIV)


(XV)

The chloro complex (XIII) separates during manufacture in the form of small brownish yellow prisms and is almost insoluble in all organic solvents, even in boiling nitrobenzene. In contrast to the basic amido complex, the chloro complex is also insoluble in glacial acetic acid, but gradually dissolves in methanolic sodium hydroxide solution, while being converted into the hydroxo complex (XIV). From the chloro complex (XIII), it is also possible, vice versa, to arrive again at the amido complex (XII) by introducing ammonia in methanolic suspension.

Of particular interest is the *ethylenediamino–diiminoisoindolino–DehydroPc—cobalt complex* (XV), which is obtained in good yield from (XIII) or (XIV) in methanolic suspension by heating with ethylenediamine. It not only dissolves in glacial acetic acid [as also does (XII)], but also in 3% aqueous acetic acid. The complex (XV) is our commercial product *Phthalogen Blue JB*.

While in the complexes (XII) to (XV) the upward-written ligands, as has just been shown, can easily be exchanged with one another (and also by other ligands), the greater bond stability of the diiminoisoindolino ligand is surprising. Only under the influence of strong reducing agents is this ligand also eliminated in solution [for example, in dilute glacial acetic acid, starting from (XV)] at temperatures around 0° with the velocity of an ion, like that of the other univalent ligands, with CoPc formation. It is found in the filtrates when the CoPc is separated and can easily be isolated from these filtrates as the difficultly soluble nitrate of the base (Xa) by adding ammonium nitrate.

The surprisingly greater adhesion of the diiminoisoindolino ligand may be ascribed to the formation of hydrogen bridges between the two imide groups of the ligand and two –C═N– bonds of the DehydroPc ring.

While the patents quoted in refs. (11) and (12) opened up the Phthalogen process of dyeing and printing, they did not yet offer any possibility of also producing on the fiber the more brilliant, more greenish blue of the *copper* phthalocyanine. Numerous attempts at obtaining complexes analogous to the cobalt compounds described above in a urea melt with phthalic anhydride and an addition of copper or nickel salts remained without success. We now know the reason: copper and nickel complexes of the general structure (IV) are far less thermostable than the analogous cobalt complexes; they decompose at temperatures around 100–120°, forming metal phthalocyanines.

Crude copper and nickel complexes showing properties similar to those of the above-described DehydroPc–cobalt complexes were obtained in the laboratories of Farbenfabriken Bayer AG (by Bienert) at the beginning of 1949 by stirring 5–6 moles of phthalonitrile in lower alcohols which adding strong alkali at 20–70°, provided—simultaneously or after short preliminary heating—1 mole of a copper salt was added. The crude suspensions of the reaction products thus obtained yielded on cotton, when processed and developed into printing inks with an addition of the auxiliaries mentioned in the patent,[12] deep and brilliant blue shades of pure CuPc.[14]

Somewhat later, it was also possible to obtain, especially well after the 1-amino- and 1-alkoxy-3-iminoisoindolenines described in Section 3 had been discovered and could be used instead of phthalonitrile in the above-described reaction, *DehydroPc–copper complexes and DehydroPc–nickel*

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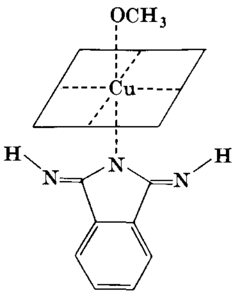
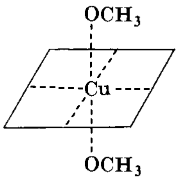
[14] See examples 7(a), 7(b), and 8 in *USP* 2,683,643.

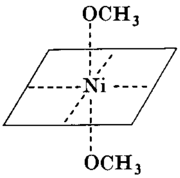
complexes in uniform, crystallized form. Structural formulas (XVI)–(XVIII) symbolize the three most interesting products of this series:



(XVI)



(XVII)



(XVIII)

(XVI) is methoxo–diiminoisoindolino–DehydroPc–copper complex, an essential constituent of *Phthalogen Brilliant Blue IF3GK*. (XVII) is the bis(methoxo)–DehydroPc–copper complex. (XVIII), bis(methoxo)–DehydroPc–nickel complex, is an essential constituent of *Phthalogen Turquoise IFBK*.

The copper complex (XVI) is obtained in good yield from 1,3-diiminoisoindoline heated with copper acetate in a molar ratio of about 5:1 during 15–20 hours in methanol under reflux with simultaneous removal of the ammonia formed. It is obtained thereby in slightly yellowish gray, microscopically small needles.

If the same mixture is heated for a considerably longer time (up to about 72 hours), then, besides (XVI) and a small quantity of finely crystalline CuPc, *conspicuously larger*, sturdy, violet-brown rhombs are formed, which quickly deposit when the reaction mixture is diluted and which finally yield by repeated flotation with methanol a pure bottom deposit of the sturdy rhombs. This product [yield in addition to (XVI) about 10–15%] proved to be a pure *dimethoxo–DehydroPc–copper complex* of structure (XVII). We had obtained the *same* complex earlier, if only in small-crystalline form, by quite a different method. It is also obtained by allowing bromine to act at 60–70° on copper phthalocyanine finely suspended in methanol and aftertreating the highly bromine-containing, unstable primary product with methanolic ammonia.

The last-mentioned method of production is only a special case of the more broadly applicable method of obtaining DehydroPc–metal complexes of the kind described from the corresponding metal phthalocyanines by reaction with suitable oxidizing agents in media which have no hydrolyzing action. We have described such reactions not only in patent examples but also in a publication[15]; the structural conceptions used there may, however, be considered superseded.

We can now summarize: There are *three methods* for the production of coordinately hexavalent DehydroPc–metal complexes:

(1) The synthesis from phthalonitrile or 1-substituted 3-imino-isoindolenines with metal salts in solvents at temperatures of mostly below 100°.

(2) The conversion of metal phthalocyanines into DehydroPc complexes by suitable oxidizing agents, such as halogens in alcohols, or nitric acid, also preferably below 100°.

(3) Only suitable for the production of *cobalt* complexes of this kind: the interaction of phthalic anhydride in a molybdate-catalyzed urea melt with cobalt salts—preferably with addition of nitrobenzene—at temperatures of 170–220°.

Regarding these subjects it should still be mentioned that the methods of producing MePc developers as mentioned under (1) and (2) were also found—*independently* of our above-described work—in the laboratories of *Du Pont* (*U.S.*). We know about 20 U.S. patents of that company—with application dates from October 1951 to 1957—which concern these fields. The essential contents of these patent specifications were later discussed in two publications by the inventors C. J. Pedersen[16] and R. A. Brooks *et al.* [16a]

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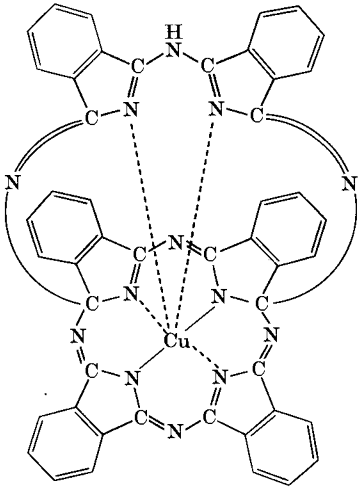
[15] See Baumann *et al.*, footnote 2, p. 145.

[16] C. J. Pedersen, *J. Org. Chem.* **22**, 127 (1957).

[16a] R. A. Brooks, J. G. Burt, B. F. Skiles, and M. S. Whelen, *J. Org. Chem.* **24**, 3 (1959). This work concerns the production of a CuPc developer of the composition $C_{48}H_{25}N_{13}Cu$ which, on reduction, yields CuPc and for whose structure the adjacent formula was presented as conceivable.



It is certain that most of the heavy metal complexes of phthalocyanine developer character described by the researchers mentioned, on the basis of their method of production and their essential properties and not least on the basis of our investigations, *are to be considered as belonging to the same class of compounds* we call today "coordinately hexavalent DehydroPc–metal complexes." From the patent points of view, they were therefore covered, partly with a view to their production, but without any exception with a view to their application, by prior patent rights of Farbenfabriken Bayer AG[17] and could therefore, with the exception of an only temporarily (1954) offered CuPc developer, Lusane Brilliant Blue, not be placed on the market by Du Pont.

C. PHTHALOGEN DYESTUFFS OF GROUP 2 (METAL-FREE 1,3-DIIMINOISOINDOLINES AND THEIR MIXTURES WITH HEAVY METAL DONORS)

This group includes as the prototypes *1,3-diiminoisoindoline* (*Xb*) which has already been mentioned, or its tautomer, *1-amino-3-imino-isoindolenine* (*Xa*). This most important and at the same time most simply structured Phthalogen is on the market under the name of *Phthalogen Brilliant Blue IF3G*. It was discovered, starting from phthalonitrile, in the very remarkable roundabout way described below:

F. Mühlbauer (Ludwigshafen works of IG) had already communicated in 1939 in IG internal reports that he had obtained from phthalonitrile by heating with copper salts in formamide difficulty soluble, orange-yellow to red-brown copper complexes which at high temperatures partly yielded CuPc. In accordance with a later description of this work in a FIAT report,[18] the products thus obtained were considered to contain 1 Cu for 2 moles of phthalonitrile.

In 1948 W. Wolf and, a short time later, also G. Rösch (Farbenfabriken Bayer, Leverkusen) again investigated the influence of Cu^1 and

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[17] Because there was no operative German patent office, on August 25, 1949, Farbenfabriken Bayer AG applied for a patent in Great Britain. At that time only one application was made to avoid overburdening Bayer's foreign exchange. Later on, this application had to be subdivided into several applications for reasons required by the patent law. In the United States the subdivision led to the following six applications:

(a) F. Baumann, B. Bienert, G. Rösch, and FBy, *USP* 2,683,643 (process of dyeing and printing and compositions therefor).

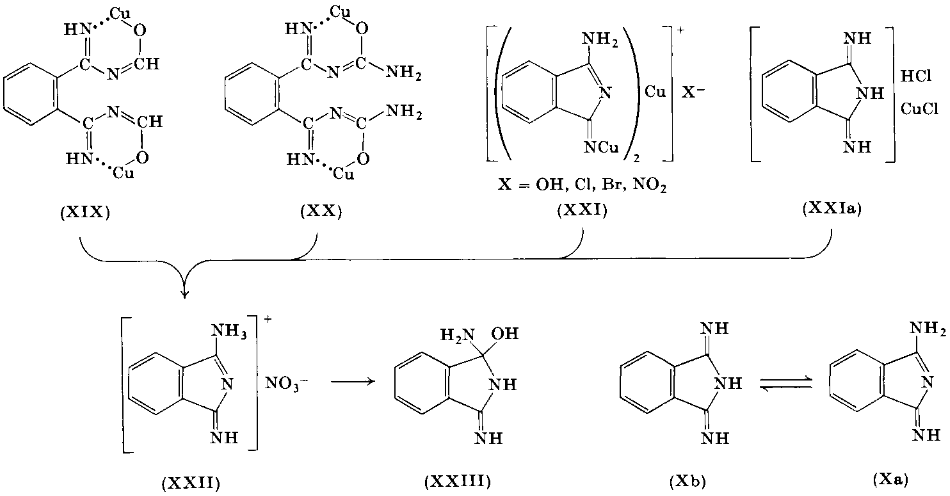
(b) G. Rösch, W. Wolf, H. Vollmann, and FBy, *USP* 2,727,043 (1-Amino-3-imino-isoindolenine).

(c) G. Rösch, W. Wolf, H. Vollmann, and FBy, *USP* 2,739,151 (process for the production of isoindolenine derivatives).

(d) *Idem. USP* 2,739,154
(e) *Idem. USP* 2,739,155
(f) *Idem. USP* 2,752,346
Additional claims and partly new examples and texts of the specification are mentioned.

[18] FIAT 1313, Vol. III, pp. 344, 342, and 345.

Cu^{II} salts on phthalonitrile in various molar ratios under conditions not yet leading to CuPc formation. Analytically pure, greenish-yellow to red-brown copper complexes[19] were thus isolated for the first time which contained 2, 1.5, to only 1 gram-atom Cu per mole of dinitrile. In accordance with their elementary composition and their properties, the structures (XIX) to (XXIa) should be ascribed to them:



In accordance with observations made by G. Rösch, experiments aiming at decoppering such complexes by means of 80–20% nitric acid always yielded ample quantities of a colorless compound which was very difficultly soluble in water and methanol and which Rösch recognized to be the *mononitrate* (XXII) *of 1-amino-3-iminoisoindolenine* (*Xa*).[19]

Addition of 1 mole of concentrated sodium hydroxide solution to about 20% ice cold aqueous suspension of this nitrate leads to temporary dissolution and then to the separation of colorless, glossy needles in the form of a thick crystal paste. The product is the *hydrate of 1,3-diimino-isoindolene* (XXIII), whose solubility in cold water is still relatively low, but shows a steep rise from 30° onwards; at 35–40° it reaches complete miscibility with water in any proportion. The base hydrate (XXIII) requires very mild drying conditions for removing the adhering water. Only then will it be possible to remove at higher temperatures the

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[19] Experimental examples for the production of the phthalo-bis(formamidine-copper) of structure (XIX) with a yield of more than 90% of the theory and for its conversion into the nitrate (XXII) by means of nitric acid are found in Baumann *et al.*[2, p. 136].

hydrate water bound in the crystal. The crystals then lose their gloss and yield the (hygroscopic!) anhydro base (Xb), tautomeric with (Xa).

The knowledge thus gained about the *not at all predictable* properties of the nitrate (XXII), of the hydrate (XXIII), and of the anhydro base (Xa) = (Xb) was of fundamental importance for finding other technically and economically useful production methods for diiminoisoindolines. Two of these methods, as well as several methods of more scientific interest, will now be discussed in more detail.

1. *The Nitrate Process*

The "nitrate process" found by W. Wolf is based on attempts at separating as a difficultly soluble nitrate [(XXII), see above] the diiminoisoindoline (derivative?) *potentially*[20] occurring in a molybdate-catalyzed urea phthalic anhydride melt by adding about 1 mole of ammonium nitrate. The first such experiments succeeded in the desired sense without any hindrance and supplied nitrate yields higher than 90% of the theory.

Subsequently, however, a second operation is required to convert the isolated nitrate (XXII) into the 1-3-diiminoisoindoline (X) (see above), on which the commercial products Phthalogen Brilliant Blue IF3G and IF3GM are based. (For the Phthalogen dyestuffs with M as their last suffix see Table I, Group 2a.)

The nitrate process can also be used to convert certain substituted phthalic acid derivatives, such as 4-phenylphthalimide (XXIV), or analogously structured heterocyclic *o*-dicarboxylic acids, such as pyridine-2,3-dicarboxylic acid (XXVI), into the corresponding diiminoisoindolines. The 5-phenyl-diiminoisoindoline (XXV) thus produced commercially is an essential constituent in the Phthalogen Brilliant Green brands IFFB and IFFBM. The Phthalogen range does not include the 4-azadiiminoisoindoline (XXVII). If developed by the Phthalogen process to the corresponding tetraaza-CuPc, it yields, however, brilliant, distinctly redder shades than CuPc.

Hitherto there has not been any satisfactory explanation regarding the mode of action of the catalysts, especially ammonium molybdate,[9] which in the metal phthalocyanine syntheses from phthalic anhydride

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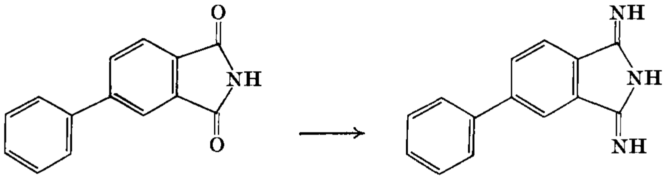
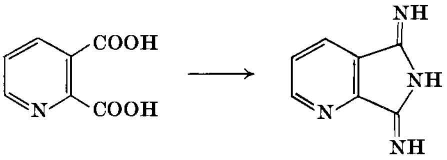
[20] It was known that in such melts 1-oxo-3-aminoisoindoline (XXXI) is obtained and can be isolated in good yield (see N. H. Haddock and ICI, *BP* 520,415). Haddock [see *J. Soc. Dyers Colourists* **61**, 70 (1945)] later mentioned that in this operation (in accordance with the well-known formation of phthalimide) "... it was only possible to isolate the imino-phthalimidine (XXXI) and that it was unknown whether after its formation the reaction (with eventual formation of CuPc) proceeds via phthalodinitrile or a compound of the type diiminophthalimide" (=Xb).



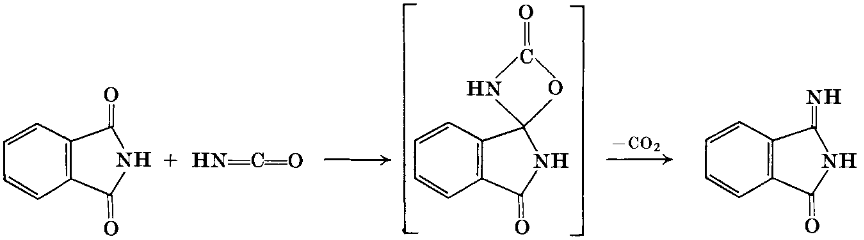
(XXIV) (XXV)



(XXVI) (XXVII)

in the urea melt very considerably accelerate the reaction and increase the yield, and which are also indispensable in the above-described production of diiminoisoindoline nitrates.

In accordance with our observations it is certain that ammonium molybdate takes an active part in the conversion of urea into isocyanic acid + ammonia or into ammonium isocyanate. We assume that it is the very reactive isocyanic acid (XXIX) which, in the ultimate analysis, causes the successive conversion of the two >C=O groups of the phthalimide into >C=NH groups.[21] We may conclude from this that temporarily there is formed from phthalimide (XXVIII) and isocyanic acid (XXIX) an unstable adduct of structure (XXX), from which 1-oxo-3-imino-isoindoline (XXXI) is formed by elimination of CO_2. The oxygen atom



(XXVIII) (XXIX) (XXX) (XXXI)

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[21] The formation of metal phthalocyanines from phthalimide and cyanuric acid, which has long been known, may be considered as supporting this opinion (see V. A. Giambalvo and Interchem. Corp., *USP* 2,375,780).

still present in this product is also exchanged, by a repetition of the same reaction sequence, for an NH group, and thus the diimide (X) is formed, which, in the presence of sufficient ammonium nitrate, is immediately converted into 1-amino-3-iminoisoindolenine nitrate (XXII), also hardly soluble in the 160–200° urea melt. The latter separates in sturdy, almost colorless crystals and, after dilution of the somewhat cooled down melt with methanol or ice water, can be sucked off, washed, and dried.

2. *Monomeric and Polymeric Alkoxy-3-iminoisoindolines and -Isoindolenines from Phthalonitrile and Their Conversion into 1,3-Diiminoisoindoline* (*X*)

The study of the action of alcoholic alkali alcoholate solutions on phthalonitrile at low temperatures[22] (H. Vollmann, 1949) led to surprising and practically meaningful results. It was found that in liquid ammonia (not under pressure) as the reaction medium—which means at temperatures around −33°—the components quickly react with each other, forming colorless, basic adducts (easily soluble in 5% acetic acid) which crystallize well. When methanol or absolute ethanol is used, 2 moles of alcohol add to 1 mole of dinitrile, forming an *1,1-dialkoxy-3-iminoisoindoline* of the formula (*XXXIIa*) or (*XXXIIb*). When isopropanol + sodium isopropylate is used, however, a *mono* alcohol adduct, the *1-isopropoxy-3-iminoisoindolenine* (*VIII*), see Chart 1, is formed.

The described addition of methanol or ethanol may also take place in excess alcohol (instead of liquid ammonia), it being advisable to add more sodium ethylate (approx. 0.5 mole), care being taken that a reaction temperature of 25–30° is maintained by cooling. When the majority of the dinitrile has dissolved, the separation of the dialkoxy compound (XXXII) in colorless, sturdy little crystals begins. The dimethoxyiminoisoindoline (a) is obtained in a yield of about 60% and the analogous diethoxy derivative (b) in a yield of more than 80% of the theory. The difference in the yields is due to the formation of larger quantities of easily soluble polymethoxyiminoisoindolenines [of the general structure (XXXVI)], as can be recognized from the more intense yellow color of the filtrates. This class of compounds will be more closely characterized further on.

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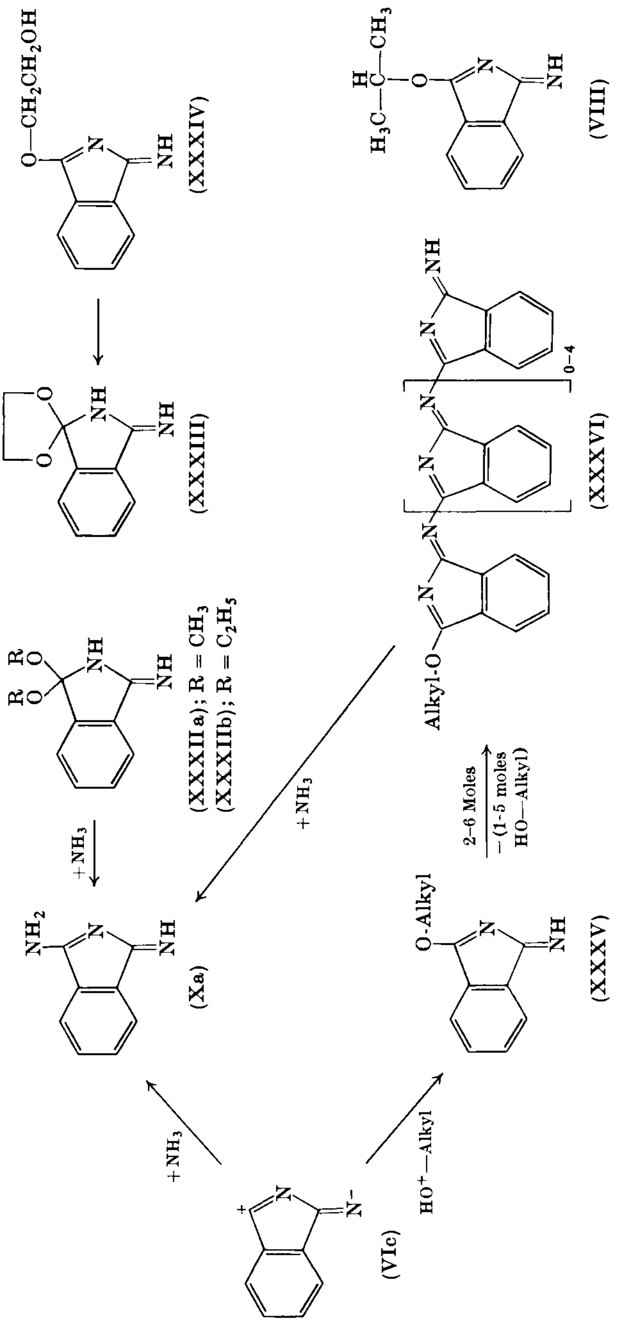
[22] As long as 35 years ago, R. P. Linstead [*J. Chem. Soc.* p. 1024 (1934)] had reacted the same components, but at the boiling temperature of ethanol. An intense yellow-brown solution was formed whose solutes showed no tendency to crystallize at all. They were isolated by evaporating the alcohol, so that a yellow-brown resin remained, which was only characterized by the fact that on heating to elevated temperatures it yielded among other products metal-free Pc. Today we know that the product described by Linstead was a mixture of polymeric alkoxyiminoisoindoline sodium salts.

CHART 1


(Xa)
+NH₃
(XXXIIa); R = CH₃
(XXXIIb); R = C₂H₅
(XXXIII)
(XXXIV)
O—CH₂CH₂OH
+NH₃
(VIc)
+NH₃
HO⁺—Alkyl
(XXXV)
O-Alkyl
2–6 Moles
−(1–5 moles HO—Alkyl)
Alkyl-O
0–4
(XXXVI)
(VIII)
H₃C—C—CH₃
H

The formula scheme in Chart 1 allows the following explanations:

(a) Phthalonitrile, here symbolized in the reactive form (VIc) (see in this connection the structural formulas in Section II,A), reacts with alcohols under the influence of anhydrous alkalis *primarily* with formation of *1-alkoxy-3-iminoisoindolenines of the structure (XXXV)*. It has not so far been possible to isolate these primary adducts, with the exception of the above-described sterically hindered 1-isopropoxy derivatives (VIII).

(b) The still very reactive monoalcohol adducts stabilize either by addition reactions or by condensation reactions. When methanol or ethanol is added under mild conditions, there is preferential formation of the geminal dialkoxyiminoisoindolines (XXXII), which, in isolated form, are rather stable. At least as stable is the adduct of 1 mole of ethylene glycol to phthalonitrile. In this case, the unstable alkoxy form (XXXIV) can stabilize by ring closure to the spiro-dioxolane ring system (XXXIII).

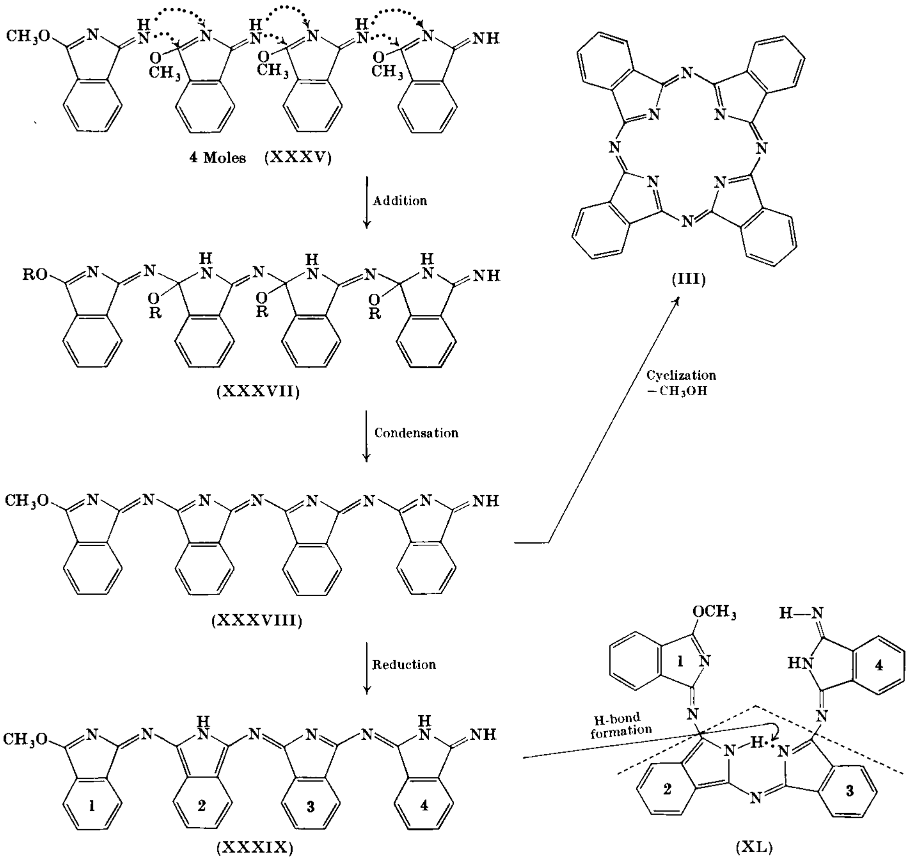
(c) 1-Alkoxyisoindolenines (XXXV) are also to be considered building blocks in the formation of those "polyiminoisoindolenines" which have already been mentioned above as by-products of the production of 1,1-dialkoxyiminoisoindolenines (XXXII). Such polyaddition products and polycondensation products [formula type (XXXVI)], mostly still having alcohol molecules added to the polyazomethine chain, as shown below in the structure example (XXXVII)] become the *main product*, if the reaction of phthalonitrile is carried out with alcohols at higher temperature or with alcohols higher than methanol and ethanol or (/and) in the presence of aromatic compounds such as chlorobenzene.

Structure examples and potential reaction mechanisms are shown by the formula survey on tetrameric links of such series given in Chart 2.

The polymethoxytetra(iminoisoindoline) (XXXVII, R = CH_3) formed in the polyaddition (structural formula upper left) dissolves in alcoholic alkali with deep yellow coloration. It can split off 3 moles of alcohol, one after the other, and—losing its solubility in methanol—convert into the monomethoxy tetra(iminoisoindolenine) (XXXVIII). This compound is also obtained from isolated dimethoxyiminoisoindoline (XXXIIa) by heating in higher boiling solvents, while the methanol distills off. By the same method, using nitrobenzene as the solvent and adding a small quantity of iodine, it is also possible to convert (XXXVIII) by its cyclization to DehydroPc (III) in moderate yield. The simultaneous formation of some H_2Pc (=metal-free Pc) has so far been unavoidable. The properties of (III) and the development of the nomenclature have already been dealt with in Section II.

A characteristic *detection reaction* for all "polyalkoxyiminoisoindole-

CHART 2



nines" dealt with above was discovered by B. Bienert and called by him the "vat reaction." It is the formation of deep blue solutions or precipitations if the products to be tested, in mixtures of water, methanol, and pyridine or dimethylformamide, are mixed, cold or warm, with sodium dithionite, while adding some sodium hydroxide solution. This "vat reaction" has been described in more detail with a view to its application for detection and the differentiation of the "polyisoindolenines."[23] The formation of the deep blue colors is chemically due to a reduction to a *dihydro stage* [in accordance with the transition from (XXXVIII) to (XXXIX)] involving a twisting of the molecule, resulting in a relatively stable resonance system with hydrogen bridge formation, as shown by

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[23] See Baumann *et al.*,[2, p. 140].

formula (XL). For the blue color of this compound, *only the part of the molecule which is below the broken line* in formula (XL) is required.

(d) The most important property common to all alkoxyisoindolenines and alkoxy indolines (both the "monomers" and the "polymers") is their capability of being converted, on exposure to ammonia, into 1-amino-3-iminoisoindolenine or 1,3-diiminoisoindoline [(Xa) $\rightleftarrows$ (Xb)], well below 100° in yields of more than 90%. The above-described knowledge resulted in the following simple *production process for (X) from phthalonitrile*:

Stir phthalodinitrile with about five times the quantity of methanol, saturate the suspension with ammonia, add sodium alcoholate, and slowly heat with further introduction of ammonia until there is no longer any dinitrile and there are no longer any polyisoindolenines. Taking into account the purity of the dinitrile used, the yield is higher than 95% of the theoretical.

(e) *The direct ammonia addition to phthalonitrile* [transition (VIc)–(Xa)] by heating the dinitrile with liquid ammonia under pressure to 140–150° can also be carried out with a high yield.[24] This result (obtained by H. Vollmann in May of 1949) was surprising insofar as it was known that the same operation, if formamide was present, only led to metal-free Pc[25]; and also introducing ammonia gas into boiling solutions of phthalonitrile in benzene or ethanol[26] or even into concentrated xylene solutions at 142° during 6 hours[27] did *not* lead to addition.

That the addition reaction when heating phthalonitrile with liquid ammonia under pressure in the presence of methanol leads in very good yield to (X) was also described in 1952 by Elvidge and Linstead.[28] According to statements by these authors, these papers are based on suggestions of ICI, which already at that time had (probably still incomplete) knowledge of our comprehensive production patent,[17] whose Indian version[29] was already published.

The above-mentioned phthalodinitrile-based processes for the production of diiminoisoindoline (X) were supplemented by A. Pugin by a further ingenious method. Pugin observed that when phthalodinitrile

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[24] G. Rösch, W. Wolf, H. Vollmann, and FBy, *USP* 2,727,043. Example 22. A laboratory experiment in this connection was published by us later on within the scope of a larger scientific paper (see Baumann *et al.*, footnote 2, p. 145).

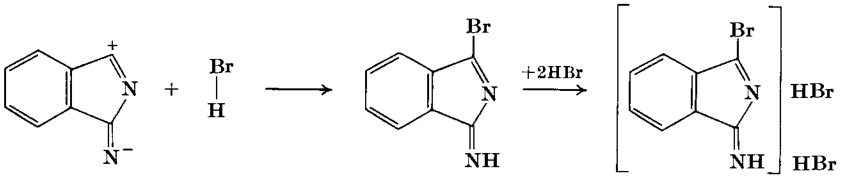
[25] F. Mühlbauer and IG, *DRP* 658,018.

[26] H. D. K. Drew and D. B. Kelly, *J. Chem. Soc.* p. 631 (1941).

[27] Unpublished work of the author (1949).

[28] J. A. Elvidge and R. P. Linstead, *J. Chem. Soc.* p. 5002 (1952).

[29] FBy, *IP* 43,679.

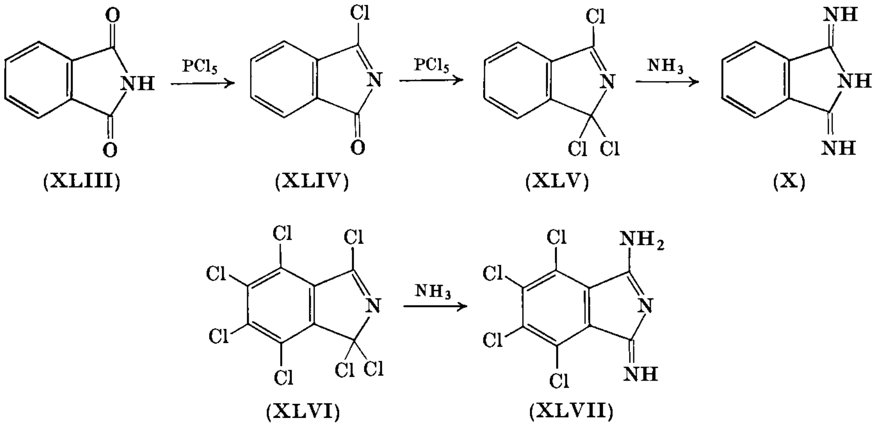


(VIc) (XLI) (XLII)

in glacial acetic acid was exposed to hydrogen bromide in an exothermal reaction (operating temperature up to about 40°), a difficultly soluble addition product of the composition $C_8H_7N_2Br_3$ was obtained, and that this product could easily be converted with ammonia into (X) or with amines into *N*-substituted diiminoisoindolines.[30] It must be assumed that in this process—in accordance with the course of the addition reactions described in Section II,A—first 1-bromo-3-iminoisoindolenine (XLI) is obtained, which, on further exposure to hydrogen bromide, precipitates in the form of the difficultly soluble dihydrobromide (XLII). The reactions take place in good yield. They cannot be applied commercially, if only because of the necessary recovery of the hydrogen bromide.

3. *Diiminoisoindolines from 1,3,3-Trichloroisoindolenine*

The process is based on the knowledge that phthalimide (XLIII) on treatment with phosphorus pentachloride in an inert solvent at temperatures of 100 to 150° yields as the main reaction product the colorless 1,3,3-trichloroisoindolenine (XLV), which distills in vacuum without



(XLIII) (XLIV) (XLV) (X)

(XLVI) (XLVII)

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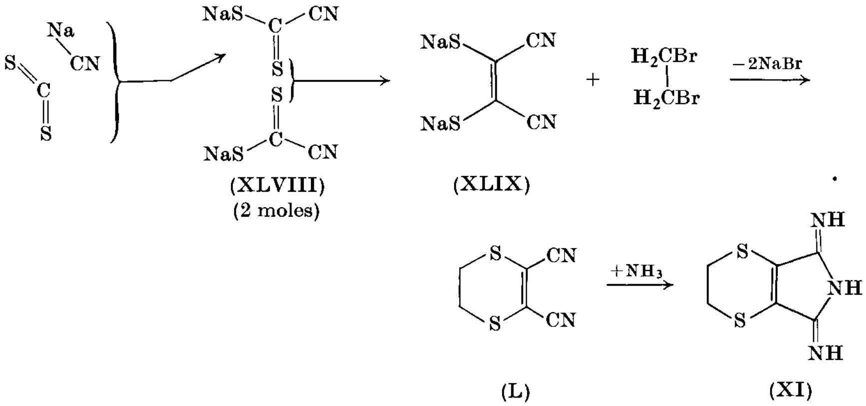
[30] A. Pugin and Gy, *FP* 1,070,912.

decomposition,[31] pure yield about 60%. The reaction takes place via the 1-chloroisoindolenone (XLIV), which can, however, only be isolated in low yield. Although (X) is obtained in good yield,[32] when (XLV) is treated with ammonia, this method is not suitable for commercial production.

While heptachloroisoindolenine (XLVI) is accessible from tetrachlorophthalimide and somewhat more than 2 moles of phosphorus pentachloride in almost quantitative yield and can also be easily reacted with ammonia to form tetrachlorodiiminoisoindoline (XLVII), the hope that it might be possible to develop from this product on the fiber the well-known green hexadecachloro-CuPc failed because of its difficult solubility.

4. *Production of 3,6-Dithiacyclohexene-1,2-dinitrile* (*L*) *and of 1,3-diimino-4,7-dithia-4,5,6,7-tetrahydroisoindoline* (*XI*)

A structural analog of phthalonitrile is the 1,3-diimino-4,7-dithia-4,5,6,7-tetrahydroisoindoline (XI), which has already been mentioned in Section II,A and which will be briefly referred to in the following as *dithia developer*. The production of this product is based on papers by Bähr *et al.*,[33] who showed that the disodium salt of dimercaptomaleic dinitrile (XLIX) is obtained from carbon disulfide and alkali cyanide in dimethylformamide via alkali cyanodithioformate (XLVIII) as an intermediate and with splitting off of sulfur from two molecules of this



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[31] H. Vollmann, F. Baumann, B. Bienert, and FBy, *DBP* 904,287.

[32] *Idem. DBP* 906,935.

[33] G. Bähr, G. Schleitzer, and H. Bieling, *Chemische Technik.* 8, 597 (1956).

intermediate. According to Degener and Petersen[34] (XLIX) easily yields 3,6-dithiacyclohexene-1,2-dicarbonitrile (L) by reaction with 1,2-dibromoethane. And, finally, it is possible according to Wolf *et al.*,[35] to produce from (L) in good yield the "dithia developer." The same methods are suitable for this purpose as have been described above for the conversion of phthalonitrile into 1,3-diiminoisoindoline (X).

In contrast to the colorless (X), the dithia developer (XI) shows a deep yellow inherent color, gives red salts with acids, and shows in concentrated sulfuric acid a deep violet color.

Mixtures of the dithia developer with diiminoisoindoline (X) yield[36] on the fiber, developed with a copper donor by the Phthalogen process, with increasing content of dithia developer increasingly *redder* and deeper shades up to dark navy blue—and when nickel donors are used even black shades. Mixtures of the kind mentioned here are commercial products of the Phthalogen range (see Table I).

III. Commercial Products of the Phthalogen Class, Including the Auxiliaries

The commercial range at present comprises 15 metal phthalocyanine developers which are broken down in Table I (first vertical column) into Groups 1, 2, and 2a in accordance with Sections B and C of this chapter:

Group 1 comprises metal complexes with a preformed DehydroPc ring.

Group 2 comprises simple 1,3-diiminoisoindolines.

Group 2a comprises the same diiminoisoindolines, but homogeneously mixed with the metal donors required for dyestuff development, in the form of Phthalogen K or Phthalogen Ni. The Phthalogen dyestuff developers Nos. 12–15 (vertical column 2) also contain quantities, increasing in accordance with the sequence given below, of the dithia developer (XI) (see Section II,C,2).

Group 3 in Table I comprises the following auxiliaries.

Phthalogen K and Phthalogen Ni are copper and nickel complexes of the structure (LI) in which R is a methyl group and R′ a β-hydroxyethyl group. These are thus *N*-substitution products of the well-known glycocoll copper (LI; R and R′ = H). Also very suitable are analogously designed complexes of the structure (LI) in which both R and R′ are β-hydroxyethyl groups or carboxymethyl groups, $-CH_2-COOH$. The latter are accessible from nitrilotriacetic acid with copper salts.

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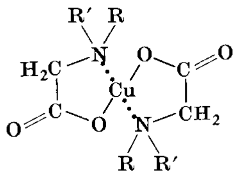
[34] E. Degener, S. Petersen, and FBy, *BeP* 565,804.

[35] W. Wolf, H. Klappert, E. Degener, and FBy, *BeP* 565,803.

[36] W. Wolf, E. Degener, and S. Petersen, *Angew. Chem.* **72**, 963 (1960).



(LI)

Phthalogen K and Ni are also offered in pure form as auxiliaries for Phthalogen dyeing (Nos. 16 and 17 of the table).

Phthalogen P is a further copper donor which only recently has been developed *especially* for Phthalogen dyeing of polyamide fibers.

Phthalotrop B is a resisting agent for printing with Phthalogen dyestuffs of Groups 2 and 2a by the preprint resist process. It is chemically a difficultly volatile, easily water-soluble di-primary amine of the aliphatic series.

Phthalofix FN is a premordant for yarn dyeing with Phthalogen Brilliant Blue IF3GK.

The Levasol brands P, PO, D, Tr, and F are difficultly volatile, water-soluble organic solvents which are indispensable for the development of the metal phthalocyanines from the Phthalogens on the fiber. There is only one exception from this rule: Phthalogen Blue IBN, described below.

Levasols P and PO are mixtures which, beside polyalcohols, also contain trialkanolamines and in many cases lead to optimum coloristic results. Levasols D (=diethylene glycol), Tr (=triethylene glycol), and F (=formamide) are technically pure, virtually uniform solvents which are used partly alone and partly in mixture with Levasols P or PO.

A new Phthalogen dyestuff developer which, strictly speaking, does not belong to any of the groups mentioned above is *Phthalogen Blue IBN*, which will now be briefly described. In accordance with our findings, this product is a complex derivative of the trivalent cobalt phthalocyanine and consequently shows, both in substance as well as in solution—for example, in 3–5% aqueous acetic acid—a deep greenish blue color. The agent required for reduction is already contained in it, built into the molecule. In Table I Phthalogen Blue IBN follows the metal DehydroPc complexes in Group 1 as No. 4.

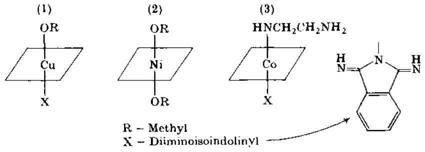
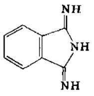
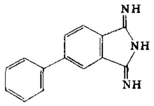
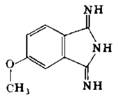
The suffixes to the names of the dyestuff developers have the following meanings:

I	Indanthrene fastness of the dyeings and printings achievable therewith.
F and FF	(Rising) brilliance of the color shades.

G and GG B and 2B R and RR	(Rising) yellow, blue, or red cast of the shades.
M	Mixtures of diiminoisoindolines with the metal donors Phthalogen K or Ni (Group 2a).
K	A preformed complex (DehydroPc metal complex) is involved.
N	A new brand.

TABLE I

Commercial Products of the Phthalogen Class

Group	*No.*	*Phthalogen*		*Composition*
1	1	Brilliant Blue	IF3GK	
	2	Turquoise	IFBK	
	3	Blue I	IB	
	4	Blue	IBN	
2	5	Brilliant Blue	IF3G	(5)  (6)  (7) 
	6	Brilliant Green	IFFB	
	7	Brilliant Green	IF2B	
	8	Brilliant Blue	IF3GM	Base No. 5 + Phthalogen K
	9	Turquoise	IFBM	Base No. 5 + Phthalogen Ni
	10	Brilliant Green	IFFBM	Base No. 6 + Phthalogen K
2a	11	Brilliant Green	IF2BM	Base No. 7 + Phthalogen K
	12	Brilliant Blue	IFGM	Mixtures of base No. 5 with dithia developer (XI) and Phthalogen K or —for No. 15—with Phthalogen Ni
	13	Blue	IRM	
	14	Marine Blue	IRRM	
	15	Blue Black	IVM	
	16	Phthalogen K		Copper or nickel complex from hydroxyethyl sarcosine (LI), $R = CH_3$; $R_1 = CH_2{\cdot}CH_2{\cdot}OH$
	17	Phthalogen Ni		
3	18	Phthalogen P		For application see Section II,C,2
	19	Phthalotrop B		
	20	Phthalofix FN		

IV. Technique and Reaction Mechanisms of the Application of Phthalogen Dyestuffs

The application methods of the Phthalogens usually correspond to those of the customary practice in pad dyeing and machine or screen printing. When preparing the dye liquors or the printing inks, it is *necessary* to add, in addition to the customary additives—such as emulsifiers and thickening agents—also certain quantities of difficultly volatile, water-miscible solvents and, as far as these solvents (like some Levasols) do not already have sufficient reducing power, also additional substances having a reducing action. Exception: for Phthalogen Blue IBN, see preceding section.

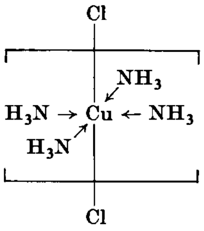
For Phthalogen dyestuffs of *Group 1* (metal DehydroPc complexes) or of *Group 2a* (mixtures of diiminoisoindolines with metal donors), the dye liquors or printing inks are ready for use. If Phthalogen dyestuffs of *Group 2* (metal-free diiminoisoindolines) are employed, an optimum quantity of a copper or nickel salt or complex salt must additionally be incorporated, in accordance with the instructions.

The padded or printed goods are then warmed, with the water rapidly evaporating, promoted by the large surface of the textile material, and the solvents becoming effective. Depending on the kind of the Phthalogen dyestuffs used, various reactions then take place on and in the fiber:

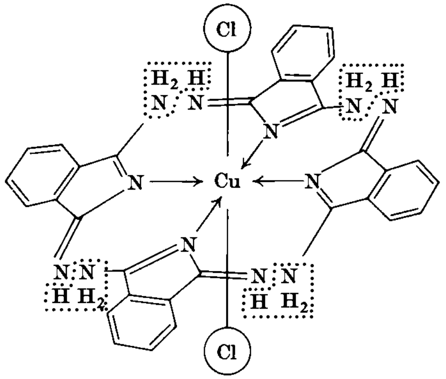
(1) Phthalogen types of Group 1 dissolve in the solvent and largely penetrate into the fiber as a solution. On higher heating, dependent upon the solvent and the reducing agent, reduction to the metal phthalocyanine then takes place rapidly, with the dyestuff being fixed. For formulation see Section II.

(2) Phthalogen types of Groups 2 or 2a, in which the required heavy metal donor—in this stage—is present, are primarily converted on drying in dissolved, now almost anhydrous form (at 60–70°) into diiminoisoindoline heavy metal complexes showing the same character as the coordinately hexavalent metal–DehydroPc complexes described in Section II,B. The "dyeings" obtained after careful drying show in this stage, if copper donors are used, washed-out yellowish to olive-colored shades. However, on spotting with a freshly prepared solution of sodium dithionite in dilute sodium hydroxide solution they *instantaneously* change to the deep, not hydrolyzable blue of the CuPc. The second step of the reaction, the reduction, and thus the fixation, then takes place at higher temperature, as under (1).

Today we think that we can best interpret our view regarding the course of the reaction of the *total synthesis* of the copper phthalocyanine *on the fiber* in the following manner:



(LII)



(LIII)

Cupric chloride is known to give with 4 moles of ammonia the complex salt copper tetrammine dichloride, for which it is customary to write $[Cu(NH_3)_4]Cl_2$. If we write it in accordance with formula (LII) (without implying any meaning other than that of the classical formulation), it becomes apparent that, if the ammonia is replaced by 4 moles of 1-amino-3-iminoisoindolenine, a precomplex of the structure (LIII) may be obtained whose steric structure *greatly favors ring closure* with elimination of 4 moles of ammonia. The reduction of the dichloro–DehydroPc–copper complex to CuPc takes place, as we know from experiments, with extreme ease. In the practice of Phthalogen dyeing, there will, however, be involved, as the final precomplexes of CuPc formation, instead of the dichloro complex [from (LIII) minus 4 NH_3]—which we selected more for didactic reasons—mostly analogously structured chlorine-free complexes, whether instead of cupric chloride Phtalogen K is used, as recommended, or from the beginning such complexes have been used [for example, as Phthalogen Brilliant Blue IF3GK of the structure (XVI)], or the primarily obtained dichloro complex is converted under application conditions (presence of excess diiminoisoindoline = Phthalogen Brilliant Blue IF3G and of difficultly volatile alcohols) into chlorine-free complexes.

CHAPTER VI

ORGANIC PIGMENTS

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I. General Survey

Chemically, organic pigments do not particularly differ from synthetic dyes, nonetheless they form a separate group. They are essentially insoluble in character. Most dyes are soluble in water, or can be made water-soluble for dyeing (e.g., vat dyes). Some dyes, although insoluble in water, are soluble in the substances to be colored (disperse dyes, solvent dyes). On the contrary the ideal pigment should be insoluble in any medium. This condition is generally not fulfilled completely, but pigments must at least be practically insoluble both in water and in the materials in which they are to be used. They are always incorporated into the materials to be colored by means of dispersion.

However, a close relationship exists between pigments and dyes. Vat dyes behave as pigments and can be used as such when not solubilized. The insoluble azo dyes that are synthesized on fibers by the azoic dyeing process are in fact real pigments formed *in situ*. Some of these dyes are also synthesized *in substance* for their use as pigments. Many acid dyes for wool can be converted into pigments by insolubilizing them as alkaline earth metal or heavy metal salts. Likewise, basic dyes can be insolubilized by precipitation with tannin and tartar emetic, or with complex acids. When soluble acid or basic dyes are precipitated on an inorganic substrate, pigments are obtained which are known as *lakes*.

Conversely, it is possible to transform pigments into soluble dyes, by sulfonation, for instance. Copper phthalocyanine can thus be converted into a water-soluble dye, used for dyeing textiles.

A. Types and Terminology of Pigments

Lakes are the oldest organic pigments, but it should be pointed out that they are not entirely organic, as they result from the precipitation of a soluble dye on an inorganic substrate.[1] Nevertheless their color is due to their organic component. The substrate is almost always colorless; most often it is composed of alumina hydrate or barium sulfate (Blancfixe or Permanent White). Alumina/Blancfixe (coprecipitated mixture) and satin white (mixture of alumina and calcium sulfate) are also used. ASTM defines a *lake* as follows: "a special type of pigment consisting essentially of an organic soluble coloring matter combined more or less definitely with an inorganic base or carrier. It is characterized generally by a bright color and a more or less pronounced translucency when made into an oil paint." And in fact lakes are prepared from dyes specially selected on account of their bright shade and the ease with which they

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[1] J. Lenoir, *Peintures, Pigments, Vernis* **35**, 303 (1959).

can be insolubilized. As important lakes derived from acid dyes, one could mention Pigment Scarlet Lake and Peacock Blue Lake, and as a lake derived from basic dyes, Methyl Violet Lake.

According to the ASTM definition, a lake always contains a substrate. In fact, the only practical way of changing most soluble dyes into suitable pigments is by precipitating them on a substrate. The latter, however, is not always indispensable and there exist numerous and very important pigments which are manufactured by precipitation of soluble dyes in the absence of any substrate. These pigments are also sometimes called "lakes," but in this case the term is incorrect. These lakes devoid of substrate are preferably named *toners*. Such pigments, in comparison to real lakes, have the advantage of possessing a higher color strength. They were formerly used for toning printing inks, whence the term "toner." The first pigment of this series was Lithol Red Barium Salt, and it is still one of the most commonly used pigments.

Of course, the manufacture of pigments does not necessarily consist in changing a soluble dye into an insoluble one. The most numerous organic pigments are neither lakes nor salts devoid of substrate. They are dyestuffs naturally insoluble by their lack of solubilizing groups. These compounds which are neither acid nor basic are nevertheless provided with phenolic, amido, and other chemical functions. They are sometimes called quasi-neutral.[2] As they are required to be insoluble not only in water but also in organic media, they must have a sufficiently high molecular weight and bear substituents such as halogens or nitro groups which particularly enhance their pigmentary properties. Pigments of this type having a high coloring strength are also known in the United States as toners. They are better designated as *pigment dyestuffs* or pigmentary dyestuffs[3] (German "Pigmentfarbstoffe," French "colorants pigmentaires"). Among the most widely used, one could mention the azo pigment dyestuffs Benzidine Yellow and Toluidine Red. Vat dyes used as pigments, e.g., Indanthrone and Flavanthrone, fall into this category. It equally includes new types of pigments such as quinacridones and dioxazines. Pigments of this type are the only entirely organic ones as they generally contain no metallic atoms. Some, however, are metallic chelates[4]; such is the case, for instance, for Green Gold and Copper Phthalocyanine.

The United States Tariff Commission recognizes three kinds of organic pigments: (*a*) lakes, (*b*) toners or full strength colors, (*c*) extended toners.

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[2] W. B. Blumenthal, *Am. Dyestuff Reptr.* **35**, 529 (1946).

[3] D. M. Stead, *J. Oil Colour Chemists' Assoc.* **43**, 124 (1960).

[4] E. R. Allen, *in* Lubs, p. 628.

The (*b*) category includes insolubilized dyes devoid of substrate and pigments insoluble by their very nature. The (*c*) category includes those compounds already classed in the (*b*) category, reduced, however, by an extender. The extender should not be mistaken for a lake substrate, as it does not act in the same way and is incorporated with the pigment only after the formation of the latter. There are a wide variety of extenders; some are organic, but most are inorganic in nature. Hydrated alumina and barium sulfate are also used as extenders, as well as calcium carbonate.

B. HISTORY

For paintings in prehistoric caves the most common colored minerals such as ochres, hematites, and limonites, which gave a color range extending from red to brown, and charcoal for black, were used. It is also known that less usual ores of brighter shades were used as pigments as far back as the third millenium B.C.: Cinnabar in China, and azurite and malachite in Egypt. Orpiment, realgar, and lapis lazuli were also used in antiquity. Great difficulties are encountered by archaeologists in determining the dates when organic pigments were first used, because they are mostly fugitive. It is almost sure, however, that since the most ancient times the need was felt by artists to complete their color range with brighter colors produced by animals and plants. These colorants, termed pigments by biologists, are very different from the pigments of the dyestuff industry. In fact, few are the true pigments, such as indigo and Tyrian Purple (6,6′-dibromoindigo), obtained from plant and animal sources.

The colorants obtained from living creatures are mainly water-soluble and among them a great number were used far back in antiquity for dyeing textiles. Man was also able to use them from the early ages in decorative coatings by transforming them into pigments through the adsorption of these dyes on clays or chalky materials. These pigments formed by a mineral substrate colored by an organic dye were later called lakes.

The first pigment to be given this name was obtained from the lac insect (*Laccifer lacca*), very widespread in India and the Far East. The insect larvae secrete a resin from which two equally precious substances are extracted: a gum, shellac, still in wide use, and lac dye, a red colorant that has been used for a long time in dyeing and painting. Lac dye mainly consists of two laccaic acids, polyhydroxycarboxy-2-phenylanthraquinones (see *CSD III*, Chapter I). Adsorbed on an inorganic substrate it gave rise to the first pigment to be called *lake*. This word was later given a wider meaning. The same applies to the word *lacquer*, which derives from lac insect, the first lacquer having been prepared from shellac. It is to be noted that, while two distinct words, lake and lacquer, are used in English, in other languages the two products are designated by the same word (*Lack* in German, *laque* in French), thus giving rise to confusion emphasized by the fact that the two products are sometimes used together, one being used to color the other.

For thousands of years, the main natural dyes selected for the manufacture of lakes belonged either to the flavone or to the anthraquinone series. Despite their lack of lightfastness, some flavones are still used as lakes in the twentieth century: yellow wood, quercitron, Persian berries, weld; the same applies to many dyes which are chemically related to those just mentioned, e.g., Indian Yellow, brazilwood, logwood. Logwood's lake is the only one which still has a notable use. The natural anthraquinone dyes gave the fastest lakes. That was especially the case with madder (mainly alizarin, which has been prepared synthetically since the nineteenth century). The other dyes belonging to this family were lac dye, kermes, and cochineal. Particularly bright, the cochineal carmine lake is still more or less in use, especially for artists' paints.

Empirically improved methods gradually replaced the original methods of preparation which consisted in simple adsorption on clay, silica, or talcum. The precipitation of dyes as insoluble salts or as complexes of aluminum, zinc, lead, iron, etc., was known. The most widespread were the aluminum compounds obtained from alum. Precipitations were carried out on a variety of mineral substrates; alumina, barytes, gypsum, and chalk. But till the middle of the nineteenth century, these improvements in the preparation of lakes represented the only appreciable progress that took place in the field of organic pigments, which were only represented by lakes of natural dyes.

When in 1856 there appeared the first synthetic dyes intended for textile dyeing, their use for lake preparations was naturally considered. These new water-soluble dyes became far more numerous than the natural dyes used previously. They had the advantage of having greater shade varieties and brightness, and often better fastness properties. Their well-defined chemical functions made possible the establishment of the present processes of lake preparation.

Acid dyes, being sulfonic or, more rarely, carboxylic acids sold as sodium salts, were precipitated from their aqueous solution on the substrate in suspension, by reaction with soluble salts of barium, calcium, and lead.

Basic dyes, sold as hydrochlorides or other water-soluble salts, were precipitated either with tannin and tartar emetic, or with natural silicates such as green earth, which acted as precipitating agents as well as substrates. Later, acids such as benzoic, phosphoric, and complex acids of the phosphotungstic type were used for bringing about the precipitation. On the other hand, lakes were also prepared by combining an acid dye with a basic dye.

Mordant dyes of the polyhydroxyanthraquinone and polyhydroxy azoic types have been converted into insoluble aluminum complexes by using alum or aluminum sulfate as laking agent, according to the already known procedure used for madder and cochineal lakes.

During the first forty years of the synthetic dye industry many new lakes appeared in that way, but the only dyes used then were those manufactured for textile dyeing. On the other hand, their number kept on increasing and, as it was noticed that the properties required of a dye to be changed into a lake were not exactly those required of one to be used for dyeing, a selection became necessary. For the same dye, even the fastness to light, a property which is always desirable, often differs (for better or for worse) according to whether it is used for dyeing wool or changed into a lake.

Because the demand for bright red lakes was particularly important, azo dyes derived from R-salt were the most appreciated. In this series, Xylidine Ponceau (*m*-xylidine → R-salt) and Pigment Scarlet (anthranilic acid → R-salt) have been selected for lakes. These azo dyes, which cannot be insolubilized without a substrate, were among the first dyes whose main outlet was their use as lakes.

It was only, however, at the very end of the nineteenth century that the synthesis of special dyestuffs for pigment usage really began. The first of this type, Lithol Red (Tobias acid → β-naphthol) appeared in 1899. This azo dyestuff had a great success, since its barium and calcium lakes had fastness properties which outclassed by far its predecessors. At first Lithol Red was sold as its sodium salt for conversion into lakes. It was then noticed (*a*) that its alkaline earth salts did not necessarily require a substrate and that this allowed the manufacture of pigments of exceptionally high coloring strength; and (*b*) that its sodium salt, which is very little soluble in water, can itself be used as pigment. This is a peculiar property in the case of a dye for lakes. However, these interesting properties were not immediately taken advantage of. Much later, Lithol Red was sold by dye manufacturers as its barium and calcium salts which were precipitated in absence of substrate, but reduced with a mineral extender (reduced toners). Finally the two salts were sold without extenders (full strength toners).

Shortly after the appearance of Lithol Red, other dyes with quite similar properties and history were produced. The main ones were Lake Red C (1902) and Lithol Rubine (1903) which, like Lithol Red, are nowadays among the most important toners.

Before the end of the nineteenth century, the idea arose of using as pigments dyestuffs devoid of acidic or basic groups and therefore insoluble in water. The first pigments of the kind were some red β-naphthol azo dyestuffs. Discovered in 1878 α-Naphthylamine Maroon (Autol Red RLP) was nevertheless only a second-rate pigment because of its solubility in organic solvents; it is classed nowadays among the Solvent Reds. Para Red (*p*-nitroaniline red) has been produced since 1870 by azoic dyeing as a substitute for Turkey Red. Later on it was manufactured in substance in order to compete with madder lake also. Although it has remained popular, Para Red, with only moderate fastness to linseed oil and solvents, is still not a good pigment. Later on, pigments of the same chemical class, but with improved fastness to oil and light, were brought out: in 1895 Orthonitroaniline Orange; in 1905 Chlorinated Para Red (from 2-chloro-4-nitroaniline) as well as Toluidine Red (from *m*-nitro-*p*-toluidine); in 1907 Dinitroaniline Orange.

β-Naphthol could only give red and orange azo dyestuffs. In the beginning of the twentieth century, to answer the need for yellow pigment dyestuffs, the idea occurred of using the condensation products of nitroarylamines and formaldehyde. The best in the series was Lithol Fast Yellow GG (1909), a derivative of 4-chloro-2-nitroaniline; it had, however, many faults. The discovery of azo dyestuffs from compounds which couple on a reactive methylene group of an aliphatic chain was more profitable. Research resulted in Hansa Yellow G, which was patented in 1909. This pigment became the prototype of the important Hansa Yellow family, many representatives of which were brought on the market in the following years. Besides acetoacetarylide azo dyestuffs, this series included Hansa Yellow R (2,5-dichloroaniline → phenylmethylpyrazolone), which is a pigment dyestuff of the pyrazolone azo dyestuff class, the first representatives of which (Tartrazine and Flavazine) had already been used as lakes for many years.

Just before World War I the only purple, blue, and green organic pigments available were lakes of triphenylmethane dyes derived either from acid dyes, e.g, Erioglaucine, which is still very popular as Peacock Blue, or from basic dyes, e.g., Methyl Violet, Victoria Blue, Brilliant Green. Those derived from basic dyes were particularly appreciated for their intensity; unfortunately they had no fastness to light when prepared with tannin. It is only in the years between the two world wars that much less fugitive lakes were brought on the market in Germany under the Fanal brand. They were phosphotungstates of basic dyes. Phosphomolybdates and phosphotungstomolybdates appeared a little later. It then became possible to eliminate the mineral substrate and these products became available as toners.

Pigment Green, the iron complex of nitroso-β-naphthol, was patented in 1921. A big gap persisted, however, in the gamut of organic pigments. This was finally filled by the sensational appearance of Phthalocyanine Blue (1935) and Green (1939).

Progress was also made in the field of red and yellow pigments in the years between the two world wars. Many toners were very much improved by the incorporation of alkaline earth rosinates, which do not act as extenders, but raise their tinting strength, their brightness, and their transparency. Some 2-hydroxy-3-naphtharylide (Naphthol AS) azo dyes, known since 1912, have added to the range of the red pigment dyestuffs. Produced at first on plant fibers by azoic dyeing, they were then brought on the market in substance under different brands of Permanent Reds. To this family of azo dyestuffs were later added a great number of Naphthol Reds.

Although patented in 1911, the yellow dichlorobenzidine and aceto-acetarylide disazo dyestuffs were only brought on the market by IG in 1935, as Vulcan Fast Yellows for use in rubber. Contrary to the Hansa Yellows, they have the advantage of not migrating in this material. Besides, they have a color strength which is about twice that of the Hansa Yellows, and this explains the great success they now have in printing inks. Well known as Benzidine Yellows, they are nowadays some of the most widely manufactured organic pigments and in this respect come second only to the phthalocyanines.

As already mentioned, phthalocyanines were discovered a few years before World War II. Thus, a new chemical class came about, the first representatives of which were pigments; this was an exceptional event in the history of dyestuffs. For thirty years now, because of their exceptional properties, these pigments have had an extraordinary commercial development. Originally known as Monastral Blue or Heliogen Blue, copper phthalocyanine in its two crystalline forms, reddish α and greenish β, ranks today first in production. Phthalocyanine Green, which now ranks second, is a polychlorinated derivative of copper phthalocyanine, while the more recent yellowish greens are both chlorinated and brominated derivatives.

Some pigments older than phthalocyanines have known spectacular commercial development since 1945, similar to that of Benzidine Yellows. These are the Permanent Red 2B toners (2-chloro-4-aminotoluene-5-sulfonic acid → 2-hydroxy-3-naphthoic acid) as calcium and barium salts (Watchung Reds, DuP) and later as a manganous salt (BON Red) which is faster to light.

Faster organic pigments were, however, required and not only reds, but of all hues other than blue and green (for the last two, phthalocyanines had solved the problem). For this purpose, it was thought of using vat dyes, some of which (indigo, indanthrone, flavanthrone) had already found some use as pigments. Most vat dyes have excellent fastness; they are, however, expensive and sold in a form which is inadequate for their use as pigments. Some treatments were invented in order to convert vat dyes into good quality pigments, and between 1955 and 1960 many of these pigments were brought on the market. Some new vat dyes have even been especially created for use as pigments. The main ones are the Perylene Reds and tetrachlorothioindigo.

On the other hand, it became possible to manufacture much faster azo pigments than those previously known and many of the new pigments of this class were commercialized. In 1946, a yellowish green nickel chelate of a 2,4-dihydroxyquinoline azo dyestuff (Green Gold, DuP) was discovered. Since 1954 the disazo condensation dyestuffs derived from 2-hydroxy-3-naphtharylides (Cromophtal Reds of Ciba) or from acetoacetarylides (Cromophtal Yellows) have appeared. Entirely new chemical classes were developed during the last twenty years; they too gave rise to some very fast pigments. They are (a) dioxazines, the first and main representative of which is the Carbazole Dioxazine Violet; (b) quinacridones, brought on the market in 1958 under the name of Cinquasia Reds and Violet (or Monastral, of DuP); (c) isoindolinone azomethines (Irgazine of Gy).

Recent patents show that some new lines will appear in the near future. The development of organic pigments has been much slower than that of dyes for textiles. At the beginning of the century it was some fifty years behind; it has now filled the gap.

C. Comparison with Inorganic Pigments

Organic pigments are in competition with inorganic pigments, which nowadays include a few natural products such as ochres, but many artificial compounds, most of which were discovered long before synthetic organic pigments. Apart from Vermilion, which was manufactured in antiquity to replace natural cinnabar, and minium, already known in the Middle Ages, the chemistry of artificial inorganic pigments began in 1704 with the discovery of Prussian Blue, followed one hundred years later by that of Cobalt Blue. Chrome Yellow, Cadmium Yellow, Ultramarine, Chrome Oxide Green, and the artificial iron oxides (yellow, red, brown, and black) all appeared at the beginning of the nineteenth century, followed a little later by Zinc Yellow. More recently some very good inorganic pigments have appeared: Cadmium Red (1910), Molybdate Orange (1935), Titanium Yellow (1960).

As most inorganic pigments show excellent durability and high hiding power, in paints (particularly exterior paints) they find little or no competition from organic pigments, which are less durable and much more transparent at equal color intensity. Inorganic pigments also have the advantage of being cheaper; one must also consider, however, the fact that the tinting strength of organic pigments is much superior. On the other hand, inorganic pigments are much less numerous and their range is much smaller in comparison to organic pigments, which have much brighter shades. A definite shade can be obtained from one organic pigment while this is not always possible with inorganic pigments, even mixed.

As the only cheap inorganic reds are iron oxides, which lack brightness and color strength, the first organic pigments needed were reds. This explains the already well established success of red lakes, followed by that of the insoluble β-naphthol azo pigments.

For inorganic yellows the range is larger. Chrome Yellows are the most important; they have quite bright shades and fairly good color strength. Their lightfastness, however, is not perfect; furthermore they are blackened by hydrogen sulfide, turn red under the action of alkalis, and are toxic. This explains the fairly serious competition existing between them and organic yellow pigments.

Prussian Blue and Ultramarine, the main inorganic blues, have an excellent durability, and Prussian Blue has a good color strength. It is nevertheless decomposed by alkalis, while ultramarine is decomposed by acids. These two pigments are now largely replaced by Phthalocyanine Blue, the first organic pigment of excellent durability. Similarly, greens obtained by mixing blue and yellow inorganic pigments are more and more replaced by Phthalocyanine Green.

Brown, black, and gray shades are almost exclusively found among inorganic pigments. A certain number of brown organic pigments also exist which, despite their high color strength, cannot compete with the very cheap brown iron oxides. As for the very few black organic pigments, they are only used in those rare applications where carbon blacks are not best suited; otherwise the latter are invariably used.

To complete this short comparison, it should be pointed out that in printing inks most mineral pigments are nowadays replaced by organic pigments, which alone can bring a high color strength and the required brightness and transparency. On the contrary, for those applications requiring a high fastness to heat, inorganic pigments are sometimes the only suitable ones. This is, of course, the case for the coloration of glass and ceramics. For plastics, however, complete ranges of organic pigments which resist molding temperatures are now available.

Apart from colored pigments one must also consider the white inorganic pigments produced and used in much larger quantities and having no rival organic counterpart. The most ancient is white lead, but its use is nowadays limited because of its toxicity. Zinc oxide and lithopone began to replace it in the nineteenth century and are still important. The use of titanium dioxide began in 1924 with the anatase form, but very rapid progress was soon made. The rutile form is much more used nowadays; it has a greater hiding power and is now by far the most important among white pigments. Titanium dioxide in particular, but also zinc oxide and lithopone, are associated with organic pigments in numerous usages, especially in paints and plastics. Indeed, except in printing inks, organic pigments are rarely used pure. Their use in tints, with often large quantities of white pigment, enables one to make the best use of their excellent color strength.

D. Usage of Organic Pigments

The fields of application of organic pigments are extremely numerous and varied. For their main usages pigments are brought into suspension in liquid vehicles: printing inks and coating compositions.

Coating compositions include oil paints, nitrocellulose lacquers, resin-based enamels (resins of alkyd, urea-formaldehyde, phenol-formaldehyde, or other types), also the natural or synthetic elastomer-based or PVA-based emulsion paints, not forgetting the alcohol-based varnishes, the lime colors, and the distempers. The competition existing in paints between organic and inorganic pigments has already been mentioned. It is to be noted that the demand for bright organic pigments of excellent fastness is particularly high for those alkyl-resin-based enamels used as automotive finishes.

At present printing inks represent the most important outlet for organic pigments. Similarly to paints, printing inks are suspensions of pigments in varnishes, though at much higher concentrations. The ink formulation is related to a large extent to the mechanical printing process in which it is to be applied. The main printing processes are the following: lithography, offset, letterpress, rotogravure, and flexography. These processes also include special applications such as the printing of wallpapers, wrappers, and tin plate. Requirements concerning pigments are not identical in these different cases.

It is interesting to note how at present pigments compete with dyes in textiles. Rayon and synthetic fibers are more and more colored in the mass through the use of pigments. Prior to spinning of rayon, a pigment is added to the viscose in a fine water dispersion. The coloration of acetate rayon by mass pigmentation prior to spinning is also easily achieved. On the other hand, the coloring of synthetic fibers (e.g., polyamides) spun in the molten state necessitates the use of pigments resisting the high temperatures involved in spinning. These pigments are scarce.

The conventional processes for textile printing are nowadays very much in competition with pigment printing, which has been considerably developed.[5] In this process, which resembles graphic printing, one uses a pigment suspension in a resinous binder-based emulsion. The binder is cured after printing. Initially water-in-oil emulsions were used, but the process was later very much improved by the usage of oil-in-water emulsions. These new formulations are even used for dyeing textiles by padding.

The classical dyeing of leather is also often replaced by the spraying of nitrocellulose lacquers or of casein paints containing organic pigments.

A great number of materials are colored in the mass by pigment dispersion. Paper was one of the first materials to which this method was applied. It is pigmented in the beater or by coating. Special properties are required of pigments for use in paper to be incorporated in laminated plastics. For a long time now rubber has also been colored with specially selected pigments which are also used for synthetic elastomers.

The first plastics, e.g., the phenol-formaldehyde plastics have been colored in a relatively easy way by classical pigments. The enormous development of modern plastics has given pigments an important outlet, but at the same time has given rise to difficult selection problems which incited a search for new organic pigments of superior quality. There exists nowadays a choice of pigments suitable for PVC, polystyrene, polyethylene, polypropylene, etc.

Finally, organic pigments have different minor but not negligible uses in artist paints, pencils, chalks, modeling clay, cosmetics, soaps, waxes, and cement.

E. Required Properties

It is easily conceivable that all pigments cannot fulfill all the often contradictory conditions implied for their various usages. The required physical properties are numerous and the pigment must further show good chemical stability in the medium in which it is used.

The hue is, of course, one of the most essential properties. Generally it is preferred bright; this is useful in order to allow possible mixing with other pigments. The required hue can be defined by its trichromatic coordinates: such is the case, for instance, for those pigments used in three-color printing.

The highest possible color strength is paramount in modern printing

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[5] CSD I, p. 292.

inks; it is also desirable in other usages where it may not be absolutely essential. It is remarkable how in this respect the requirements have changed since the appearance of the first toners and pigment dyestuffs, their tinting strength being far greater than that of the usual inorganic pigments and lakes used at that time. When they first appeared, toners were considered too strong. They were therefore reduced with extenders. For the same reason azo pigment dyestuffs such as Para Red and Toluidine Red were made as lakes by coupling in the presence of an inorganic substrate. The tendency today is to demand higher and higher color strengths.

It is also to be noted that the color yield of a pigment in the medium in which it is to be used does not depend exclusively on its chemical constitution, but also on it physical form and on the nature of the medium itself. The pigments must be readily dispersible in that medium, which can be a varnish, a plastic, or an elastomer. The dispersibility is related to the size and texture of the pigment particles, as well as to their agglomerate state and to their surface properties (organophilic and hydrophilic). As a general rule, a pigment must be in fine particles, agglomerated as little as possible and the agglomerates must be very friable. In order to avoid clogging the holes of the spinneret, the mass coloration of synthetic fibers necessitates the use of fine particles and of well-dispersed pigments. The ease of grinding is important for usage in paints and inks: it is desirable that the maximum intensity of the coloration be attained after the shortest possible grinding time.

Fastness to light is desirable as a general rule, and even more so, of course, for those applications which are to be exposed for a prolonged period to broad daylight. In certain cases, pigments of lower lightfastness, but possessing other interesting properties can be accepted.

It is to be noted that fastness to light often depends on the medium in which the pigment is dispersed. Benzidine Yellows and Lake Red C, for instance, show greater fastness in rubber than in paints and printing inks. On the other hand, pigments are in general less fast to light in pale tints than in dark tints. An important factor in exterior paints is the pigment durability; it not only implies fastness to light, but also weathering resistance.

Fastness to heat is required for pigments used in baking enamels and in those plastics molded at more or less high temperatures. Few organic pigments are unaffected by temperatures above 150°. Some, however, will resist short exposure up to 200° and sometimes more. Those chemically stable to high temperature sometimes, however, change in shade, following a modification of their crystalline form. On the other hand, for almost all applications (in particular for printing inks) it is necessary that pigments show no tendency to sublimation.

As was said previously, an ideal pigment should be insoluble in all media. Generally this condition is not completely fulfilled, and the insolubility requirements are based in fact on the application. Nonbleeding properties in water are not only necessary in water paints, but in almost all applications. Except for some slightly water-soluble toners (namely, the sodium toners), pigments are quite insoluble in water. Some, however, are very hydrophilic and can bleed in water in the form of a colloidal suspension. Others change shade by hydration through contact with water. Pigments presenting these faults are not suitable for offset printing.

Of course, pigments used in drying oil-based paints and inks must not bleed in oil. Nonbleeding in a certain number of solvents is very often required, in particular for those used in lacquers, whether nitrocellulosic, glycerophthalic, or alcoholic. The main solvents to be considered are alcohol, acetone, butyl acetate, glycol ethers, toluene, xylene, and petroleum hydrocarbons. Pigments to be used in textile printing must resist trichlorethylene dry cleaning. Insolubility in plasticizers is important for those used in plasticized lacquers and plastics. The pigment must particularly not bleed in PVC plasticizers, namely, dioctyl phthalate, which has very strong dissolving power. Insolubility in even stronger solvents such as dimethylformamide is not generally required; very few pigments have this property, which in certain cases (acrylic textiles) can nevertheless be of interest.

Other properties required from pigments are closely related to the insolubility in organic media. Overspray fastness is often required from those used in paints. It implies the nondiffusion of the pigment contained in a bottom coat into a second coat of a different color. Migration resistance is necessary for usage of pigments in plastics and elastomers. Migration consists in the diffusion of a pigment from one point to another in the material in which it is dispersed, or from that material into another with which it is in contact.

When certain pigments are used in inks, fine particles, which can be wiped with the finger, appear on the printed surface. This sort of efflorescence gives a flat aspect to the print. The pigment is said to be "powdering" or "hazing." Another phenomenon which is more or less related to the first is the bronzing of pigments in printing. It is an effect of light reflection giving the print different shades depending on the observation angle. This effect is sometimes desirable, most often it is not. These faults can be corrected by surface treatments or by other modifications of the pigment.

For their use in paints, it is desirable that pigments have a high hiding power (opacity). It is generally said that organic pigments are much less opaque than inorganic pigments. Were they used at equal weights, this statement would not be correct, but practically, because of their much greater color strength, much less organic pigment is used in an application. In general, the organic pigment is used in conjunction with a white pigment such as titanium dioxide; the latter ensures the desirable opacity in the paint. On the contrary, in other applications, a certain transparency is required of pigments. Such is the case, for example, in printing inks, especially for three-color printing. The desirable transparency of organic pigments can often be obtained by varying the conditions of preparation, or else by incorporating a metallic salt of rosin.

The oil absorption (or in a general way, the vehicle absorption) is an important property of pigments. On it depend the rheological properties of inks and paints. In general it should not be high. An ink prepared with a pigment having a high oil absorption can become unusable due to its high viscosity.

Fastness to alkalis is not always necessary. It is required of those pigments to be used in lime or silicate paints, or for the coloration of cement, soap, and wrappers of alkaline products. It is also necessary for the mass coloration of viscose and for application in those textiles liable to be submitted to alkaline treatments.

Pigments must be acid-fast if they are to be used in acid media or if they have to be exposed to acid vapors.

One particular pigment cannot fulfill all the aforementioned requirements. To satisfy all needs a great number of organic pigments belonging to most of the different classes of dyestuffs have been developed.

F. Chemical Classification

The traditional classification of dyes, based on the chromophores, could also be adopted for organic pigments. Pigments, however, are very unevenly distributed in the various chemical groups defined by the chromophores. A reasonable classification should take into account the preponderance of the azo dyestuffs, which is even more marked in the case of pigments than in that of dyes. Among the azo pigments, different families should be distinguished by the nature of the coupling component, which has a very marked influence on the pigment properties (hue and fastness). On the other hand, pigments of different chromophores but of similar properties such as the anthraquinone and the indigoid pigments could be united in the same class. Finally, it is useful to mention the new classes separately, even if their pigments have not yet appeared on the market.

The following classification can be advocated and is followed in Section II of this chapter.

A. *Acetoacetarylide azo pigments,* principally the monoazoic Hansa Yellows and the disazoic Benzidine Yellows. This class supplies the great majority of yellow pigments. It is still the object of active research.

B. *Pyrazolone azo pigments,* chiefly disazo pigments such as Benzidine Orange and some Pyrazolone Reds.

C. *β-Naphthol azo pigments,* including the oldest and commercially still the most important red pigments. Some, like Toluidine Red, are of the pigment dyestuff type; the others, such as the Lithol Reds, are of the toner type.

D. *2-Hydroxy-3-naphthoic acid azo pigments,* red toners among which the rubines and the maroons are the most numerous. This class, which includes, among others, Lithol Rubine and the Permanent Red 2B toners, is still being developed.

E. *2-Hydroxy-3-naphtharylide azo pigments,* very numerous monoazo (Naphthol Reds) and disazo pigments, some of very high quality. Intensive research is being carried out in this class.

F. *Naphtholsulfonic acid azo pigments,* essentially red lakes, were very numerous at one time. Nowadays those still in use are very few.

G. *Triphenylmethane pigments and related compounds,* including a few lakes derived from acid or basic dyes, but principally formed by the Alkali Blues as well as the phosphotungstic and/or phosphomolybdic toners; mainly violet and blue (e.g., Methyl Violet and Victoria Blue toners).

H. *Phthalocyanine pigments,* high grade blues and greens. Between them they represent in weight almost one-quarter of the total organic pigments produced.

I. *Anthraquinone, indigoid, and related pigments,* principally "vat pigments," i.e., specially treated vat dyes for use as pigments. Among these pigments of various hues are found some new and very fast products such as the Perylene Reds.

J. *Quinacridone pigments,* reds and red-violets of high quality. They have recently been developed commercially.

K. *Dioxazine pigments,* whose principal representative is a violet. Further research is being carried out in this class.

L. *Azamethine pigments* }
M. *Fluorubine pigments* } The newest classes.
N. *Naphthindolizinedione pigments* }

O. *Miscellaneous pigments* belonging to different chemical classes which have very few representatives.

The advantage of this classification is that the different chemical categories are approximately arranged in increasing bathochromic order, at least in Classes A to H. Furthermore, Classes H to N include pigments which by their outstanding fastnesses are extremely interesting and to which one can only compare the best and more recent azo pigments from Classes A and E. It is to be noted that among all these exceptional organic pigments, only those from Class H now have a well-established commercial position.

G. RELATIONSHIP OF CHEMICAL CONSTITUTION TO PROPERTIES OF PIGMENTS

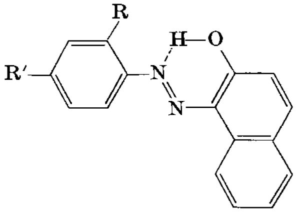
In pigments the relationship between chemical constitution and hue is the same as for dyes (see *CSD I*, Chapter VIII). Nevertheless the shade of a pigment also depends on its physical state, and the color it communicates to the medium in which it is dispersed depends more or less on that medium itself. Furthermore, the chemical constitution of a pigment has, of course, an influence on its fastness properties.

Without entering into theoretical considerations beyond the scope of this chapter, it is useful to point out some aspects regarding the relations existing between the chemical constitution and the properties of pigments (hue and fastnesses).

The influence of the nature of the coupling component on the hue in the case of azo pigments has been shown in the classification given in the preceding section. Yellows and oranges are obtained with compounds coupling on a reactive methylene group in an aliphatic chain (acetoacetarylide, Class A) or to a nonaromatic heterocycle (pyrazolone, Class B). These coupling components contain, however, aromatic nuclei which are necessary for the pigment fastnesses.

For the production of other azo pigments, in particular red (but also orange and purple), the coupling components used are β-naphthol (Class C) or its derivatives: 2-hydroxy-3-naphthoic acid (Class D), 2-hydroxy-3-naphtharylides (Class E), 2-naphtholsulfonic acids (Class F). All these compounds couple in the 1-position. It is to be noted that phenolic functions in pigments must in general be avoided, mainly because they confer on the pigment a certain solubility in alkaline media. In pigments belonging to Classes C to F, however, the phenolic function is made inactive by hydrogen bonding with a nitrogen atom as shown in Formula (I).

The size of the molecule is of great importance. A sufficiently high molecular weight is necessary to ensure nonsublimation and an acceptable degree of insolubility in dispersion media. Almost all organic pigments have molecular weights ranging between 300 and 1000, although some macromolecular pigments are also in existence. Compared



(I)

to Hansa Yellows (molecular weights below 400), Benzidine Yellows (molecular weights above 600 and sometimes above 800) show better resistance to solvents and to migration. Azo condensation pigments have molecular weights ranging from 800 to 1000; their fastness properties are outstanding. Pigments having the smallest molecules are Indigo (Mol. wt. 262) which is easily sublimed, and Para Red (Mol. wt. 293) which shows little fastness to solvents. In such pigment, however, the substituents present and the skeleton of the molecule can ensure good fastness in spite of the relatively low molecular weight. Toluidine Red (Mol. wt. 307), which belongs to the same family as Para Red, is distinctly faster because of its substituents. Quinacridone, with only 312 as molecular weight, is one of the fastest pigments; this is explained as resulting from an intermolecular association by hydrogen bonds. The heaviest common pigments are the polyhalogenated Phthalocyanine Greens (mol. wt. 1100 to 1300); Phthalocyanine Blue of lower molecular weight (576) is just as fast. The outstanding properties of these high-grade pigments are attributed to the macrocycle of porphyrazine rather than to their nature as metallic complexes; indeed the fastness properties of the metal-free phthalocyanine compare very well with those of copper phthalocyanine.

Apart from phthalocyanines, very few commercial pigments are metallic complexes, although many others have been patented. As a general rule, the transformation of an azo pigment into a metallic complex greatly improves fastness to light and solvents, as is the case for Para Brown, the copper chelate of Para Red, and even more so for Green Gold (CI Pigment Green 10), the nickel chelate of a yellow azo dyestuff presenting no interest by itself. Nevertheless metallic chelation often leads to duller shades.

Amide functions (carboxamide and sulfonamide) in general strongly favor fastness to light and solvents. This explains why among azo pigments the most interesting and those on which research is still carried out are the ones belonging to classes A and E in which the coupling components are aryl amides. Pigments of high molecular weight are obtained by condensation reactions capable of giving rise to amide linkages (azo condensation pigments): thus fastness to light and to solvents are simultaneously improved.

The substituents most usually introduced into the aromatic nuclei in order to modify the shade and improve the fastness properties are chlorine atoms and groups such as nitro, methyl, methoxy, and ethoxy. Chlorine atoms have a favorable effect on fastness to light and solvents, a fact which has for a long time been demonstrated by the superiority of Chlorinated Para Red over Para Red itself. In recently introduced pigments derived from tetrachloroisoindolinone, the chlorine atoms play a fundamental part (see Section II,L,2). These pigments are very fast to overspray, migration, and light, while the corresponding derivatives of unchlorinated isoindolinone lack these properties. Chlorine atoms have a variable effect on the shade of pigments, sometimes hypsochromic and sometimes bathochromic. It is well known that the introduction of chlorine atoms in phthalocyanines progressively displaces their shade from blue to green.

It is interesting to note that in polyhalogenated phthalocyanines the partial replacement of chlorine by bromine leads to much yellower greens. Apart from this example, commercial pigments containing bromine are relatively rare; nonetheless some do exist among vat pigments, e.g., dibromoanthanthrone of excellent lightfastness.

In general, nitro groups have a very marked bathochromic effect which enhances the color strength; but in certain cases their introduction into the molecule can lead to duller shades. Their action with respect to resistance to migration and solvents is almost always favorable; lightfastness may be improved or decreased.

It must also be stressed that the influence of the substituents on the pigment properties depends on their position in the molecule. In azo pigments, for example, the bathochromic effect of the nitro group is strong if it is in the ortho or para position to the amino group of the diazo component; the effect is much weaker if the nitro group is in the meta position. Similarly, derivatives of *m*-chloroaniline are more yellowish than those of *o*- and *p*-chloroanilines.

In general the presence of one methyl group has only a weak bathochromic effect and a slight influence on the fastness properties. Two methyl groups (in the ortho and para positions) have a more perceptible effect. Higher alkyl groups, at least in commercial pigments, are rare. Methoxy and especially ethoxy groups have very strong bathochromic effects and generally a favorable influence on lightfastness. Their effect on the fastness to solvents is variable; in certain cases it is unfavorable.

The sulfo group found in toners and lakes is usually present as a salt of barium, calcium, manganese, and less often of strontium or lead. It thus ensures the insolubility of the pigment in most organic media and lack of tendency to sublimation even if the molecule is small. Pigments of this type are also in general insoluble or very little soluble in water. They are not, however, fast to alkalis. Sodium salt toners sufficiently insoluble in water are exceptional (Sodium Lithol and Lake Red C toners). The nature of the metal has a very marked influence on the shade, sodium salts being the most yellowish. Calcium salts are more bluish than barium salts, and manganese salts are often even more bluish. The sulfo group has an adverse effect on lightfastness; this effect is less noticeable for manganese salts than for the others. There even exist some very lightfast manganese salts, e.g., Permanent Red 2B Manganese Toner.

Amino groups are only found in lakes and toners of basic dyes particularly appreciated for their bright shades. These pigments are sensitive to acids and show low fastness to light. The lightfastness of even the phosphotungstomolybdic toners, which are considered the best, is only moderate.

H. Relationship of Physical State to Shade of Pigments

As has already been said, the apparent color of a pigment in the medium in which it is dispersed does not depend on its chemical constitution alone, but also on its physical structure and on the nature of the medium itself.

In all applications, the pigment is present as microcrystalline particles, more or less large and more or less agglomerated, which scatter and reflect incident light. The refractive index of a pigment and the surface of its particles play an important part. The medium in which it is dispersed also exerts an influence by its optical characteristics. If the refractive index of the pigment is higher than that of the medium, as happens most often, light is partially reflected on the surface of the pigment. The greater the difference between the refractive index of the pigment and that of the medium, the greater will be the rate of reflection and the more will the pigment appear opaque.

The hiding power and the tinctorial strength of a pigment depend, furthermore, on the shape and size of its particles. The opacity and the color strength increase with decreasing particle size, because of the resulting increase in surface area. It is nevertheless conceded that this tendency is reversed for particle sizes below the wavelength of light.[6]

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[6] D. Patterson, "Pigments, An Introduction to their Physical Chemistry," p. 130. Elsevier, Amsterdam, 1967.

Because of all these factors a modification of the spectral characteristics of the pigment with respect to those solely due to light absorption becomes more or less apparent. Shade, brilliance, hiding power, and color strength can vary within wide limits according to the fineness of the pigment particles and the nature of the material that is to be colored.

On the other hand, polymorphism is frequent in all classes of organic pigments. From what has been said above, it becomes apparent that chemically identical pigments belonging to different crystalline systems may have very distinct shades. Indeed their microcrystals differ by their shape and their refractive index. The crystalline form and the degree of crystallinity can also influence other properties, particularly lightfastness. In most cases, among the different crystalline forms that can be assumed by a pigment some are unstable and only one is interesting for its shade and properties.

The best known and, practically, the most important polymorphisms are those of pigments which have been commercialized in different crystalline forms; such is the case, for instance, with copper phthalocyanine the α form of which is reddish blue and the β form greenish blue. It is also the case with linear *trans*-quinacridone in which the β form is reddish violet and the γ form red.

The influence of the physical structure on the shade is sometimes more important than the normal effect of a bathochromic substituent. This explains why predictions on the effect of introduction of a substituent in a pigment molecule are often invalidated. It happens, in fact, that in trying to modify a pigment by introducing a bathochromic substituent one obtains on the contrary a hypsochromic shift due to the change in the crystalline system of the pigment taking place simultaneously. Very characteristic examples of this phenomenon have been observed in the dioxazine class (see Section II,K,3), but analogous cases also exist in azo pigments.[6a]

The above-mentioned differences in shade that arise between toners that are salts of different metals of the same acid dye are also explained by the difference in physical structure. Lithol Red salts, for example, all give the same absorption spectrum when the measurements are made by transmission through solutions in pyridine.[7]

I. INFLUENCE OF MANUFACTURING CONDITIONS

Since the physical structure of pigments is determined by the conditions of preparation, it is easily conceivable that their manufacture

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[6a] A. Pugin, *Chimia* (*Aarau*) Suppl., p. 60 (1968).

[7] L. S. Pratt, "Chemistry and Physics of Organic Pigments," pp. 18 and 304. Wiley, New York, 1947.

requires particular care. In a series of batches, production of the pigment with constant shade and properties can only result from strict control of all factors involved in the process.

The first indispensable condition concerns the purity of the intermediates used in the pigment manufacture. In the preparation of an azo pigment, for instance, if the diazo component contains a minute amount of another amine as impurity, this will give rise to a foreign pigment which will be intimately mixed with the main one, thus altering its properties and shade. In other cases an insoluble and colorless impurity is obtained which may alter the technological properties of the pigment or act as an extender by lowering the color strength. The elimination of such impurities after pigment formation is seldom feasible. At the most it could be done in certain cases through a costly treatment (by using an organic solvent, for instance); on the other hand, this treatment could have an unfavorable influence on the physical structure of the pigment.

A pigment of normal purity and of well-defined chemical structure can be obtained in fairly different shades, depending on the manufacturing conditions. In this respect Toluidine Red (CI Pigment Red 3) is one of the most typical. This pigment comes on the market in a great number of brands, ranging from yellowish scarlet to bluish red. It is not a matter of polymorphism, since in all these brands the crystalline system is the same. They only differ by the size and the state of aggregation of their particles. Those with the finest particles are the most yellowish and have the highest color strength. This versatility arises from variations in the coupling conditions of diazotized *m*-nitro-*p*-toluidine with β-naphthol, such as concentrations of diazo and naphthol solutions; temperature; pH and rate of coupling; presence, nature, and quantity of surfactant; and eventual heating of the reaction mixture after coupling. The influence of these factors is more or less felt in the manufacture of all azo pigments, hence the necessity for great precision when carrying out the operation.

Obviously, a similar high degree of precision is necessary in the manufacture of other classes of pigments. Conditions for their preparation are indeed often more complex since, unlike the azo pigments, they are rarely obtained directly in a form suitable for use as pigments. They have to undergo a pigmentary conditioning treatment. The principal treatments of this type are *acid pasting* (dissolving in concentrated sulfuric acid, followed by reprecipitation in water) and *salt milling* (ball milling with an inorganic water-soluble salt, which is then removed by washing with water). In certain cases, grinding is carried out in the presence of an organic solvent, or the pigment is treated hot with an organic liquid. If the pigment is polymorphous, the nature of the pigmentary conditioning has a decisive effect on the crystalline form obtained.

In preparing pigments, use is often made of dispersing agents, especially anionic or nonionic ones, though they are occasionally cationic. By using them, particularly in the preparation of an azo pigment, it is possible to obtain a fine suspension of a coupling component which is insoluble under the conditions of the operation. The essential part played by these surfactants is to ensure the formation of the pigment in fine particles; however, they should be used with care.[8] It is not always possible to remove, by washing, a surfactant which has been strongly adsorbed on the pigment and which by its presence can modify the technological properties of the pigment. While organic pigments are generally hydrophobic, a surfactant adsorbed on their surface can render them hydrophilic, a property which is sometimes required, but is more often undesirable. On the other hand, the presence of a surfactant, even a nonionic one, in a pigment may have an unfavorable effect on the dielectric properties of an insulator colored with that pigment.

Certain preparations of pigments are carried out in the presence of sodium rosin soap, which acts as a surfactant. Most often, however, the rosin soap is converted into an insoluble metallic rosinate incorporated in the pigment, the properties of which are thereby favorably modified. The first resinated pigments were the Lithol Reds and the Lithol Rubines, resination being carried out by coprecipitation of the toner and the rosinate of the same metal. Resination has the advantage of imparting a soft texture to the pigment, while increasing its brightness and transparency and reducing its tendency to bronzing. It should be noted that rosinates do not act as true extenders, since very often the coloring power is not reduced but is indeed increased (at least, up to a certain degree of resination). Today, resination is widely practiced, not only on toner-type pigments, but also on pigment dyestuffs, such as Toluidine Red and quinacridones. In place of rosin, use is often made of modified rosins (notably, hydrogenated), and sometimes of other natural or synthetic resins. In 1959, Fran patented the use of resinates of certain metals such as zirconium, which have the effect of imparting gloss to pigments used in printing inks (Luxiane pigments),[9] a result which is particularly useful for those which have a tendency to "powdering" (see Section I,E).

In most cases, the manufacture of a pigment is finished off in an aqueous medium. The pigment in suspension in this medium has taken on the physical form which it must retain, as far as possible, when it is delivered as a powder to the user. It still has to be filtered, washed, dried, and ground. Unless care is taken, changes in the physical structure may still occur in the course of these operations. It is important that the pigment

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[8] A. Permut, *Am. Ink Maker* **45,** No. 11, 20 (1967).

[9] J. Lenoir, J. Ligot, M. Maigrot, and Fran, *FP* 1,226,652; 1,246,922; 1,253,937.

should be cleared, by washing, of all soluble impurities present in the mother liquor, especially mineral salts which could, on drying, stick the particles of pigment together.

Most frequently, the pigment is dried in a heated air circulation dryer or under vacuum. The temperature of drying should be carefully controlled; in general, it should not exceed 65–70°, although the pigment may be stable at higher temperatures. Certain pigments must be dried at a very exact temperature in order to acquire the final shade and have the requisite properties. Drying may also be carried out, with advantage, by atomization in a spray dryer. Except in the latter case, the dry pigment is obtained in the state of more or less friable lumps, which have to be ground. Grinding in a disintegrator should break down these lumps as far as possible, which is relatively easy for pigments of soft texture but is much less easy for those of hard texture. In any case, the particles of pigment are more or less agglomerated in clusters containing air.

After drying and grinding, the pigment has often lost some of its coloring power. To get over this drawback, pigments are sometimes sold to the user in the form of aqueous pulp (presscake, washed and, if required, diluted). However, these pastes are inconvenient to use; they have a tendency to settle on storage, and they may form crusts by partial drying out in containers which are not closely sealed. The best way to avoid loss of coloring power is to transfer the pigment directly from the aqueous phase to the organic vehicle in which it will be used. This method, the so-called flushing process, is widely used for pigments intended for printing inks. It consists in mixing the wet presscake of pigment, in a kneading trough, with an oily vehicle, e.g., a lithographic varnish. The pigment passes into the organic phase and the water separates. This technique has the advantage of preserving the original fineness of the particles. Generally, the flushed pigment in the ink has a tinctorial yield superior to that of the dried and ground pigment.

J. Present Trends

Over the last twenty years, world production of organic pigments has greatly increased, to keep pace with the growing number of outlets for these products. In United States, the only country for which exact statistics of pigment production are given, about 50 million pounds per annum are now manufactured. By way of comparison, American production of dyes is of the order of 200 million pound per annum, and it must be emphasized that these dyes contain much more diluent than do pigments. In most cases, indeed, the latter are not extended at all.

In fact, as a result of the modernization of methods of application, full strength pigments are in increasing demand, while lakes and extended toners are steadily losing ground. This tendency, which is general throughout the world, is particularly shown up in the American statistics.

Table I shows, for some years which are taken as typical, the percentages calculated from statistics of toners and lakes manufactured in the United States. It should be remembered that under the designation "toners," the U.S. Tariff Commission includes all organic pigments other than lakes. Up to 1960, the statistics gave separate indications of the quantities of full-strength toners and extended (or reduced) toners produced. Since the latter have assumed minor importance, statistics since 1961 give only the total production of toners.

TABLE I

UNITED STATES PERCENTAGE PRODUCTION OF DIFFERENT PIGMENT CATEGORIES

	1951	*1954*	*1957*	*1960*	*1966*
Full-strength toners	52.7	67.2	73.5	75.7	—
Extended toners	25.8	19.5	14.6	13.8	—
Toners, total	78.5	86.7	88.1	89.5	91.2
Lakes	21.5	13.3	11.9	10.5	8.8

As can be seen, the share of lakes and extended toners declined strongly between 1951 and 1957. Since that time, this trend has developed more slowly, but the share of lakes has fallen to below 9%. It should also be noted that Peacock Blue Lake (CI Pigment Blue 24) alone accounts for half the production of lakes, and that four red lakes taken together make up one-quarter of the production. The poor demand for the other lakes can be explained not only by their relatively poor coloring power, but also by their general lack of fastness.

It is interesting to recall, however, that while lakes with an inorganic substrate have become for the most part obsolete, a new type of lakes, with an organic substrate, has appeared during the last twenty years. These are fluorescent pigments consisting of a substrate which is a synthetic resin and a fluorescent dye such as Rhodamine, Thioflavine, or Brilliant Sulfoflavine. As examples of this type of pigment, we may mention Day-Glo (Switzer), Fluolac (Fran), Hi-Viz (Lawter), Lumigraphic (IMP), and Velva-Glo (Radiant).

Other more important changes in the nature and quantity of pigments used supervened over the same period. The present production in the

United States of organic pigments of various shades can be estimated approximately, as a percentage, as is shown in Table II.

The share of blues and greens has become very important as a result of the success of the phthalocyanines, which are now the pigments manufactured in the greatest quantity and which together represent one-quarter of the total production of organic pigments. The yellows are essentially acetoacetarylide azo pigments, among which the Benzidine Yellows have become much more important than the yellows of the Hansa type. Red pigments always predominate and half of those which are used are still β-naphthol azo pigments, the production of which does not diminish. The 2-hydroxy-3-naphthoic acid azo pigments represent about one-quarter of the reds, and their production is increasing.

TABLE II

PERCENTAGE PRODUCTION OF DIFFERENT COLORS

Yellows	15.5	Blues	25
Oranges	2	Greens	11
Reds	43	Browns	0.5
Violets	2.5	Blacks	0.5

Many pigments have disappeared from industry, but in their place new ones have appeared. Thus, the number of organic pigments on the market is still considerable: about 370, of which three-fifths are azoics. Reds are the most numerous—about 180. Such a number may appear surprising; however, these pigments differ in shade, in properties, and, last but not least, in cost. It is fortunate that there is a choice, from which the one best suited for a specific application can be selected. As M. Saltzman has said "The selection of a colorant is always a compromise between the properties desired by the designer and the cost of imparting a given hue, value and chroma to a particular paint. There are very few pigments which are suitable for all materials, and those which are suitable for all systems seldom offer the best money value."[10]

The case of the phthalocyanines, universal pigments at an acceptable price, is exceptional. That is why the old pigments continue to be used, notably yellows and reds which have sufficient fastness for ordinary applications and which are of interest because of their cheapness.

Nevertheless, it has been necessary to create new high-grade pigments

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[10] M. Saltzman, *Offic. Dig., J. Paint. Technol. Eng.* **35**, 245 (1963).

capable of meeting the highest requirements. Research has taken place along many lines: (a) chemical classes already represented in the field of pigments: 2-hydroxy-3-naphtharylide and acetoacetarylide azo pigments, vat dyes, dioxazines; (b) known coloring matters which had not been exploited commercially: quinacridones, fluorubines; (c) entirely new coloring matters: naphthindolizinediones, azomethines (derivatives of isoindolinone and others).

At the present time, we know of universal pigments of all hues, but in general their uses are limited by their price. On the other hand, efforts are being made to improve the classic pigments, in order to meet the requirements for purity of shade, coloring power, fineness of texture, and ease of dispersion. New presentations of old pigments have been put on the market. The principal pigments existing in industry appear under a large number of brand names, each of which represents pigments specially prepared for a specific application.

Rubber was the first material for which special series of pigments were created, under the names Rubber, Vulcan (FH,G), Vulcanosin (BASF), Vulcafix (Fran), Vulcafor (ICI), Vulcol (Acna), Irgaphore (Gy), etc. These pigments are sold either as a powder, or in paste form with an artificial rubber or a fatty vehicle, or finally, as master batches. These latter consist of a very concentrated dispersion of pigment in rubber or in a synthetic elastomer. From a suspension of pigment in latex, a master batch, in which the pigment gives its maximum tinctorial yield, can be obtained by coagulation.

For plastics, there are ranges of pigments such as Irgaplast (Gy), Polymon (ICI), Plasticone (SW), Plastol (Pol), and Polymo (KKK). The principal ones, which are intended for polyvinyl chloride, are designated by the letters PV, PVC, or by names such as Vinyloplast (S) and Vynamon (ICI). Certain of these pigments are sold coated with a vinyl polymer or copolymer and are distinguished by such names as Vinyl Disp., Euvinyl (BASF), Microlith K (Ciba), and Vynolour (HAR).

There is a general tendency to provide users with pigments which have been predispersed in a small quantity of the material to be colored, or at least in a vehicle which is miscible with it. Flushed pigments, referred to above, can also be regarded as a type of master batch. Certain pigment manufacturers, notably in America, sell flushed pigments in various printing ink vehicles. However, flushing is often done by the ink manufacturers themselves, starting from the presscakes which are sold to them. We could also mention, as another type of master batch, nitrocellulose chips in which the pigment is dispersed, and which are used for the coloration of lacquers. The first chips of this type were the Ence colors (BASF). Generally speaking, all these compositions of pigments have several advantages: The work of the user is made easier and cleaner, and the perfectly dispersed pigment in these products gives its maximum tinctorial yield.

Where the pigment is sold in powder form, its manipulation can be made less likely to cause soiling by compressing it into friable granules. A certain number of pigments are now offered in this form.

For many uses, pigments are sold in the form of special compositions, either pastes or liquids. This is especially the case with products intended for textile printing and pad dyeing (see Section I,D), and there are many brands in the world: Acramin (FBy), Aridye, Aquaprint (IC), Bedafin (ICI), Helizarin (BASF), Hiltone (HD), Imperon (FH), Imprint (IMP), Neopralac (Fran), Oremasin (Ciba), Printofix (S), Pyratex (MM), Ryudye (DIC), Sherdye (SW), Tinolite (Gy), etc.

The compositions used for coloration of viscose in the mass are more or less fluid pastes, containing the pigment in a finely dispersed state, with a surfactant: Celloide (Fran), Heliofil (FBy), Microsol (Ciba), Microfil (Acna), Monolite V (ICI), Novofil (FH), Spin (G), Tinofil (Gy), Visco (DIC), Viscofil (S). The fineness of the pigments and the stability of their dispersion are of paramount importance for the mass coloration of all artificial or synthetic textiles; improved processes, using special dispersing agents, have been patented in recent years.[11]

For certain applications in aqueous media, e.g., the coloration of paper, the pigments are made hydrophilic by kneading with surfactants in high proportion. There are powder compositions of this type, designated by the letters WD (water dispersible), or by names such as Pigmosol (BASF) and Solupoudre (Fran). Similar products are sold for the pigmentation of latex: Vulcanosol (BASF), Latexol (Fran), Vulcatex (ICI). The present tendency is to use aqueous predispersions similar to the compositions for viscose, in preference to these powders. Among these fluid pastes which are suitable for paper, and some of which are specially intended for emulsion paints, we may mention Accosperse (CCC), Artilene (S), Colanyl (FH), Imperse, Super Imperse (IMP), Irgalite SPV, CPV, (Gy), Monolite HD (ICI), Pergantine (Ciba), Solupate, Ultrapate (Fran).

For the manufacture of other paints and of inks, users increasingly demand pigments which are easy to grind and which will disperse very rapidly. This requirement has brought forth recently patented inventions, according to which use is made of, notably, oleic acid and sodium oleate[12]; an insoluble amine rosinate[13]; amines such as octadecyl-

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[11] ICI, *BP* 855,657; FH, *FP* 1,391,541; 1,396,714; Monsanto, *USP* 3,354,111.

[12] Gy, *FP* 1,438,075.

[13] Gy, *FP* 1,476,138.

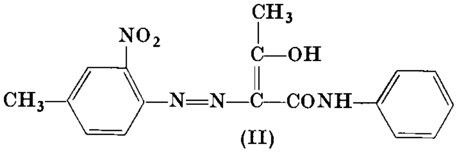
propylenediamine in various forms[14]; other amines of the same type[15]; and resin amines.[16] Special predispersed pigments for inks and paints have recently been put on the market under the brands Irgalite PR (Gy), Lutetia ST (Fran), Monolite EDI, EDP (ICI).

II. Chemistry and Properties of Organic Pigments

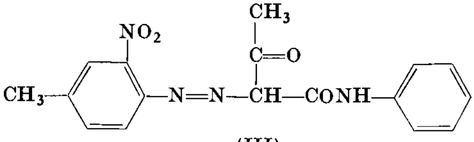
A. ACETOACETARYLIDE AZO PIGMENTS

This class includes pigments ranging from greenish yellow to orange.[17] Hansa Yellow G (*m*-nitro-*p*-toluidine → acetoacetanilide), patented in 1909 and put on the market in 1910, was the first pigment of this class to be produced.

Coupling of acetoacetarylides with diazonium salts takes place on the reactive methylene group of their aliphatic chain, between the two carbonyl groups. As acetoacetarylides are assumed to couple in their enolic form, the formula of the corresponding azo compounds is commonly written (see *Colour Index*) in that form (II). Often, however, it is written in the ketonic form (III).[18]



(II)



(III)

This series includes many monoazo pigments, universally known as Hansa Yellows, although the word Hansa is a trademark which in Germany is also applied to pigments belonging to other chemical classes.

Other acetoacetarylide pigments include symmetric disazo compounds. Among these some are prepared by coupling 2 moles of a diazotized amine with a bis acetoacetarylide, and the others by coupling a tetrazotized diamine with 2 moles of an acetoacetarylide. The most important

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[14] ICI, *DP* 66,11718; *FP* 1,481,733; 1,489,564; 1,490,126; FH, *FP* 1,496,298; 1,559,870.

[15] KVK, *DP* 64,12115; 66,11672.

[16] KVK, *FP* 1,491,740.

[17] J. Lenoir, *Peintures, Pigments, Vernis* **35**, 442 (1959).

[18] On the other hand, for a discussion of azo-hydrazone tautomerism, see Vol. III, Chapter VI.

ones belong to the latter type; they are prepared from 3,3′-dichlorobenzidine and are called Benzidine Yellows.

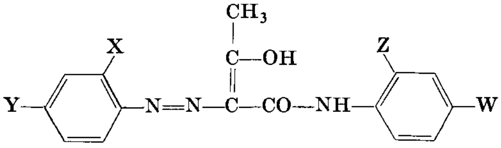
These pigments are all prepared according to the general method of preparation of azo pigments.[19] Though acetoacetarylides can couple in an alkaline medium, it is almost always necessary to carry out the coupling reaction either in an almost neutral medium, in the presence of chalk, or in an acid medium buffered by sodium acetate or formate, in order to obtain a useful pigment. More often the coupling reaction is carried out by introducing the diazonium salt solution into a suspension of the arylide, the latter having been precipitated from its sodium enolate solution by acidification, if necessary in the presence of a surfactant. The azoic dyestuff obtained by this process is immediately usable as pigment, without further treatment. It may be useful, sometimes, to heat at an appropriate temperature and pH after the coupling reaction has taken place.

1. *Hansa Yellows*

Hansa Yellows correspond to the general formula (IV) in which X or Y is a nitro group. Most of these pigments derive from diazotized *o*-nitroanilines. Those indexed in *Colour Index* are listed in Table III.

TABLE III

HANSA YELLOWS



(IV)

CI Pigment	*CI*	*X*	*Y*	*Z*	*W*
Yellow 1	11680	NO_2	Me	H	H
Yellow 2	11730	NO_2	Cl	Me	Me
Yellow 3	11710	NO_2	Cl	Cl	H
Yellow 4	11665	H	NO_2	H	H
Yellow 5	11660	NO_2	H	H	H
Yellow 6	11670	NO_2	Cl	H	H
Yellow 9	11720	NO_2	Me	Me	H
Orange 1	11725	NO_2	OMe	Me	H
Yellow 65	11740	NO_2	OMe	OMe	H
Yellow 74	11741	OMe	NO_2	OMe	H

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[19] CSD I, pp. 409, 430.

They are sold under different brand names: Hansa (FH and others), Fanchon (HAR), Graphtol (S), Irgalite (Gy), Lithosol (DuP), Lutetia (Fran), Monolite (ICI), Permansa (SW), etc. These are also brand names for pigments of other classes.

The most important in this series is the original Hansa Yellow G, CI Pigment Yellow 1, often just called Hansa Yellow or Toluidine Yellow. The second most important one is the very greenish Pigment Yellow 3 (its original name being Hansa Yellow 10G). The most reddish one is CI Pigment Orange 1, sometimes known as Hansa Orange (its original name being Hansa Yellow 3R).

Till very recently, there could only be found in the market the classical Hansa Yellows, including the first nine in Table III, as well as some mixed pigments obtained either by coupling a single diazonium salt with a mixture of two arylides, or more often by coupling a mixture of two diazonium salts with a single arylide. These mixed pigments have very different characteristics in shade, transparency, and oil absorption, compared with mixtures of the two pigments prepared separately and then mixed in the right proportions. The better known ones are obtained by coupling diazotized mixtures of 3-nitro-4-aminotoluene and 3-nitro-4-aminoanisole with acetoacetanilide (Monolite Fast Yellow 2RS and various American brands under the name of Hansa Yellow M).

The classical Hansa Yellows show excellent fastness to light, water, linseed oil, acids, and alkalis. However, their fastness to heat above 150° is poor; furthermore, they bleed in most solvents and migrate in rubber and plastics. They have found important use in paints and printing inks. On the other hand, in printing inks the tendency is to use more and more Benzidine Yellows, the reason being that these pigments, although less fast to light than Hansa Yellows, nevertheless have a coloring strength which is at least twice as great. Through new manufacturing techniques the coloring strength of some classical Hansa Yellows has recently been improved; but considerable research has been carried out in this series in order to develop Hansa Yellows of far better quality.

As CI Pigment Yellow 3 particularly lacked coloring strength, stronger greenish yellows were needed; many have been found in which the diazo component is again 4-chloro-2-nitroaniline. In 1960 FH marketed Hansa Yellow 8G (CI Pigment Yellow 82), using as coupling component 6-chloro-2-acetoacetamidotoluene. Some time later Hansa Brilliant Yellow 10GX was brought out, in which the coupling component is 5-chloro-2-acetoacetamidotoluene.[20] In 1961 and 1962 Gy patented similar azo pigments in which the coupling component is 4-chloro-3-

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[20] FH, *DBP* 1,212,237.

acetoacetamido-acetophenone or isobutyrophenone.[21] Some less greenish ones, which also possess high coloring strength, are obtained through the use of acetoacetyl *o*-anisidine and *p*-phenetidine as coupling components.[22]

5-Nitro-2-aminoanisole was found to be a very interesting diazo component, giving coloring strength in Hansa Yellows comparable to those of Benzidine Yellows. The first of this type (Table III, Yellow 74) was patented in 1959[23]; it is known as Dalamar Yellow (DuP), Brilliant Hansa Yellow 5GX (FH). Recently, similar pigments were patented in which the coupling components are acetoacetyl derivatives of *o*-chloraniline,[24] 5-chloro-2-aminotoluene,[25] 5-chloro-2-aminoanisole,[26] *p*-aminobenzamide,[27] 4-chloro-2,5-dimethoxyaniline,[28] 4-cyano-2,5-dimethoxyaniline,[28a] α-naphthylamine.[28b] 4-Chloro-2,5-dimethoxyacetoacetanilide reacts with diazotized *p*-nitroaniline to yield a golden yellow pigment used in the mass coloration of viscose rayon (CI Pigment Yellow 70).[29]

Some attempts have been made to obtain nonbleeding and plastic-usable Hansa-type pigments of yellow and orange hues. This was attained by the use of heavier azo molecules, particularly through the introduction of further amido groups. In 1958 FBy[30] patented a series of azo pigments in which the diazo component is 2-nitro-4-acetamidoaniline and the coupling component an acetoacetylated Fast Blue or Fast Violet Base (CI Azoic Diazo Comp. 20, 24, 41, 43). In 1961 FH[31] patented the use of acetoacetamidobenzimidazolinones as coupling components. PV Brown HFGG (FH) derives from a compound of this type.

2. *Other Monoazo Pigments*

The acetoacetarylide monoazo pigments lacking a nitro group in their diazo component, unlike the Hansa Yellows, are in general greenish in shade and possess low color strength and low fastness properties. Fast-

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[21] Gy, *SP* 393,586; 424,024.

[22] IMP, *FP* 1,309,211.

[23] DuP, *USP* 3,032,546.

[24] Toyo Ink Man., *JP* 14,432 ('66); *CA* **66**, 19817f.

[25] Gy, *DP* 67,07574.

[26] Gy, *FP* 1,486,225.

[27] *RP* 184,991; *CA* **66**, 86732n.

[28] Gy, *FP* 1,517,252.

[28a] Gy, *FP* 1,558,622.

[28b] Fran, *FP* 1,599,578.

[29] *CI Add. & Am.*, July 1961 (discontinued generic name).

[30] FBy, *FP* 1,219,730.

[31] FH, *USP* 3,109,842.

ness properties can be enhanced by the introduction of halogen atoms into the molecule, while the introduction of bathochromic groups will increase the color strength. Up to now, however, very few of the monoazo pigments of this type can be found on the market. In the two less recent ones the diazo component is 5-chloro-2-aminotoluene, while the second component is acetoacetyl-α-naphthylamide in CI Pigment Yellow 25 and 4-chloro-2,5-diethoxyacetoacetanilide in CI Pigment Yellow 49, which is particularly used in the mass coloration of rayons as well as in paper for laminated plastics. In 1959, ICI patented some acetoacetarylide azo pigments in which the diazo component is a 6- or 7-amino-2-hydroxy-4-methylquinoline.[32] Monolite Fast Yellow 6GS belongs to this series.

Permanent Yellow FGL (FH), which first appeared in 1960, owes its coloring strength and its remarkable fastness properties to both its coupling component (CI Azoic Coupling Comp. 44) and its diazo component (2,5-dimethoxysulfanilanilide).[33] FH patented other pigments of this type, in which the diazo component is a sulfonamide[34] or a sulfone.[35] The use of carboxamides was also patented.[36] Such monoazo pigments sometimes have good overspray fastness and migration resistance.

Some pigments of simpler structure but of rather low color strength also possess these properties. This enables their use in poly(vinyl chloride). They are barium salts of acetoacetarylide azo coloring matters containing a sulfonated diazo component. Some have been known since 1913[37] but found their use only forty years later. They derive from *o*-nitraniline-*p*-sulfonic acid, e.g., CI Pigment Yellow 61 and 62, Graphtol Yellow 3GL, RL, Irgaplaste Yellow GL, RL. Some others were patented by S in 1957[38]; they derive from 2-amino-4-chloro-5-methylbenzenesulfonic acid, e.g., CI Pigment Yellows 85 and 86, and Graphtol Yellow 3GLN and GRL.[39]

3. *Benzidine Yellows*

The coupling of tetrazotized benzidines (1 mole) with acetoacetarylides (2 moles) results in the formation of disazo pigments known as Benzidine

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[32] ICI, *BP* 896,472; 904,794.

[33] FH, *DBP* 845,374.

[34] FH, *DBP* 1,021,104; 1,200,979.

[35] FH, *DBP* 1,085,985.

[36] FBy, *FP* 1,218,055; FH, *FP* 1,306,941.

[37] AGFA, *FP* 455,312.

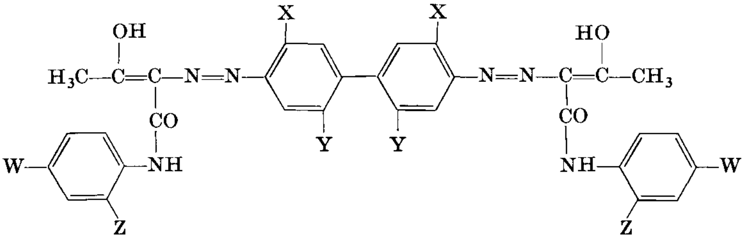
[38] S, *FP* 1,203,865; see also DIC, *JP* 15,306 ('68); *CA* **69**, 87966r.

[39] According to *CA* **64**, 16018f.

Yellows. Benzidine itself is not used; instead 3,3′-dichlorobenzidine is used in most cases, and sometimes *o*-tolidine or *o*-dianisidine. The last two give rise to orange rather than yellow pigments. The classical pigments of this family which are mentioned in *Colour Index* correspond to the general formula (V) and are listed in Table IV. The nature of their substituents is given in the table.

TABLE IV

ACETOACETARYLIDE DISAZO PIGMENTS



(V)

CI Pigment	CI	X	Y	Z	W
Yellow 12	21090	Cl	H	H	H
Yellow 13	21100	Cl	H	Me	Me
Yellow 14	21095	Cl	H	Me	H
Yellow 15	21220	OMe	Cl	Me	Me
Yellow 17	21105	Cl	H	OMe	H
Yellow 55	21096	Cl	H	H	Me
Orange 14	21165	OMe	H	Me	Me
Orange 15	21130	Me	H	H	H
Orange 16	21160	OMe	H	H	H

Although they have been known since 1911,[40] twenty-five years had to pass before the first pigments belonging to this family appeared on the market. They were sold by IG in a range of pigments for rubber, under the denomination Vulcan Fast Yellows and Oranges, which included only Yellows 13, 14, 15, and Orange 14 (Table IV). They were superior to the Hansa Yellows in their nonbleeding properties in solvents, their lack of migration in rubber, and their better resistance to vulcanization temperature. On the other hand, their fastness to light was inferior; following this, Yellow 13 (Permanent Yellow GR), the best in the series, was the only one to be sold for use in paints and inks.

The simplest pigment of the series, the acetoacetanilide derivative,

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[40] GrE, *DBP* 251,479.

was not included in the Vulcan range because of its slight migration. Nevertheless this compound, Yellow 12, of less reddish shade than Yellow 13 is nowadays by far the most important because of its shade, its intense color strength, its brilliancy, its aptitude for production in a transparent form, and its relative cheapness. These properties correspond, in effect, to the needs of modern printing methods whether lithographic or heliographic. This pigment is often called "Benzidine Yellow AAA" (from Aceto Acet Anilide); its production, which increases year after year, ranks it nowadays as third among organic pigments, after Phthalocyanine Blue and Green. The production of other Benzidine Yellows has also increased so much that the American production of Benzidine Yellows now amounts to four times that of the Hansa Yellows. Together Benzidine and Hansa Yellows represent 95% of all yellow organic pigments.

CI Yellow 14, known as Benzidine Yellow AAOT (Aceto Acet *Ortho* Toluidide), ranks second in importance; it is slightly greener in shade and slightly faster to light compared to the first. CI Yellow 17, known as Benzidine Yellow AAOA (Aceto Acet *Ortho* Anisidide), is even a shade greener and slightly faster.

Among the orange pigments in this family, CI Orange 16 is really the only important one; it is usually known as Dianisidine Orange (the name "Benzidine Orange" denotes a particular pyrazolone azo pigment; see Section II,B).

Apart from their use in inks and rubber, the pigments listed in Table IV are particularly used in pigment printing and sometimes in plastics. Most of them, however, are not suitable for poly(vinyl chloride) as they have a tendency to migrate, and, on the other hand, their fastness to light is insufficient for many applications. Finally, their greenish yellow range of color is not wide enough and the greener pigment, CI Yellow 15, is too costly.

Because of these drawbacks research was carried out in order to produce new nonbleeding and nonmigrating Benzidine Yellows faster to light than the previous ones. Among those commercialized the most noteworthy is a reddish yellow pigment patented by FH in 1952,[41] and known as Permanent Yellow HR, in which the coupling component is 4-chloro-2,5-dimethoxyacetoacetanilide. S patented similar pigments in which the coupling component is fluorinated or brominated instead of chlorinated,[42] or is a derivative of 4-halogeno-2-methyl-5-methoxacetoacetanilide,[43] or 2-acetoacetamidobenzothiazoles.[44]

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[41] FH, *DBP* 921,404.

[42] S, *FP* 1,294,427; *SP* 400,419.

[43] S, *SP* 386,592; 400,418.

[44] S, *SP* 397,914; 398,841.

The presence of nitro groups in the molecule has been shown to be an effective way of eliminating migration in PVC. In pigments patented by Fran[45] in 1961, one of the Z or W substituents in formula (V) is NO_2, the other is Cl, Me, or OMe. In 1961 and 1962 S patented disazo pigments derived from *o*-dinitrobenzidine.[46] The introduction of acylamino substituents in the coupling component can ensure nonbleeding properties. Some orange and yellow pigments bearing such substituents have been patented.[47]

Many greenish yellow pigments derived from tetrahalogenobenzidines have been discovered. One of those, Permanent Yellow H10G, was patented by FH[48] in 1958 and derives from 2,5,2′,5′-tetrachloro-4,4′-diaminobiphenyl. Some similar ones were also patented by FH.[49] Some greenish and reddish yellows derived from 3,5,3′,5′-tetrahalogenobenzidines were patented by GS (tetrachloro)[50] and by S (tetrabromo or dichlorodibromo).[51]

4. *Other Types of Disazo Pigments*

By coupling acetoacetarylides with tetrazotized diamines other than the benzidines, some interesting pigments can be obtained. Ciba in particular patented in 1952 some nonmigrating yellow pigments prepared in this way and derived from 1,5-diaminoanthraquinone.[52] According to a Gy patent,[53] fast greenish yellow pigments are obtained when use is made of 4,4′-dichloro-3,3′-diaminobenzil or of the corresponding hydrobenzoin or bibenzyl. Irgalite Fast Yellow 6GLT very probably belongs to this series. In an S patent[54] a bright yellow pigment is mentioned for use in viscose rayon. It is prepared from 2,5,2′,5′-tetrachloro-4,4′-diaminodiphenylurea and CI Azoic Coupling Component 44. In certain patents ICI claims some yellow pigments derived from quite complex diamines such as *N*,*N*′-bis(4-amino-2-chloro-phenyl)terephthalamide and 1,4-xylylenebis(3-amino-4-methoxyphenyl sulfone).[55] In a more recent patent ICI uses bis-1,4-(3′-amino-4′-chlorobenzoyl)-

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[45] J. Lenoir, M. Maigrot, and Fran, *FP* 1,299,094; 1,338,314.

[46] S, *FP* 1,342,539; 1,294,427.

[47] CIBA, *USP* 2,807,609; *SP* 331,213; Toyo Ink Man., *JP* 22,396('66); *CA* **66**, 86599z.

[48] FH, *DBP* 1,088,634.

[49] FH, *DBP* 1,131,838; 1,153,844.

[50] GS, *DBP* 1,098,124.

[51] S, *SP* 395,393.

[52] CIBA, *SP* 309,180.

[53] Gy, *BP* 803,985.

[54] S, *USP* 2,936,305.

[55] ICI, *BP* 849,376; 895,948.

benzene as tetrazo component.[55a] HAR patented a yellow disazo pigment suitable for plastics and derived from 3,7-diaminodibenzothiophene dioxide.[56]

Some commercial disazo pigments are obtained by coupling two molecules of a diazonium salt with a molecule of bis acetoacetarylide. In the older pigments the second component is CI Azoic Coupling Component 5 [bis(acetoacetyl)*o*-tolidine]. The only ones in this series of any importance are CI Pigment Yellow 16 (CI 20040) and 77 (CI 20045), in which the respective diazo components are 2,4-dichloroaniline and 5-chloro-2-aminotoluene. Despite the fact that like Benzidine Yellows these pigments have a biphenyl nucleus, their color strength is nearer to that of Hansa Yellows than that of Benzidine Yellows. A similar pigment of superior strength and greater fastness but lacking the aforesaid nucleus was patented in 1965 by HSH[57] and possesses the following formula: 5-chloro-2-aminotoluene (2 moles) ⇉ 2,5-dichloro-1,4-bis(acetoacetamido)benzene.

5. *Azo Condensation Pigments*

The aforementioned research has shown the interesting fact that pigments with large molecules do not migrate in plasticized PVC. It was further demonstrated that large numbers of amide links in pigment molecules increase their fastness properties. On the other hand, when attempts are made to synthesize azo pigments of very large molecular size by normal coupling methods, one is limited by the low solubilities of the high molecular weight components taking part in the reaction. It is very difficult, in particular, to quantitatively obtain a disazo pigment by coupling a second diazonium salt molecule onto a previously formed insoluble monoazo color.

This difficulty can be overcome by preparing in the first stage a low molecular weight azo color, followed by a condensation giving rise to a high molecular weight pigment through a carboxamide link.

Many Ciba patents, the first one of which dates back to 1951,[58] involve preparations of this type, in which carboxy azo dyestuffs are transformed into acid chlorides and condensed in a solvent medium with amines or diamines. This method was mainly developed for the production of red disazo pigments of the 2-hydroxy-3-naphtharylide class (see Section II,E,7). It is also used, however, for manufacturing yellow

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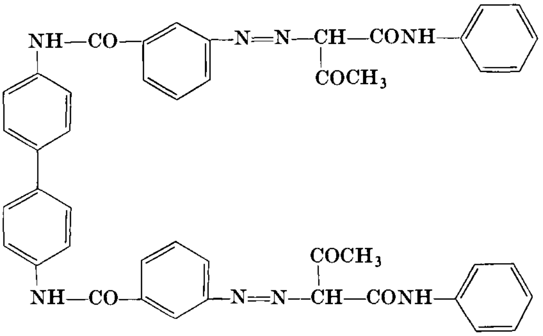
[55a] ICI, *BP* 1,139,296.

[56] HAR, *USP* 2,879,266: see also S, *FP* 1,552,521.

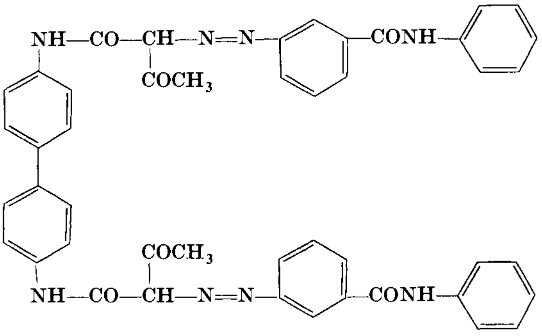
[57] HSH, *FP* 1,471,620.

[58] CIBA, *FP* 1,054,935; *DBP* 921,223.

pigments derived from acetoacetarylides, the two main types of which according to Gaertner[59] correspond to formulas (VI) and (VII).



(VI)



(VII)

In these formulas the aromatic nuclei may bear substituents such as halogen, alkyl, alkoxy, or nitro. The molecular weights of these pigments may reach 900 to 1100. To prepare a pigment of type (VI), 4-chloro-3-aminobenzoic acid, for example, is diazotized and then coupled with an acetoacetarylide. The monoazo product obtained is filtered, washed, dried, and put in suspension in chlorobenzene; the suspension is then heated and treated with thionyl chloride at the boil. The carboxychloride is formed. It is filtered, washed, and dried and then brought into suspension in chlorobenzene containing some pyridine. A benzidine is then introduced (1 mole for 2 moles of carboxychloride) and the mixture heated to boiling for a prolonged period. Finally the pigment (VI) is

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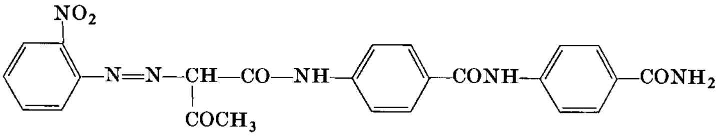
[59] H. Gaertner, *J. Oil Colour Chemists' Assoc.* **46**, 37 (1963).

filtered, washed, and dried.[60] Cromophtal Yellow 2G (CI Pigment Yellow 79)[61] was a pigment of this type.

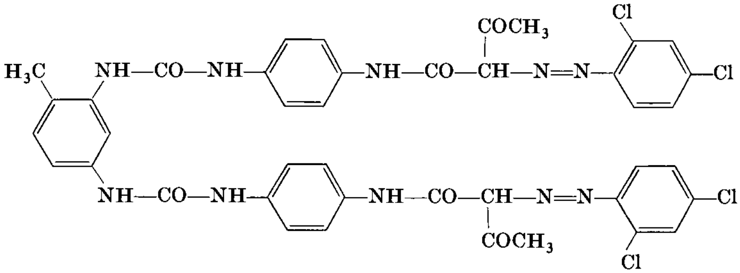
To prepare a pigment of type (VII), 4-chloro-3-aminobenzoic acid can again be used. It is diazotized and 2 moles of the diazonium salt are coupled with 1 mole of Azoic Coupling Component 5, or rather with a substituted 1,4-bis(acetoacetyl)phenylenediamine (2,5-dimethyl, 2-methyl-5-chloro, or 2,5-dichloro). The disazo dyestuff so formed is separated and treated with thionyl chloride to obtain the carboxychloride, which is finally condensed with an amine such as chlorotoluidine.[62] The Cromophtal Yellows GR, 3G, and 6G belong to this series.

Laptev and Vysokosov[63] used a similar method to prepare the yellow pigment (VIII) by coupling diazotized *o*-nitroaniline with *p*-acetoacetamidobenzoic acid; the azo dyestuff is then treated with thionyl chloride to obtain the carboxychloride which is then condensed with *p*-aminobenzamide.



(VIII)

In 1962 and 1966, FBy patented[64] disazo pigments of large molecules obtained by condensing aminoazo or hydroxyazo dyestuffs with diisocyanates. For example, [2,4-dichloroaniline → *p*-aminoacetoacetanilide] (2 moles) condensed with toluylene-2,4-diisocyanate gives rise to the yellow pigment (IX). According to a Japanese patent[64a] disazo pigments are prepared by condensing aminoazo dyes with terephthaloyl chloride.



(IX)

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[60] CIBA, *SP* 305,022; 305,023.

[61] *CI Add. & Am.*, January 1962 (discontinued generic name).

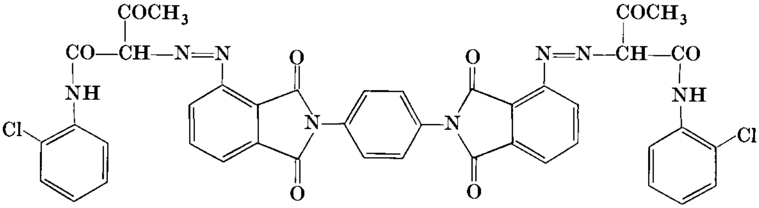
[62] CIBA, *SP* 359,498.

[63] N. G. Laptev and A. N. Vysokosov, *RP* 120,624; *CA* **58**, 8061f.

[64] FBy, *DBP* 1,213,553; *FP* 1,544,475.

[64a] Daito Chem. Ind. & Toyo Ink Man., *JP* 17,308('68); *CA* **70**, 38888d.

In 1965 FBy also patented[65] phthalic diimide disazo dyestuffs such as the yellow pigment (X) which is obtained by condensing *p*-phenylenediamine with 2 moles of the monoazo dyestuff: 3-aminophthalic anhydride → acetoacet-*o*-chloroanilide.

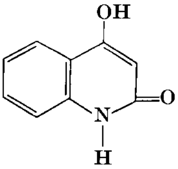


(X)

6. *Related Pigments*

Yellow azo pigments in which the coupling component is not an acetoacetarylide have been known for a long time. However, apart from the pyrazolone derivatives, which will be treated further on, most of them have not been marketed. Such is the case with the indanedione derivatives[66] and with those of sulfazone,[67] patented, respectively, in 1910 and 1912.

Two commercial azo pigments derived from 2,4-dihydroxyquinoline are available. It is to be noted that 2,4-dihydroxyquinoline couples in its tautomeric form, 4-hydroxy-2-quinolone (XI), and that this cyclic amide bears a great resemblance to acetoacetarylides which are open-chain amides.



(XI)

The oldest pigment derived from 2,4-dihydroxyquinoline is CI Pigment Yellow 7 (CI 12780) with *o*-nitroaniline as diazo component. The most important is CI Pigment Green 10, the nickel chelate of the dyestuff: *p*-chloroaniline → 2,4-dihydroxyquinoline (XII). This very

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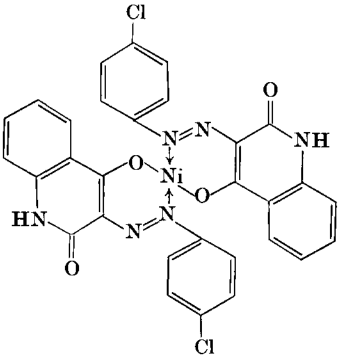
[65] FBy, *FP* 1,490,373.

[66] BASF, *DBP* 241,723.

[67] MLB, *DBP* 273,342.

yellowish green pigment was patented in 1941 by DuP[68] and put on the market under the name of Green Gold. It is now manufactured by many firms. Despite its relatively weak color strength, it is much appreciated for its outstanding fastness to solvents, heat, light, and weathering. It is particularly used in automotive finishes and in textile printing.

Other pigments having 2,4-dihydroxyquinoline as the coupling component were recently patented.[68a] In orange pigments, the diazo component is 6-amino-2,4-dihydroxyquinazoline or 6-amino-2,3-dihydroxyquinoxaline; in a yellow it is 1-aminoanthraquinone.



(XII)

In recent patents, the use of new coupling components having reactive methylene groups is mentioned. In 1961 S[69] patented some yellow pigments derived from 1,2-diphenyl-3,5-dioxopyrazolidine with various amines as diazo components. In 1965 BASF patented[70] some yellow pigments in which the diazo component is 1-aminoanthraquinone and the coupling component barbituric acid or 2-iminobarbituric acid.

In 1963 and 1965 IC patented some azo pigments having as coupling component a malonanilide optionally substituted on its benzene rings.[70a]

B. Pyrazolone Azo Pigments

Although containing fewer examples compared with the previous one, this class constitutes a larger gamut, extending from yellow to red and maroon.[71]

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[68] DuP, *USP* 2,396,327.

[68a] BASF, *FP* 1,510,398; 1,527,378.

[69] S, *SP* 399,622; 421,343.

[70] BASF, *FP* 1,469,919.

[70a] IC, *USP* 3,252,968; 3,382,228.

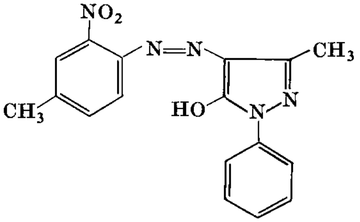
[71] J. Lenoir, *Peintures, Pigments, Vernis* **35**, 612 (1959).

Tartrazine, CI Acid Yellow 23,[71a] which is the oldest pyrazolone dye, is still used nowadays for preparing bright and transparent lakes (CI Pigment Yellow 100). Many other pyrazolone dyes have been used in lakes: CI Acid Yellows 11 and 13, and Saturne Yellows.[71b] Although still used fifteen years ago, these lakes are now quite obsolete.

On the other hand, there are two series of pyrazolone pigment dyestuffs, the monoazo and the disazo pigments. Most of them are derivatives of the most usual pyrazolone: 1-phenyl-3-methyl-5-pyrazolone. The preparation of these pigments is similar to that of acetoacetarylide azo pigments. However, by using a pyrazolone hydrochloride solution the coupling reaction can often be carried out at lower pH.

1. *Monoazo Pigments*

Some monoazo pigment dyestuffs having 1-phenyl-3-methyl-5-pyrazolone as coupling component have been on the market since 1910, but very few of these are still in use. The diazo component in those which have been retained is *o*-chloroaniline in CI Pigment Yellow 60; 2,5-dichloroaniline in CI Pigment Yellow 10; and *m*-nitro-*p*-toluidine in CI Pigment Orange 6. The first one is almost obsolete, while the second is still relatively important as a reddish yellow. The fastest to light and oil is CI Pigment Orange 6 (XIII), which like the Hansa Yellows has a nitro group in the ortho position of the azo linkage. In a general way, monoazo pigments in this series have the drawback of being relatively soluble in solvents (alcohols, aromatic hydrocarbons, glycol ethers).



(XIII)

According to a recent patent, very much improved fastnesses are obtained by using 1-(4′-carbamoylphenyl)-3-methyl-5-pyrazolone as coupling component.[71c]

2. *Disazo Pigments*

Disazo pigments are solvent-faster than monoazo pigments and are much more used. They are oranges and reds derived from 3,3′-

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[71a] CSD I, p. 608.

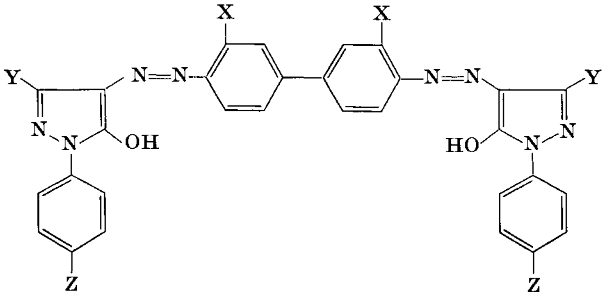
[71b] CSD I, p. 611.

[71c] N. G. Laptev and A. N. Vysokosov, *RP* 151,738.

dichlorobenzidine or other 4,4′-diaminobiphenyls. They correspond to the general formula (XIV). Those indexed in *Colour Index* are listed in Table V.

TABLE V

PYRAZOLONE DISAZO PIGMENTS



(XIV)

CI Pigment	*CI*	*X*	*Y*	*Z*
Orange 13	21110	Cl	Me	H
Orange 34	21115	Cl	Me	Me
Red 37	21205	OMe	Me	Me
Red 38	21120	Cl	CO_2Et	H
Red 39	21080	H	CO_2Et	H
Red 41	21200	OMe	Me	H
Red 42	21210	OMe	CO_2Et	H

The most important one in the series is Orange 13. This pigment, initially commercialized in Germany as Vulcan Fast Orange G and universally known as Benzidine Orange, is nowadays one of the most manufactured oranges. In rubber, it is sufficiently fast to light, but less so in its other numerous applications. Besides, it lacks fastness to certain solvents. Therefore, for such uses as textile printing, its homolog Orange 34, brought on the market not long ago, is preferred. This "Ditolyl Orange" has indeed better lightfastness and dry cleaning properties.[72]

The red pigments in this series owe their shade to the bathochromic effect of the methoxy groups of dianisidine or of the ester group of ethyl 1-phenyl-5-pyrazolone-3-carboxylate. The oldest ones, Reds 37 and 38, were brought on the market in 1933 by IG for coloring rubber.

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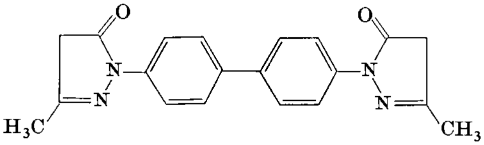
[72] *Am. Ink Maker* **39**, No. 5, 74 (1961); A. Permut, *Ibid.* **45**, No. 4, 12 (1967).

Red 38, which is the best one, is nowadays very much used not only in rubber, but also in plastics, although its resistance to migration is often insufficient. Other Pyrazolone Reds have appeared: CI Pigment Reds 39 and 41, the second being important; and CI Pigment Reds 110 and 111, pigments synthesized by coupling a mixture of tetrazotized 3,3′-dichlorobenzidine and *o*-dianisidine with 1-*p*-tolyl-3-methyl-5-pyrazolone.[73] The series was completed by the Pyrazolone maroons, which include Red 42 and an analogous disazo pigment in which the diazo component is *o*-tolidine.

It is doubtful whether new pyrazolone azo pigments will appear on the market. Nonetheless, in patents claiming new diazo components, examples are sometimes mentioned in which pyrazolones are used as coupling components. On the other hand, a recent patent from FH[74] is especially concerned with pigments of this class, in which 2 moles of diazotized anthranilic acid are coupled with the bis pyrazolone (XV). By converting the azo dyestuff into a Ni or Cu chelate, yellow pigments suitable for PVC are obtained.



(XV)

C. β-Naphthol Azo Pigments

The β-naphthol azo compounds, which are among the oldest organic pigments, are essentially reds, ranging from orange to maroon.[75] Commercially, this class is almost as important as the phthalocyanines. By weight, it represents about one-fifth of the organic pigments made and about one-half of the reds. It includes (1) pigment dyestuffs in which the diazo component is free from solubilizing groups; (2) toners and lakes in which the diazo component is sulfonated or carboxylated.

1. *Pigment Dyestuffs*

The red and orange pigments in this series almost all correspond to the general formula (XVI). They are summarized in Table VI. To prepare

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[73] ICI, *FP* 959,045; 983,719.

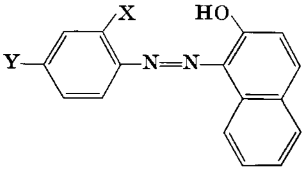
[74] FH, *DBP* 1,153,843.

[75] J. Lenoir, *Peintures, Pigments, Vernis* **36**, 144 (1960).

these azoics, it would be easy to carry out coupling in alkaline medium, with the β-naphthol in solution as sodium naphtholate. However, to produce good pigments, it is generally necessary to couple in an almost neutral medium or in a buffered acid medium. Indeed, Pigment Orange 5 is prepared in a strongly acid medium. In fact, since 2,4-dinitroaniline is diazotized by nitrosylsulfuric acid, a large quantity of acid is introduced into the coupling with the diazonium sulfate, and this does not hinder the reaction. In these various cases, coupling is done with a suspension of β-naphthol reprecipitated from the naphtholate solution by acidification.

TABLE VI

β-NAPHTHOL AZO PIGMENT DYESTUFFS



(XVI)

CI Pigment	*CI*	*X*	*Y*
Red 1	12070	H	NO_2
Red 3	12120	NO_2	Me
Red 4	12085	Cl	NO_2
Red 6	12090	NO_2	Cl
Red 40	12170	α-Naphthylamine	
Red 93	12152	OMe	Cl
Orange 2	12060	NO_2	H
Orange 3	12105	Me	NO_2
Orange 5	12075	NO_2	NO_2

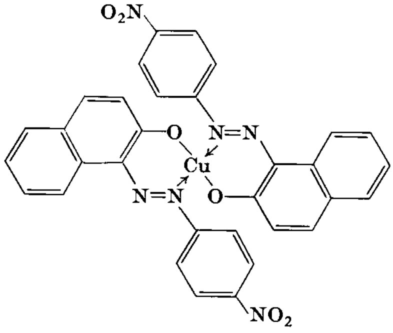
Pigment Red 1 is Para Red (from *p*-nitroaniline), of which there are two varieties: Para Red Light, yellowish, and Para Red Dark, bluish and brighter. The second is prepared by replacing 5 to 7% of the β-naphthol with 2-naphthol-7-sulfonic acid (F-acid). These cheap pigments are still widely used in paints, but their commercial importance has greatly diminished because of their poor fastness to solvents and their poor fastness to light in tint.

Pigment Red 3, Toluidine Red (from *m*-nitro-*p*-toluidine), is much faster. This is the pigment of which the greatest number of brands exist in industry, covering a wide range from yellowish scarlet to bluish red. Differences in shade result essentially from variations in the size of microcrystalline particles, which can be regulated by varying the conditions of coupling (see Section I,I). However, the bluest brands (extra dark) are prepared by mixing a little *m*-nitro-*p*-anisidine with the *m*-nitro-*p*-toluidine during diazotization. Toluidine Red is still today one of the most used pigments, though its consumption has diminished by half in the last 20 years. It is very fast to light, but has several defects. Its lack of overspray fastness precludes its use in modern paints based on alkyd resins. Nevertheless, it has many applications, particularly in oil and emulsion paints.

Pigment Red 4, Chlorinated Para Red, or Chlor Para Red (from *o*-chloro-*p*-nitroaniline) has better fastness than Para Red, due to the chlorine atom in the ortho position. It is still of importance as a fire red pigment. Its isomer Pigment Red 6, Parachlor Red (from *p*-chloro-*o*-nitroaniline), was at one time made under the name Hansa Red GG (MLB), but was abandoned. During the last fifteen years, this pigment has enjoyed an astonishing recovery. A little bluer and very slightly faster to light than Red 4, it is appreciated for its transparency.

Pigment Orange 5, Dinitroaniline Orange, is the most used of the orange pigments. Its fastness properties are at least equal to those of Toluidine Red. On the other hand, Pigment Orange 2, Orthonitroaniline Orange, is falling more and more into disuse, and Pigment Orange 3 is obsolete. The same applies to Pigment Red 93. Pigment Red 40, α-Naphthylamine Maroon, is still used in phenoplasts, but it is more of a solvent dye (CI Solvent Red 4).

CI Pigment Brown 2, or Para Brown (XVII), is the copper chelate of Para Red. It is incomparably faster to light and to solvents than the



(XVII)

latter. It has the drawback that it easily catches fire in dry grinding, but this can be remedied.[76]

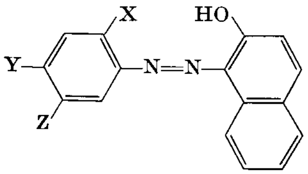
Similar brown pigments, also chelates of copper, were patented by FBy in 1953.[77] In one of these, the diazo component is 4-nitro-4′-aminobenzanilide.

2. *Toners and Lakes*

Most of these red or orange pigments correspond to the general formula (XVIII). They are summarized in Table VII, with their substituents and the metals of the commercial salts.

TABLE VII

β-NAPHTHOL AZO TONERS AND LAKES



(XVIII)

CI Pigment	*CI*	*X*	*Y*	*Z*	*Metals*
Red 49	15630		Tobias acid		Ba, Ca, Na, Sr
Red 50	15500	CO_2^-	H	H	Ba, Na
Red 51	15580	H	SO_3^-	Me	Ba
Red 53	15585	SO_3^-	Cl	Me	Ba, Na, Ca
Red 68	15525	SO_3^-	Cl	CO_2^-	Ca
Red 69	15595	SO_3^-	Me	Cl	Na
Red 70	15590	SO_3^-	Me	H	Ba
Red 117	15603	SO_3^-	Cl	*i*-Pr	Ba
Orange 7	15530	SO_3^-	Cl	Cl	Na
Orange 17	15510	H	SO_3^-	H	Ba, Na

These azo compounds are prepared in the form of sodium salts by coupling in alkaline medium with β-naphthol in solution as sodium naphtholate. After separation of the dye, conversion into a toner is brought about by double decomposition with barium or calcium chloride. To resinate these toners, if required, a solution of rosin soap is

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[76] J. Lenoir, J. Luna de Prada, and Fran, *FP* 1,103,480.

[77] FBy, *DBP* 870,303.

added to this preparation; the rosin precipitates at the same time as the toner in the form of a salt of the same metal intimately mixed with the pigment.

Because of their nature as insolubilized acid dyes, these pigments differ in properties from previous pigment dyestuffs. They are faster to solvents, but less so to light, and they have rather poor resistance to alkalis. They are of very unequal commercial importance. By far the most used are Pigment Reds 49 and 53.

Red 49, or Lithol Red, which is the oldest of the series, has Tobias acid (2-aminonaphthalene-1-sulfonic acid) as its diazo component. It is sold in the form of salts of several metals, which are toners, including the sodium salt, which is sufficiently insoluble in water to be usable as a pigment. These toners constitute a range from orange red to maroon. This versatility results not only from the various metals, but also from the polymorphism of the pigments, and from the possibility which exists of modifying them by varying conditions of preparation and incorporating with them alkaline earth soaps of rosin.[78] The most widely used is Lithol Red Barium toner. It is a medium red, of which more than 3 million pounds are made per annum in the United States, which places it in the first rank of reds and gives it fourth place among organic pigments. The Calcium Toner, of which 1.5 million pounds are made in the United States, exists in two crystalline forms which are very different in shade, one bluish red and the other dark maroon (Lithol Maroon). The Sodium Toner is an orange red, of less importance. The Strontium Toner has appeared more recently. The principal outlet for all these pigments is in printing inks, but they have other uses, notably the coloration of rubber.

Pigment Red 53, first sold as a dye for lakes, is still called Lake Red C or Red Lake C, although it is no longer used except in toners. The principal one is Barium Toner, bright scarlet in shade and having very high coloring power. There are opaque bronzing brands and transparent brands of this toner. It has the same uses as the Lithol Reds, whose production it has surpassed in Europe. In the United States, where it has doubled in the last fifteen years, it has now reached nearly 2 million pounds. The Sodium Toner, a brilliant orange, is less important, and the Calcium Toner is very little used. In the manufacture of the diazo component of Lake Red C, 2-amino-6-chlorotoluene-4-sulfonic acid is obtained as a by-product and is used to manufacture an isomer of Lake Red C, similar in shade but of inferior quality.[79]

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[78] A. Permut, *Am. Ink Maker* **45** No. 5, 12; No. 6, 12 (1967).

[79] A. Permut, *Am. Ink Maker* **35**, No. 5, 45 (1957).

Among the other reds in this series, the only one of any importance is Pigment Red 51, scarlet in shade. Pigment Red 50, or Lake Red D, derived from anthranilic acid, was formerly a great success; today, it is almost as derelict as Lake Red P, derived from 4-nitroaniline-2-sulfonic acid, which was at one time important, but is now obsolete.

Pigment Red 69 and Pigment Orange 7 are dyes for lakes which are almost obsolete, and the only orange of importance in this series is CI Pigment Orange 17, the sodium salt of which is none other than Orange II (CI Acid Orange 7), still used for the preparation of lakes. The Barium Toner is also made from it, and is known in the United States under the name Persian Orange.

The newest pigments in this series are homologs of Lake Red C: CI Pigment Red 117, derived from 2-chloro-5-aminocumene-4-sulfonic acid, patented by SW in 1957[80]; and Clarion Red (CCC) derived from 2-chloro-5-aminoethylbenzene-4-sulfonic acid, patented in 1952.[81]

There are hardly any other novelties to expect in the class of β-naphthol azo pigments, which was thoroughly studied at the end of the nineteenth century and at the beginning of the twentieth century.

D. 2-Hydroxy-3-naphthoic Acid Azo Pigments

This class, which provides about one-fourth of all commercial red pigments, extends and completes the preceding class of toners. While the Class C pigments range principally from medium to yellowish red, the present class includes mainly rubines, although the range extends from scarlet to maroon.[82] These pigments are often called BON Rubines, Reds, and Maroons (BON arising from Beta-Oxy-Naphthoic acid, the trivial name of their coupling component).

Since a carboxyl group is present in their molecule, these pigments are all metallic salts of the toner type (or lake), particularly as the diazo component is almost always an aminosulfonic acid. It does not therefore seem strange to see that in general they have the same qualities and faults as the β-naphthol azo toners, i.e., very good resistance to solvents and lack of fastness in alkalis; their lightfastness, however, is often superior. This is particularly the case for manganese toners, which in this series are numerous.

The preparation of these pigments is very similar to that of β-naphthol azo toners. After having coupled in an alkaline medium the dye is changed into a toner by double decomposition with the chloride of an alkaline earth metal or with manganese sulfate. These toners are very

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[80] SW, *USP* 2,796,415.

[81] CCC, *USP* 2,598,483.

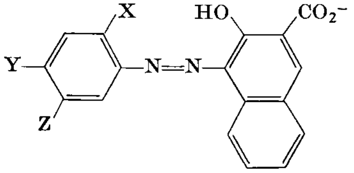
[82] J. Lenoir, *Peintures, Pigments, Vernis* **36**, 388 (1960).

often resinated by coprecipitation of the corresponding metallic salt of rosin. There also exist some one-step processes for the manufacture of these pigments.

Most pigments of this class have the general formula (XIX) in which the carboxylate ion as well as the sulfonate ion carried by the diazo component are bound to the metallic cation. In Table VIII are indicated the substituents and metals of those toners listed in *Colour Index.*

TABLE VIII

2-Hydroxy-3-naphthoic Acid Azo Pigments



(XIX)

CI Pigment	*CI*	*X*	*Y*	*Z*	*Metals*
Red 48	15865	SO_3^-	Me	Cl	Ca, Mn, Ba, Sr
Red 52	15860	SO_3^-	Cl	Me	Ca, Mn, Ba
Red 55	15820	CO_2^-	H	Cl	Mn
Red 56	15870	OMe	SO_3^-	Me	Ba
Red 57	15850	SO_3^-	Me	H	Ca, Ba, Na
Red 58	15825	H	Cl	SO_3^-	Ca, Mn, Sr, Ba
Red 63	15880		Tobias acid		Mn, Ca, Ba, Sr
Red 64	15800	H	H	H	Ba, Ca
Red 115	15861	H	Me	SO_3^-	Mn

The oldest representative of this family is Pigment Red 57, the original names of which are Permanent Red 4B and Lithol Rubine B. This last name is still commonly used. Lithol Rubine Calcium Toner is the most manufactured pigment of this class in Europe. This is not the case in the United States, but its annual production has doubled in the last twenty years and now reaches 1 million pounds. Many brands exist, most of them resinated to different degrees. Resination increases transparency and gives a more bluish shade in tint, without diminishing the color strength. On the contrary, it is increased, at least up to a certain limit of resination. A special resination process patented in 1959 by

Fran[83] enables its transformation into a good magenta pigment for use in three-color printing (Luxiane Magenta P). Lithol Rubine Calcium Toner has a large outlet in printing inks and has many other usages. On the contrary, the Barium Toner is very little used. The sodium salt formerly used as dye for lakes is a bright orange dyestuff almost insoluble in water, sometimes used as pigment.

In the United States Pigment Red 48 or Permanent Red 2B is the most important. In this country its annual production keeps on increasing and has now reached 2.6 million pounds, thus ranking it second among the red pigments. This production is shared, however, between many toners, the principal ones being the salts of calcium and manganese. The calcium toner is a rubine, less bluish and a little faster to light than Lithol Rubine. This pigment, which appeared in 1928 in Germany, at first had very little success. Its tremendous commercial development began twenty years later when it was marketed by DuP as Watchung Red. Since then it has been manufactured in the whole world. Its main outlets are printing inks and plastics. The yellowish red Barium Toner has the same usages, but is less important. The bluish red Manganese Toner differs from the others in its very superior fastness to light; it is very much used in paints. Some more transparent brands are also known; they are mixed salts of manganese and calcium. The recently produced strontium toner is fire red. There also exists a Watchung Maroon, which is the calcium toner of the mixed azo dyestuff prepared from a mixture of 2-chloro-4-aminotoluene-5-sulfonic acid and 2-chloro-4-aminoanisole-5-sulfonic acid; it was patented in 1952 by DuP.[84]

Pigment Red 52, an isomer of Red 48, is sometimes named Naphtoic Red C as it has the same diazo component as Lake Red C. It is better known in the United States as Lithol Red 2G, an improper name arising from the first edition of *Colour Index*, in which by mistake this constitution was attributed to Lithol Red 2G of IG (the latter was in fact CI Pigment Red 69, Table VII). Pigment Red 52, which up to then had not been manufactured, appeared on the market in the United States in 1951 and underwent an extremely rapid commercial development. Its production now amounts to over 1 million pounds per annum, essentially shared between the Calcium Toner, a rubine, and the Manganese Toner, which is a garnet.

None of the other pigments belonging to this class can compare in importance with the preceding ones. Pigment Red 58, however, is distinguished by the variety of its toners. The most interesting is the manganese toner of crimson shade. Pigment Red 77 (CI 15826) (not listed

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[83] J. Lenoir, J. Ligot, M. Maigrot, and Fran, *FP* 1,226,652.

[84] DuP, *USP* 2,744,027.

in Table VIII) is also a manganese toner derived from a chlorinated metanilic acid, the diazo component being 2,3-dichloroaniline-5-sulfonic acid. It was patented in 1954 by SW.[85]

Pigment Red 63 has the same diazo component as Lithol Red; its main toners are those of calcium (claret) and of manganese (maroon). Other manganese toners, also maroon, are known; they have anthranilic acid or its chlorinated derivatives as diazo component. Pigment Red 55 or Maroon Gold derives from 4-chloroanthranilic acid; it was patented in 1950 by DuP[86] and is suitable for automotive finishes. Pigment Red 118, Monolite Maroon GS, is the chromium chelate and manganese salt of the same azo dyestuff. It was patented in 1954 by ICI.[87]

Pigment Red 64 is the only one in this series that does not have an anionic group in its diazo component (which is aniline). Its barium and calcium toners are old pigments of low fastness to solvents and of no interest other than their cheapness. The copper toner, on the contrary, is an interesting brown pigment of recent commercial development; it is CI Pigment Brown 5.

This class of pigments is today in full expansion: Not only are its principal representatives more and more in use, but also, in less than twenty years many new toners have been put on the market. Others may appear, since research in this series is still being carried out, as shown by the patents that have been issued.

For example, in a patent from DuP[88] a bluish red strontium toner is mentioned, which is said to be suitable for automotive finishes. It has the monoamide derived from aminoterephthalic acid and 2,4-dimethoxy-5-chloroaniline as diazo component. Diazo components more akin to those of the classical pigments have been proposed: dichloroaniline or toluidinesulfonic acids,[89] xylidinesulfonic acids,[90] 2-naphthylamine-4-sulfonic acid,[91] aniline-2,5-disulfonic acid,[92] and 1-sulfomethyl-2-aminonaphthalene.[92a] In 1966 BASF patented[93] some toners belonging to this class which were modified by the association of 1% of a metal such as nickel with 99% of the alkaline earth metal; the color strength is then said to be

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[85] SW, *USP* 2,694,055.

[86] DuP, *USP* 2,649,383.

[87] ICI, *BP* 776,873.

[88] DuP, *USP* 2,808,400.

[89] CCC, *USP* 2.765,300; 2,821,525.

[90] Toyo Ink Man., *JP* 17,754('66); 5,550('67); *CA* **66**, 30018s; **67**, 44834n.

[91] *RP* 133,962; *Chem. Zentra.* No. 6, 2725 (1965).

[92] FBy, *FP* 1,513,911.

[92a] CCC, *FP* 1,564,369.

[93] BASF, *FP* 1,511,993.

enhanced. In 1966 FBy patented[94] pigments analogous to Reds 52 and 57 in which the coupling component is no longer 2-hydroxy-3-naphthoic acid, but its 6-sulfo derivative.

E. 2-HYDROXY-3-NAPHTHARYLIDE AZO PIGMENTS

These pigments are almost all reds of the pigment dyestuff type.[95] They differ from those of the previous class by having the carboxyl group of the 2-hydroxy-3-naphthoic acid changed into an arylamide. The coupling components, the original name of which is Naphthol AS, are well known for their use in azoic dyeing.[95a] Pigments of the present class are often made from azoic diazo components (Fast Bases). Many of them, however, are prepared with arylides which are not sold as azoic coupling components and/or with diazo components that are not used in azoic dyeing.

The first pigments of this class were patented in 1911,[96] and a short time later two of these were sold as Grela Reds. They were not successful due to their high cost. The AS Naphthols were later manufactured in larger quantities for azoic dyeing, and consequently their price dropped. This made it possible to use them for good quality pigments. In the 1930s IG brought on the market a whole series of Permanent Reds principally selected from those combinations which were formed in situ on textiles in azoic dyeing. In the 1940s, there appeared in the United States a series of Naphthol Reds primarily created to answer the needs for alkali-resistant red pigments. They belonged to the same class, but did not possess the same formulas as the German Permanent Reds.

Since then, whether in Europe or in America the number of these pigments has kept on increasing. However, although this class includes today more than 80 commercial pigments, it still produces only a relatively small proportion of the red pigments used (only 4% in the United States for 1965, more in Europe). A very considerable amount of research is being carried out with the aim of creating very fast pigments with the help of new diazo components and/or special hydroxynaphtharylides. Some are already on the market, and there is little doubt that the commercial importance of this class will increase in the near future. It is further to be noted that this class includes not only monoazoic, but also disazoic pigments. Furthermore, although it principally includes a rich gamut of reds, a small number of oranges, browns, purples, and blues are also found in the market.

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[94] FBy, *BP* 1,108,249.

[95] J. Lenoir, *Peintures, Pigments, Vernis* **36**, 700 (1960).

[95a] CSD I, p. 668.

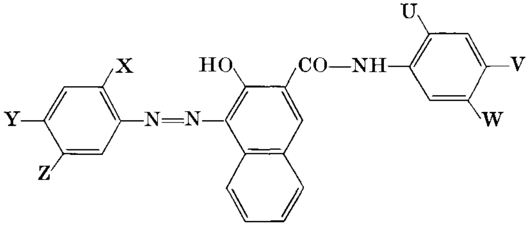
[96] GrE, *DBP* 256,999.

1. *Classical Monoazo Pigments*

These pigments have the general formula (XX). Apart from some relatively new ones this series consists essentially of the German Permanent Reds and the American Naphthol Reds of the initial varieties. This is the reason why these pigments of simple structure can be considered as classical. Those indexed in *Colour Index* are tabulated in Table IX.

TABLE IX

2-HYDROXY-3-NAPHTHARYLIDE AZO CLASSICAL PIGMENTS



(XX)

CI Pigment	*CI*	*X*	*Y*	*Z*	*U*	*V*	*W*
Red 2	12310	Cl	H	Cl	H	H	H
Red 7	12420	Me	Cl	H	Me	Cl	H
Red 8	12335	Me	H	NO_2	H	Cl	H
Red 9	12460	Cl	H	Cl	OMe	H	H
Red 10	12440	Cl	H	Cl	H	Me	H
Red 11	12430	Me	H	Cl	Me	H	Cl
Red 12	12385	Me	NO_2	H	Me	H	H
Red 13	12395	NO_2	Me	H	Me	H	H
Red 14	12380	NO_2	Cl	H	Me	H	H
Red 15	12465	NO_2	Cl	H	OMe	H	H
Red 16	12500	OMe	NO_2	H	α-Naphthylamide		
Red 17	12390	Me	H	NO_2	Me	H	H
Red 18	12350	NO_2	Me	H	H	H	NO_2
Red 19	12400	OMe	NO_2	H	Me	H	H
Red 21	12300	Cl	H	H	H	H	H
Red 22	12315	Me	H	NO_2	H	H	H
Red 23	12355	OMe	H	NO_2	H	H	NO_2
Red 112	12370	Cl	Cl	Cl	Me	H	H
Red 114	12351	Me	H	NO_2	H	H	NO_2
Red 162	12431	Me	H	NO_2	Me	H	Cl
Orange 22	12470	Cl	H	Cl	OEt	H	H
Orange 24	12305	H	H	Cl	H	H	H
Brown 1	12480	Cl	H	Cl	OMe	H	OMe

One of the difficulties in the preparation of this class of azoic dyestuffs is the solubilization of the coupling components. To dissolve their monosodium salts (naphtholates) a mixture of alcohol and water is usually necessary. Most of these products, however, can be dissolved in hot water as disodium salts (the second acid group being the enolic form of the amide function). An excess of caustic soda may be useful; care should be taken, however, to avoid hydrolysis of the amide group. The coupling reaction is sometimes carried out in an alkaline medium. However, just like many other azo pigments, those belonging to this class must often be prepared in a neutral or slightly acid medium to obtain the desirable pigment properties. Under these conditions the coupling component, having been reprecipitated from its alkaline solution in the presence of a surfactant, is in a state of fine suspension. In some cases the coupling reaction must take place at temperatures of the order of 60 or 70°.

Among the classical pigments CI Reds 2, 7, 8, 9, 10, 11, 12, 16, 21, Orange 24, and Brown 1 are those which formed with Red 5 (which we see later) the original German "Permanent" series. With the exception of Red 21, which is obsolete, they are important in Europe but not much manufactured elsewhere. Red 2 is the only one to be manufactured in large quantity even in the United States. These pigments are used in printing inks and for mass coloration of rayons. It is important to note that in these fibers their fastness properties are superior to those of the same azo compounds formed by azoic dyeing.

Those pigments of the series having 2,5-dichloroaniline as their diazo component range from scarlet to orange red; the most important are Reds 2 and 10. Derivatives of chlorotoluidines (Reds 7 and 11) are bluish reds. Reds 12 and 16, which derive from nitrotoluidine or nitroanisidine, are bordeaux. Red 112, more recent than the preceding ones, is a derivative of 2,4,5-trichloroaniline; this beautiful scarlet of excellent fastness properties is more and more used, in particular in emulsion paints and in textile printing. Another derivative of 2,4,5-trichloroaniline was patented by FBy in 1963[97]; it is a brown pigment with paraphenetidide as its coupling component. Permanent Red FGG (FH) first appeared in 1958 (CI Pigment Red 148). It is made from diazotized 2,4-dichloroaniline and Naphthol AS-D; its shade approaches that of Lake Red C, and its fastness properties are superior. CI Pigment Red 136 is a bordeaux derived from 2,4-dinitroaniline; it was patented by FBy in 1957.[98]

The American Naphthol Reds are CI Reds 13, 14, 15, 17, 18, 19, 22, and 23. It is interesting to note that while the preceding series contains

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[97] FBy, *DBP* 1,273,728.

[98] FBy, *DBP* 925,122.

only few nitro compounds, the Naphthol Reds all have nitro aryl amines as their diazo components. They range from scarlet to maroon. They are important in the United States, but little manufactured elsewhere. The oldest and also the most used are Red 17 (Naphthol Red Medium), Red 22 (Naphthol Red Light), and Red 23 (Naphthol Red Dark). Red 13 (Toluidine Maroon Light) and especially Red 18 (Toluidine Maroon Dark) have been used in automotive finishes, but they are much less used nowadays. Reds 14, 15, and 119 are more recent maroons. The most interesting is Red 14 (Naphthol Maroon Light); it is now manufactured also in Europe.

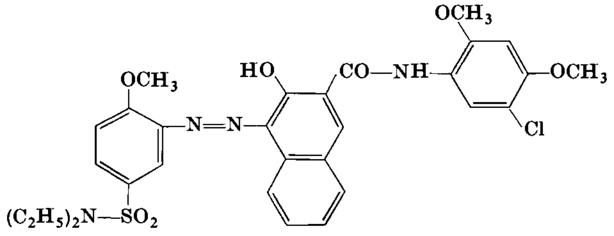
There also exist on the market some 15 other pigments of formula type (XX) which are not in *Colour Index*. They are oranges, reds, and browns, most of them especially manufactured for mass coloration of rayons. Just like CI Orange 24, oranges in general have the low bathochromic *m*-chloroaniline as their diazo component. In some browns the coupling component is an arylide of hydroxycarboxylic acids derived not from naphthalene, but from carbazole (Azoic Coupling Component 15) or from dibenzofuran (Azoic Coupling Component 16).

In general, pigments of the classical type owe their good fastness properties towards oil and alkalis to the carboxamide function of their coupling component. They are therefore suitable for printing inks and viscose rayon, but their relatively high price is often an obstacle to their use in oil paints. Many of them are very fast to light and sufficiently resistant to trichloroethylene to allow their use in textile printing. Due to their insufficient solvent resistance, however, they cannot be used in baking enamels, and because they migrate in plastics and rubber they are not suitable for these materials.

2. *Pigments in Which the Diazo Component is a Sulfonyl Compound*

In some pigments of excellent fastness properties, the diazo component is an *o*-anisidine or toluidine or chloroaniline having on the benzene ring a substituent such as sulfonamide, sulfone, or sulfoester.

The oldest in this series is CI Pigment Red 5 (CI 12490) brought on the market by IG before World War II as Permanent Carmine FB (XXI).



(XXI)

This pigment has now found many manufacturers in the world. It is very much appreciated for its excellent lightfastness in pale tint and its good resistance to numerous solvents. Because of its low migration it is even sometimes used in plastics. A similar pigment, CI Pigment Red 132 of scarlet shade, derives from 4-(dimethylamino)sulfonyl-2-aminotoluene.[99] Another analogous pigment was patented in 1966 by Kuznetsov *et al.*[99a]

In 1958 FH patented[100] some red-violets derived from 4(cyclohexylmethylamino)sulfonyl-2,5-dimethoxyaniline; in the same year FBy[101] patented some reds fast to overspray and derived from 4-acetamidosulfonyl-2-aminoanisole. Diazo components bearing a $-SO_2NHCH_2CONH_2$ group are used in certain pigments that were patented by FH[102] in 1963. Similar pigments, with $-SO_2NHC(=NH)NH_2$ groups, were patented by S[102a] in 1967. Some simpler sulfonamides are also found in recent patents such as that of HD[103] regarding the azo pigment sulfanilamide → 2-hydroxy-3-naphth-*o*-anisidide, and that of Ciba,[103a] with *o*-aminobenzenesulfonanilide as diazo component.

Pigments derived from sulfones are more scarce; the only one that still exists on the market is CI Pigment Red 163 (CI 12455). The analogous CI 12450 is obsolete.

In two FBy pigments the diazo component is a 2-aminoanisole-(or toluene)-sulfonic acid aryl ester. These are Helio Fast Carmine G, patented in 1950,[104] and Helio Fast Red FG, patented in 1956.[105] They are very fast to light and solvents. Nonetheless their ester function endows them with a certain sensitivity towards alkalis which is unusual for this class of pigments.

3. *Pigments in Which the Diazo Component Is a Benzamide*

Some commercial pigments as well as many recently patented pigments derive from an aminobenzanilide. They correspond to the general formula (XXII), in which the benzene ring A may bear substituents. The three oldest pigments of this series are listed in Table X.

[99] *CI Add. & Am.*, July 1961 (discontinued generic name).

[99a] Tambov Chem. Combine, *RP* 192,997; *CA* **68**, 70164j.

[100] FH, *DBP* 928,242.

[101] FBy, *DBP* 1,087,302.

[102] FH, *DBP* 1,235,468.

[102a] S, *FP* 1,551,511.

[103] HD, *USP* 3,127,391.

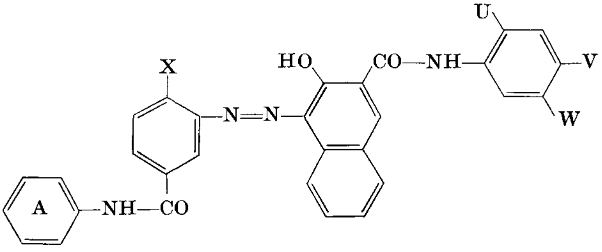
[103a] CIBA, *SP* 452,749.

[104] FBy, *DBP* 849,149.

[105] FBy, *DBP* 1,087,300.

These pigments are principally sold for coloring rubber, in which they do not migrate. 3-Amino-4-methoxybenzanilide, the diazo component of the last two in the table, is also that of more recent pigments. In 1953 Permanent Carmine FBB (CI Pigment Red 146; U = W = OMe, V = Cl) was brought out by FH; it is more bluish and brighter than CI Red 5. A similar pigment, Permanent Pink F3B, which is even more bluish, was patented in 1958.[106] Analogous pigments were again patented in 1966.[106a]

TABLE X



(XXII)

Benzanilide and Hydroxynaphtharylide Azo Pigments

CI Pigment	CI	X	A	U	V	W
Red 30	12330	Me	2,4-diMe	H	Cl	H
Red 31	12360	OMe	Unsubst.	H	H	NO_2
Red 32	12320	OMe	Unsubst.	H	H	H

Two other pigments patented in 1961 and 1962 by FH[107] differ from Red 146 solely by the substituents on nucleus A (XXII): the first by a $-CONH_2$ group in the para position, the second by two chlorine atoms in the 2,5-positions. A certain number of pigments patented by Gy between 1961 and 1964[108] have X = Cl and two or three chlorine atoms on the A nucleus.

It is interesting to notice that in many pigments patented during recent years the A nucleus disappears, the diazo component becoming a

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[106] FH, *DBP* 1,088,632.

[106a] GS, *FP* 1,539,578; T. I. Orlova *et al.*, *RP* 201,290.

[107] FH, *DBP* 1,208,435; 1,221,382.

[108] Gy, *FP* 1,328,646; *SP* 418,493; 426,056; 435,501.

non-*N*-substituted benzamide. These simple components are 4-aminobenzamide,[109] 3-amino-4-methylbenzamide,[110] 3-amino-4-methoxybenzamide,[111] 4-amino-3-methylbenzamide,[112] 3-amino-4-chlorobenzamide,[113] and 5-amino-2,4-dichlorobenzamide.[114] As a general rule, these pigments in which the coupling components are usual arylides, are said to be fast to solvents, and interesting for textile printing and for plastic coloring. Permanent Red F5RK (FH) belongs to this series.[109] Its very good fastness properties most likely result from intermolecular association by hydrogen bonds between carbamoyl groups. Reds derived from 3-amino-4-methoxycarbonyl-benzamide would also have the advantage of not migrating in PVC.[115] According to an older patent from FBy[115a] very solvent-fast reds are obtained with 3-amino-4-methoxybenzoylurea as diazo component.

It is also to be noted that in 1958 FBy patented[116] pigments ranging from orange to maroon, fast to overspray, and in which the diazo component is 2-amino-5-nitro-*N*,*N*-dimethylbenzamide. Finally, one could also include in this series PV Carmine HR (FH), which was patented in 1952.[117] Here the A nucleus is in the diazo component, but its coupling component is the nonsubstituted 2-hydroxy-3-naphthamide.

4. *Various Monoazo Pigments*

Apart from the preceding series, which are largely represented commercially, there also exist a great number of monoazo pigments of the same class, showing some constitutional peculiarities either in the diazo or in the coupling component, or in both.

Most of these pigments were patented during the last few years. In some of the oldest, however, the diazo component is a monoacyl-*p*-phenylenediamine of the general formula (XXIII). Many violet and blue pigments used for mass coloration of rayons or for textile printing belong to this series. They derive from Fast Violet and Fast Blue Bases, well known for their usage in azoic dyeing (R = Ph, X = Me or alkoxy, Y = alkoxy). The *Colour Index* only mentions CI Pigments Violet 13 and 25, but others exist on the market. One could also include in this series Helio

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[109] FH, *BP* 1,033,917; FBy, *DP* 64,09644.

[110] IC, *BP* 949,741; *USP* 3,322,932; FH, *DBP* 1,230,151; HD, *FP* 1,496,429.

[111] HD, *USP* 3,330,819.

[112] FBy, *FP* 1,411,277.

[113] FH, *DBP* 1,019,416; 1,153,841.

[114] Gy, *USP* 3,197,457.

[115] FH, *DBP* 1,199,305.

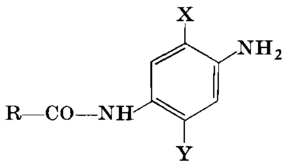
[115a] FBy, *DBP* 965,917.

[116] FBy, *DBP* 1,098,645.

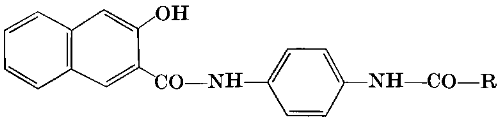
[117] FH, *DBP* 1,052,970.

Fast Maroon R (CI Pigment Violet 17) ($R = Me$, $X = NO_2$, $Y = H$) a pigment patented by FBy[118] in 1955.

In many pigments patented by FH[119] between 1959 and 1961 the coupling component has the formula (XXIV), where $R = Me$ or Ph. These pigments have, in general, a benzamide or a benzenesulfonamide as their diazo component and are very fast to light and to solvents. Other pigments patented by ICI in 1959[120] and by GS in 1963[121] have a phthalimido or a naphthalimido group either in the diazo or in the coupling component.

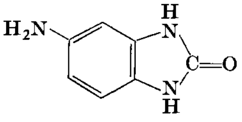


(XXIII)

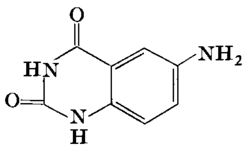


(XXIV)

In some recently patented pigments –NHCO– or –NHCONH– groups, which improve fastness, are included in the rings. In an important series of pigments patented by FH[122] the coupling component is the 2-hydroxy-3-naphthoyl derivative of either 5-aminobenzimidazolinone (XXV) or of its 4-amino isomer. They are reds, maroons, and browns fast to light and overspray. Some pigments patented by FBy and by FH[123] have as their diazo component 6-amino-2,4-dioxotetrahydroquinazoline (XXVI) or as coupling component its 2-hydroxy-3-naphthoyl derivative. In another patent[124] the diazo component is 3-methyl-6-amino-4-oxo-dihydrobenzotriazine (XXVII).



(XXV)



(XXVI)

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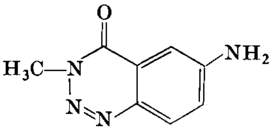
[118] FBy, *DBP* 963,458.
[119] FH, *DBP* 1,146,604; 1,153,841; 1,225,321.
[120] ICI, *BP* 901,420.
[121] GS, *DBP* 1,227,173; 1,229,214.
[122] FH, *DBP* 1,188,229; 1,215,839; 1,216,460; 1,217,008; *BeP* 713,053; 723,711.
[123] FBy, *FP* 1,164,476; FH, *USP* 3,118,870; *DBP* 1,235,467; 1,289,928.
[124] FBy, *DBP* 1,101,658.



(XXVII)

Other heterocyclic compounds are also mentioned as diazo components, e.g., 7-amino-2-hydroxy-4,6-dimethylquinoline in an ICI patent[125]; 3-(3′-amino-4′-methoxy)phenyl-4-methyl 1,2,5-oxadiazole in a patent from FH[126]; and 2-(2′-aminophenyl)-4-quinazolone in a patent from FBy.[126a] Coupling components bearing heterocycles are also mentioned in recent patents, e.g., in a Ciba patent[127] the 2-hydroxy-3-naphthoyl derivative of 2-(3′-aminophenyl)amino-4,6-diamino-1,3,5-triazine is mentioned. In one of the patents by IC[128] concerning reactive pigments for polymer textiles, mention is made of the 2-hydroxy-3-naphthoyl derivative of propylene-1,2-imine.

2-Hydroxy-3-naphtharylides substituted on the naphthalene nucleus are rare. However, in patents by IC[129] new pigments are claimed to be faster to light than CI Pigment Red 5, the coupling component of which is the 7-bromo or 7-cyano derivative of CI Azoic Coupling Component 12.

Some anthraquinone derivatives have been proposed as diazo components: 2-amino-3-chloroanthraquinone in some patents by G[130] and 1-amino-5-benzamidoanthraquinone in one of FBy patents[131] concerning a red pigment suitable for plastics. As coupling component, the 2-hydroxy-3-naphthoyl derivative of 2-aminoanthraquinone has found a mention in Ciba patents.[132]

5. *Toners and Chelates*

It may seem strange to find in this class some toners which are insolubilized sulfonic acid dyes. Despite their drawbacks (lower fastness to light, sensitivity to alkalis), pigments of this type have the advantage of not migrating in plastics such as PVC. They can be prepared from classical hydroxynaphtharylides and from cheap diazo components,

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[125] ICI, *BP* 896,472.

[126] FH, *DBP* 1,047,342.

[126a] FBy, *BP* 1,129,849.

[127] CIBA, *SP* 389,128.

[128] IC, *USP* 3,297,677.

[129] IC, *USP* 3,153,032; 3,335,168.

[130] G, *USP* 2,871,234; 3,079,376.

[131] FBy, *FP* 1,461,884.

[132] CIBA, *FP* 1,172,849; Add 73,266.

which is not the case for the new high-quality pigments of this class. These toners, however, have appeared only recently. The first ones seem to be those patented in 1953 by BASF[133]; they are manganese toners with chlorotoluidinesulfonic acids as diazo components.

The principal commercial toners are CI Pigment Reds 133, 134, and 151. Irgaplaste Reds HBL and HGL were patented by Gy in 1955; they are barium or calcium toners having aniline-2,5-disulfonic acid as diazo component.[134] PV Red H4B belongs to a series of pigments patented by FH in 1957, the two components of which bear sulfo groups, the second one being, for instance, 2-hydroxy-3-naphthoylsulfanilic acid.[135] The same coupling component is found in a recent Ciba patent,[136] the diazo component being 2-amino-4-trifluoromethylbenzenesulfonic acid. The corresponding barium toner is an intense red suitable for PVC.

Metallic chelates of hydroxynaphtharylide azo dyestuffs are rare. A mention should be made, however, of Newport Maroon (DuP), which is the copper chelate of 4-nitroanthranilic acid → 2-hydroxy-3-naphthoyl-*p*-phenetidide.[137] Furthermore, chelates of disazo dyestuffs are mentioned in some patents.[138]

6. *Various Disazo Pigments*

Tetrazotized 4,4′-diaminobiphenyls coupled with two molecules of 2-hydroxy-3-naphtharylide give rise to blue pigments which could be called "Benzidine Blues." In fact, the only diaminobiphenyl to be used is dianisidine, in order to obtain pigments for the mass coloration of rayons. Only three or four of these pigments are still available commercially, two of which are listed in *Colour Index*: CI Pigment Blues 25 and 26 (CI 21180 and 21185), their respective coupling components being the anilide and the *o*-anisidide of 2-hydroxy-3-naphthoic acid.

Other blue disazo pigments patented in 1957 by S[138] derive from 4,4′-diamino-2,5,2′,5′-tetramethoxydiphenylurea. Among others they include a navy blue which is a copper chelate with 2-hydroxy-3-naphthanilide as coupling component; and a migration-resistant dark blue in which the unsubstituted 2-hydroxy-3-naphthamide is the coupling component.

Since less than twenty years ago a great number of disazo pigments of

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[133] BASF, *DBP* 949,077.

[134] Gy, *FP* 1,145,768.

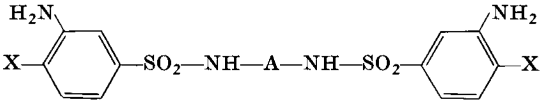
[135] FH, *DBP* 1,078,259.

[136] CIBA, *SP* 423,039.

[137] According to H. Raab, *in* Ullmann, **13**, p. 809; *USP* 2,416,248.

[138] S, *FP* 1,194,450.

high molecular weight, most of them red, have been invented to answer the urgent need for pigments of this hue suitable for PVC and for baking enamels. As will be seen later, such pigments are mainly obtained by what is known as the azo condensation method. Many patents, however, claim pigments prepared by double coupling of heavy tetrazotized diamines with two molecules of hydroxynaphtharylides. FBy in 1957[139] and S in 1958[140] patented pigments fast to overspray and derived from diamines of the general formula (XXVIII) in which, for instance, A = $-CH_2CH_2-$ or *p*-phenylene and X = Me or OMe.



(XXVIII)

In an ICI patent[141] the diamine is *N*,*N*′-bis(5-amino-2,4-dichlorophenyl)terephthalamide; and in one of FH patents[142] it is bis(3-amino-4-chlorobenzoyl)-*p*-phenylenediamine.

Another type of disazo pigment is found in a patent recently taken out by Gy.[143] It concerns a bordeaux pigment prepared by coupling 2 moles of diazotized 5-nitro-2-aminoanisole with 1 mole of bis(2-hydroxy-3-naphthoyl)-*p*-phenylenediamine.

7. *Azo Condensation Pigments*

In fact, double couplings on bis(hydroxynaphthoyl)arylenediamines are in general very difficult to execute. It is true that some are carried out on textile fibers in azoic dyeing, particularly with bis(2-hydroxy-3-naphthoyl)dianisidine. A disazo pigment of the same type, however, cannot be properly prepared in substance by the usual coupling process in aqueous medium. The insoluble monoazo dyestuff formed with the first mole of diazonium salt will with difficulty react with the second one, so that double coupling cannot, in general, be quantitative.

A method known as "azo condensation,"[144] which has already been mentioned for the preparation of yellow pigments (see Section II,A,5) overcomes this difficulty. This general method has been described in

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[139] FBy, *DBP* 1,058,175.

[140] S, *SP* 380,268.

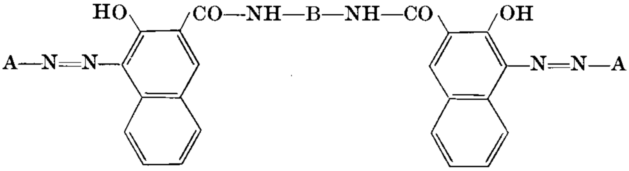
[141] ICI, *BP* 894,602.

[142] FH, *DBP* 1,133,052.

[143] Gy, *SP* 460,991; see also Gy, *DP* 68,09766; 68,09767; 68,09768.

[144] H. Gaertner, *J. Oil Colour Chemists' Assoc.* **46**, 33 (1963).

numerous Ciba patents, the first ones dating back to 1951 and 1952.[145] It enables not only the preparation of disazo pigments of the above-mentioned type (XXIX), but also of other types of azo dyestuffs formed by large molecules containing two to four amide links giving rise to excellent fastness qualities.



(XXIX)

In this method, pigments of general formula (XXIX) are prepared as follows: The diazonium salt of an amine A—NH_2 is coupled with 2-hydroxy-3-naphthoic acid. The resulting monoazo pigment is separated, dried, and then converted to the acid chloride by treatment with thionyl chloride in chlorobenzene or *o*-dichlorobenzene under heat and in the presence of dimethylformamide. The dye in the form of acid chloride is eventually purified; 2 moles are then condensed with 1 mole of a diamine H_2NBNH_2 under heat and in the same medium.

Ciba brought on the market a dozen "Cromophthal" pigments corresponding to formula (XXIX), in which the amine A—NH_2 is a chloro- or a dichloroaniline, a chlorotoluidine, a chloromethoxytoluidine, a chlorodimethoxyaniline, or methyl anthranilate. The diamine H_2N—B—NH_2 is benzidine, 3,3′-dichlorobenzidine, *o*-tolidine, *p*-phenylenediamine, chloro-*p*-phenylenediamine, or 1,5-diaminonaphthalene. Cromophtal Reds R, 2RF, 2R, BR, GR, B, Scarlets R, 2R, Orange 4R, Rubine B, Bordeaux B, and Violet R belong to this series. These pigments have outstanding fastness to light and solvents, enabling their use in PVC and baking enamels.

It is to be noted that according to some patents pigments of formula (XXIX) can be prepared by processes other than condensation. A patent taken out by Ciba[146] describes the direct coupling of the dehydrated and

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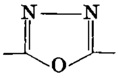
[145] CIBA, *SP* 297,020; 303,155; 304,984-305,028; *DBP* 921,223; *FP* 1,054,935; 1,089,809; among more recent patents concerning disazo pigments of type (XXIX), see also CIBA, *BP* 942,431; 942,432; 988,973; *USP* 3,137,688; *SP* 424,027; 434,520.

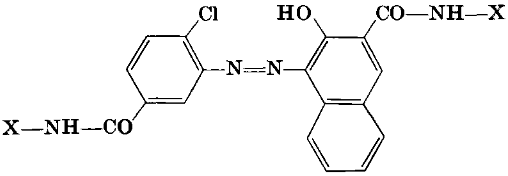
[146] CIBA, *USP* 2,912,428; see also coupling of a diazoamino compound at the boil, in acetic acid or in *o*-dichlorobenzene containing acetic acid: CIBA, *FP* 1,537,367; 1,537,423; 1,539,446.

stabilized diazonium salt and the bis(hydroxynaphthoyl)arylenediamine which is carried out by mixing in a kneading trough. In a more recent patent[146a] Ciba described another direct process, in which an acid solution of the diazonium salt is continuously mixed with an alkaline solution of the bis(hydroxynaphthoyl)arylenediamine in 2-ethoxyethanol, at pH 4.5–5.0 with vigorous stirring, the pigment suspension formed being continuously withdrawn. According to a patent taken out by Gy[147] coupling can be carried out in a sand mill. FH patented in 1959[148] a very different process using a Mannich base prepared by treating the bis(hydroxynaphthoyl)arylenediamine with formaldehyde and dimethylamine. This base, having $-CH_2N(CH_3)_2$ groups in 1,1′-positions, is very soluble in water as its hydrochloride. It reacts with the diazonium salt at pH 4–5; the coupling takes place in the 1,1′-positions with elimination of the dimethylaminomethyl groups, giving rise to the desired disazo pigment.

Ciba patents regarding azo condensation pigments are so numerous that not all can be mentioned. One of these patents[149] describes disazo pigments related to type (XXIX) which are prepared by using hydrazine instead of diamine $H_2N—B—NH_2$. Red pigments with an oxadiazole ring (XXX) instead of the –CONH—B—NHCO– group are prepared by cyclization of these dyes with thionyl chloride. Some patents describe pigments ranging from red to violet which are copper, cobalt, or nickel chelates of disazo dyestuffs of type (XXIX) in which the amine $A—NH_2$ is an *o*-aminophenol.[150]



(XXX)



(XXXI)

Many monoazo pigments are described in other patents. Those of general formula (XXXI) are prepared from a 3-aminobenzoic acid and 2-hydroxy-3-naphthoic acid. The dye is converted to the bis acid

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[146a] CIBA, *BP* 1,143,727.

[147] Gy, *SP* 397,913.

[148] FH, *DBP* 1,257,913.

[149] CIBA, *USP* 2,838,486; see a pigment of similar type: Toyo Ink Man., *JP* 829('68); *CA* 68, 106071t.

[150] CIBA, *FP* 1,162,066; *SP* 347,915.

chloride and then condensed with 2 moles of an amine X—NH_2 which can be a heavy amine such as 3-aminopyrene,[151] a benzoyl-*p*-phenylenediamine,[152] or an aminobenzanilide.[153] Even acid chlorides of monoazo dyes of the type: heavy diazo component without carboxyl → 2-hydroxy-3-naphthoic acid are condensed with amines such as an acyl-*p*-phenylenediamine,[153a] an aminophenylurea,[153b] 4-aminonaphthostyril,[153c] an aminobenzotriazole,[153d] an aminobenzanilide,[153e] or aminoterephthalanilide.[153f] Similarly, acid chlorides of monoazo dyes, aminobenzoic acid → 2-hydroxy-3-naphtharylide, are condensed with heavy amines.[153g] Red, violet, and blue tetrakisazo pigments can also be prepared by condensing a diamine with two molecules of the carboxychloride of a disazo dyestuff of the type: amine → amine → 2-hydroxy-3-naphthoic acid.[154]

Ciba has also patented pigments containing sulfonamide links, which are obtained by the same process used for the preparation of carboxamide links.[155] For instance, the azo pigment sulfanilic acid → 2-hydroxy-3-naphthanilide is converted to the sulfochloride with thionyl chloride and condensed with *o*-tolidine, giving thus a scarlet pigment.

Azo condensations of different types have recently been invented. According to a patent taken out by FBy,[156] a red pigment very fast to migration can be obtained by condensing in sulfuric acid at low temperature *N*,*N*′-di(hydroxymethyl)urea with the azo pigment *m*-chloroaniline → 2-hydroxy-3-naphthoyl-*o*-anisidine. Two molecules of the latter are said to be united by a $-CH_2NHCONHCH_2-$ bridge between the benzene nuclei of the coupling component.

General formula (XXXII) represents pigments prepared by condensation of a diamine $H_2N—Y—NH_2$ with 2 moles of the monoazo pigment 3-aminophthalic anhydride → 2-hydroxy-3-naphtharylide. These pig-

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[151] CIBA, *DBP* 1,115,864.

[152] CIBA, *DBP* 1,235,465; 1,247,510.

[153] CIBA, *FP* Add 68,658.

[153a] CIBA, *FP* 1,445,002; 1,445,004; 1,445,804; 1,530,953; 1,542,171; *SP* 422,193; 458,578; *DBP* 1,278,040; *BP* 1,050,806.

[153b] CIBA, *FP* 1,474,394; 1,545,185.

[153c] CIBA, *FP* 1,557,266.

[153d] CIBA, *BP* 1,122,559.

[153e] CIBA, *FP* 1,356,646; 1,437,518; *SP* 434,515; 459,409; 459,415; 471,203; *DBP* 1,274,261.

[153f] CIBA, *SP* 428,032.

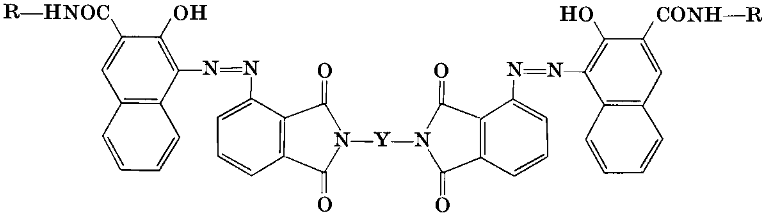
[153g] CIBA, *BP* 949,736; *FP* 1,437,518; *SP* 471,204; see also SCW, *JP* 21,190('68).

[154] CIBA, *SP* 347,917.

[155] CIBA, *USP* 2,759,921.

[156] FBy, *FP* 1,470,735.

ments are described in several FH patents.[157] The diamine can be ethylenediamine, a *p*-phenylenediamine, a benzidine, 4,4′-diaminodiphenylmethane, etc. Condensation takes place in *o*-dichlorobenzene at 150° and gives rise to red pigments very fast to light, migration, and heat.



(XXXII)

Condensation of aminoazo dyestuffs with dichlorotriazines, which are well known for their use in dyes, can also be used for azo condensation pigments. A patent taken by CFM[158] describes a red pigment used for the mass coloration of viscose. It is prepared by condensing 2,6-dichloro-4-(*o*-chloro)phenoxy-1,3,5-triazine with 2 moles of the azo dyestuff obtained by reduction of *p*-nitraniline → 2-hydroxy-3-naphthoyl-α-naphthylamine.

According to a recent FBy patent,[158a] urethane pigments are obtained by condensing a diisocyanate with 2 moles of an azo dye of the present class bearing an alcoholic hydroxy group either in its diazo or in its coupling component.

F. Naphtholsulfonic Acid Azo Pigments

This class, which has played a very important part for half a century, has provided many (about 70) red and orange lakes, and also some toners.[159] Although about 20 of these are still in use, most of these lakes and toners are disappearing. Only two lakes and one toner have retained any notable commercial importance. The coupling components of these dyes are either a 2-naphtholsulfonic acid coupling in position 1, or a 1-naphtholsulfonic acid coupling in position 2.

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[157] FH, *FP* 1,490,372; 1,490,374; *DP* 67,01983.

[158] CFM, *FP* 1,441,147.

[158a] FBy, *BP* 1,141,654.

[159] J. Lenoir, *Peintures, Pigments, Vernis* **37**, 331 (1961).

1. *Derivatives of β-Naphtholsulfonic Acids*

The pigmentary representatives of this group derive essentially from 2-naphthol-6-sulfonic acid (Schaeffer acid) or from 2-naphthol-3,6-disulfonic acid (R-acid). Today, there is only a single derivative of 2-naphthol-8-sulfonic acid (Crocein acid), one from 2-naphthol-6,8-disulfonic acid (G-acid), and no derivative from naphtholtrisulfonic acid.

TABLE XI

β-NAPHTHOLSULFONIC ACID AZO LAKES AND TONERS

CI	*CI*	*Diazo component*	*Coupling component*
Pigment Orange 18	15970	Aniline	Schaeffer acid
Pigment Orange 19	15990	*o*-Chloroaniline	Schaeffer acid
Acid Orange 16	16011	*o*-Toluidine	Schaeffer acid
Acid Orange 17	16020	*m*-Xylidine	Schaeffer acid
Pigment Yellow 104	15985	Sulfanilic acid	Schaeffer acid
Mordant Red 60	15975	Anthranilic acid	Schaeffer acid
Acid Red 25	16050	Naphthionic acid	Crocein acid
Acid Red 26	16150	*m*-Xylidine	R-acid
Acid Red 17	16180	α-Naphthylamine	R-acid
Pigment Red 60	16105	Anthranilic acid	R-acid
Acid Red 27	16185	Naphthionic acid	R-acid
Pigment Red 61	24830	Diaminotriphenylmethane	R-acid
Pigment Red 62	23295	*m*-Tolidine	R-acid
Acid Red 73	27290	4-Aminoazobenzene	G-acid

The lakes and toners of this series are summarized in Table XI, with their CI numbers. It should be noted that *Colour Index* has not given all of them a CI Pigment number, but for certain CI Acid and CI Mordant dyes it has indicated that they are used in lakes.

Pigment Orange 18 is a calcium toner (CI shows it wrongly as a barium toner). It was still important fifteen years ago, but is now almost as obsolete as CI Pigment Orange 19. It should be noted that when the sulfo group is situated in the β-naphthol ring, it is more unfavourable to lightfastness than when it is found in the diazo component. This is one of the causes of the steady decline of this class of pigments.

However, two derivatives of R-acid remain important today, the chief of which is CI Acid Red 26 (Xylidine Ponceau or Scarlet 2R), the barium lake of which is a beautiful brilliant red. More than 600,000 pounds are made annually in the United States. The other important lake, though falling behind, is CI Pigment Red 60 or Pigment Scarlet 3B, a brilliant bluish red relatively fast to light, but having too weak coloring power for modern printing inks. Two lakes which are not shown in Table XI, and which derive also from R-acid, were put on the market by FBy fifteen years ago; these are Helio Fast Red Toners R and 3B. Their diazo components are, respectively, 2,4,5-trichloroaniline and 4-chloro-2-aminodiphenyl ether. The disazo Pigment Reds 61 and 62 are almost nonexistent now; the diazo component of Red 61 is 4,4′-diamino-2,2′,5,5′-tetramethyltriphenylmethane.

2. *Derivatives of α-Naphtholsulfonic Acids*

Toners and lakes in this series derive from 1-naphthol-5-sulfonic acid, 1-naphthol-4-sulfonic acid (NW acid), or 1-naphthol-8-benzamido-3,5-disulfonic acid (Benzoyl-K acid). They are assembled in Table XII.

TABLE XII

α-NAPHTHOLSULFONIC ACID AZO LAKES AND TONERS

CI	*CI*	*Diazo component*	*Coupling component*
Pigment Red 54	14830	α-Naphthylamine	1-Naphthol-5-sulfo. acid
Acid Red 34	14720	Naphthionic acid	NW-acid
Pigment Red 65	18020	*m*-Chloroaniline	Dichlorobenzoyl-K-acid
Pigment Red 66	18000	*m*-Toluidine	Benzoyl-K-acid
Pigment Red 67	18025	*o*-Anisidine	Dichlorobenzoyl-K-acid
Pigment Violet 8	18005	α-Naphthylamine	Benzoyl-K-acid

Since the disappearance of Helio Red BL (CI 14810), the diazo component of which was *o*-toluidine, CI Pigment Red 54 is the only derivative of 1-naphthol-5-sulfonic acid used. This pigment, well known as Helio Bordeaux, is sold almost only in the form of its calcium toner. It has been reported, however, that the manganese toner is also used.[160] Helio Bordeaux is of interest because of its attractive shade and its cheapness; it is still important, but has begun to fall off because of its moderate fastness.

CI Pigment Reds 65, 66, and 67 and Violet 8 are barium lakes or toners of Anthosines,[161] dyes which have been known since 1912. The coupling component of Reds 65 and 67 is 2,4- or 2,5-dichlorobenzoyl-K-acid. They are of interest for their brilliiant shade, but they have not many manufacturers today.

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[160] *Am. Ink Maker* **38**, No. 8, 37 (1960).

[161] CSD I, p. 489.

G. TRIPHENYLMETHANE PIGMENTS AND RELATED COMPOUNDS

The triphenylmethane pigments should be divided into three distinct groups: (1) lakes and toners of basic dyes; (2) lakes and toners of acid dyes; (3) Alkali Blues. To groups (1) and (2) can be added lakes and toners of dyes which are not derived from triphenylmethane, but from xanthene or other more or less related compounds.[162]

1. *Toners and Lakes of Basic Dyes*

For a long time, lakes have been made by precipitating basic dyes on an inorganic substrate by means of tannin, plus an additional treatment with tartar emetic, which is necessary to obtain a pigment which does not bleed. Other lakes have been prepared with green earths, arsenious acid, or aluminium benzoate. These lakes are interesting for the brilliance of their hues, but they are as devoid of lightfastness as the same dyes on textiles. This is why these fugitive lakes are almost unused today, except that of Methyl Violet, of which more than 400,000 pounds are made annually in the United States.

It must not be forgotten, however, that several fluorescent basic dyes (notably Rhodamines and Thioflavine) are widely used at present to prepare lakes of a special type: fluorescent pigments, the substrate of which is a synthetic resin (see Section I,J)

On the other hand, basic dyes are used to make lakes and even toners which are much faster to light than their parent dyes, while still retaining their brightness of shade. These pigments are obtained by using complex acids from precipitation, the principal ones being phosphotungstic acid (PTA) and phosphomolybdic acid (PMA), often in association as phosphotungstomolybdic acid (PTMA). The first pigments of this type were the Fanal colors of IG, the preparation of which is described in Volume II.[163] The old type Fanal colors were PTA lakes containing an aluminum hydroxide substrate. The Fanal extra are PMA toners, and the Fanal supra are PTMA toners.

The comparative advantages of phosphotungstic acid and phosphomolybdic acid have been much discussed. The PMA pigments are tinctorially stronger, but a little less brilliant and harder in texture than the PTA pigments. In general, the PTA pigments fade and the PMA pigments darken on exposure to light. A compromise is achieved in the PTMA pigments. A study made by IG showed that the maximum lightfastness was obtained with an Mo_2O_7/W_2O_7 ratio of the order of 1/5 to 1/4.

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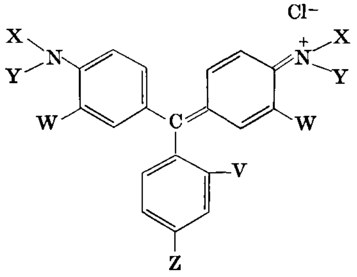
[162] J. Lenoir, *Peintures, Pigments, Vernis* **39**, 68 (1963).

[163] CSD II, pp. 736–739.

This is why PTMA is often preferred. However, today PMA is much used solely because of its lower price, while PTA alone is hardly used at all.

These pigments are now manufactured in all countries which make coloring matters. While the name Fanal has been retained by BASF, special names have been given to these pigments by most other makers: Brillfast (JWTS), Consol (LB), Fanatone (KKK), Fastel (ICI), Forthbrite (ABF), Halopont (DuP), Heliostable (Spcm), Helmerco (CCC), Hollway and Moly (HAC), Kromal (CBC), Lamprolac (Fran), Nyco (NYC), Perma (BCW), Pyramid and Tropical (MM), Sicilian (IMP), Solar and Tintofen (G), and Symulex (DIC). Some manufacturers distinguish these pigments by the words Tungstate, Molybdate, or "Permanent" (as against "Fugitive" lakes of the same dyes); other manufacturers sell them under the same brand names as their other pigments.

The principal pigments in this group are summarized in Table XIII; their parent dyes correspond to one of the general formulas (XXXIII)–(XXXV). The principal outlet for these pigments is the printing industry, in which they are very much esteemed for their brilliance of shade and their very high coloring power. They are fast to oil and to the principal solvents, except the alcohols. Their fastness to light is only relatively



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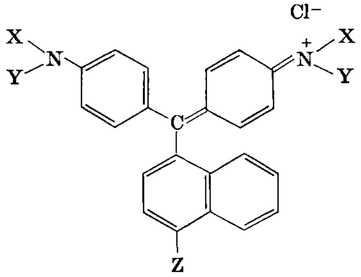

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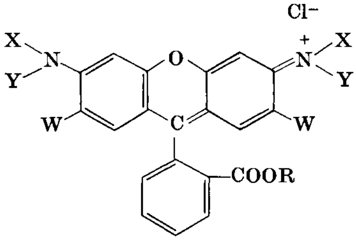

(XXXV)

good, though it is very much better than that of the fugitive lakes. It is agreed that this advantage is due to an excess of acid complex adsorbed on the surface of the pigment, which gives protection against the action of light.

The most important pigments in this series are Red 81, derived from Rhodamine 6G extra; Violet 3, derived from Methyl Violet; Blue 1, derived from Victoria Pure Blue BO; and Violet 1, derived from Rhodamine B. Blues 3 and 9 (Permanent Peacock Blues) have been used as the "cyan" element (greenish blue) in inks for three-color printing; they have now been almost entirely replaced by Copper Phthalocyanine, β form. The same applies to CI Pigment Blue 8, a coprecipitated mixture of Blue 3 and Green 1. Greens 1 and 4, which are derived, respectively, from Brilliant Green and Malachite Green, have also become of little importance, being replaced by the Phthalocyanine Greens. However, CI Pigment Green 2, a yellow-green coprecipitated from a mixture of Brilliant Green and Thioflavine, is still much used. Another yellow green (CI Pigment Green 3) derives from a mixture of Brilliant Green and Auramine O. Several pigments which are not shown in Table XIII have only minimal importance; this is the case with derivatives of Thioflavine T (CI Pigment Yellow 18), Fuchsine (CI Pigment Violet 4), and Crystal Violet.

TABLE XIII

PTA, PMA, and PTMA Toners and Lakes of Basic Dyes

CI Pigment	*CI*	*Formula*	*X*	*Y*	*Z*	*W*	*V*	*R*
Red 81	45160	(XXXV)	Et	H	—	Me	—	Et
Red 82	45150	(XXXV)	Et	H	—	H	—	H
Violet 1	45170	(XXXV)	Et	Et	—	H	—	H
Violet 2	45175	(XXXV)	Et	Et	—	H	—	Et
Violet 3	42535	(XXXIII)	Me	Me	NHMe	H	H	—
Blue 1	42595	(XXXIV)	Et	Et	NHEt	—	—	—
Blue 2	44045	(XXXIV)	Me	Me	NHPh	—	—	—
Blue 3	42140	(XXXIII)	Et	H	H	Me	Cl	—
Blue 9	42025	(XXXIII)	Me	Me	H	H	Cl	—
Blue 10	44040	(XXXIV)	Me	Me	NHEt	—	—	—
Blue 14	42600	(XXXIII)	Et	Et	NEt_2	H	H	—
Green 1	42040	(XXXIII)	Et	Et	H	H	H	—
Green 4	42000	(XXXIII)	Me	Me	H	H	H	—

It should be noted that about 10 years ago there appeared on the market similar pigments prepared with phosphosilicic acid. Mention should also be made of the copper ferrocyanide lakes or toners of basic dyes. The first pigments of this type were the Fanal M colors,[164] made during World War II by IG, who at that time had no tungsten or molybdenum. These pigments were regarded as substitutes for the other Fanal colors, inferior to them in quality. Nevertheless, they were of interest because of their relative cheapness; they have been improved and are being made in increasing quantities. At the present time, copper ferrocyanides of Rhodamine 6G extra (CI Pigment Red 169), of Methyl Violet (CI Pigment Violet 27), of Ethyl Violet, and of Brilliant Green are to be found in industry.

2. *Lakes and Toners of Acid Dyes*

Triphenylmethane acid dyes have been widely used to prepare violet, blue, and green lakes of poor lightfastness, though less fugitive than those of the basic dyes. Insolubilization in the form of the barium salt on a substrate of aluminum hydroxide is not always sufficient, since these dyes are amphoteric, having amine functions as well. It is sometimes necessary to neutralize these basic groups by means of tannin or a complex acid.

Only one of these lakes remains important today: CI Pigment Blue 24 which is the lake of Erioglaucine A.[165] Despite its low coloring power (high alumina hydrate content), its sensitivity to acids and alkalis, and its moderate lightfastness, this pigment, which is well known under the name of Fugitive Peacock Blue Lake, is widely used in inks for three-color printing. Its importance was emphasized in 1953, in an article by C. H. Allen[166] and its annual production still exceeds 2 million pounds in the United States. Some other acid dyes from triphenylmethane are still used to a small extent for making lakes; these are CI Acid Violets 9 and 17, Blues 7 and 104, and Greens 3 and 16.

A lake can also be made from Eosine, or tetrabromofluorescein,[167] but it is preferably used for a toner, CI Pigment Red 90, which is the lead salt of this dye. This pigment is sometimes called Eosine Toner or Bromo Acid Toner, but it is better known under the name Phloxine Toner (a deceptive name, since it is not derived from Phloxine). Although it is expensive, toxic, and of poor lightfastness, this beautiful, very brilliant toner is widely used in the printing industry as the "magenta" component for three-color printing. Its annual production in the United States remains at about 1.2 million pounds.

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[164] CSD II, p. 738; M. Michels, *DBP* 657,740.

[165] CSD II, p. 715.

[166] C. H. Allen, *Ind. Eng. Chem.* **45**, 1610 (1953).

[167] CSD II, p. 748.

3. *Alkali Blues*

These dyes are sulfonated derivatives of phenylated rosanilines. Their preparation has been described in Volume II of this series.[168] In spite of their strange name (which arises from the conditions in which they were at one time used for dyeing wool), the Alkali Blues are free sulfonic acids. Being insoluble in water and in oil, they are used just as they are as pigments, which is exceptional for sulfonated dyes.

There is a whole series of Alkali Blues which differ in the parent Rosaniline, in the degree of phenylation, and in the degree of sulfonation. The more highly phenylated are the greenest. Two principal types can be distinguished: green shade and red shade. The Rosaniline should be at least fully monosulfonated, but sulfonation should not be carried so far as to diminish the coloring power and aggravate the sensitivity of the pigment to alkalis.

In any case, the Alkali Blues lack resistance to alkalis and soap; they bleed in alcohol and have only moderate lightfastness. However, they are fast to water, acids, oil, and hydrocarbons. They are distinguished by a bronzy luster, hence the name "Reflex Blue" given to some of their brands. They appear in *Colour Index* under CI Pigment Blues 18, 19, 56, and 57. They have a considerable outlet in printing inks, being chiefly used in black inks for toning carbon blacks. They are almost always flushed before use.

H. PHTHALOCYANINE PIGMENTS

The phthalocyanine class includes pigments and dyes the chemistry and properties of which have been largely dealt with in Volume II of this series (Chapter XXXVII), and in Chapter IV of this volume. Nevertheless, the phthalocyanines cannot be omitted from the present chapter devoted to pigments. In fact, the Phthalocyanine Blues and Greens are of particular value and technical importance.[169] Although the distinct chemical compounds in this class are very few in number in industry, they represent, in total weight, about one-quarter of the organic pigments manufactured.

1. *Phthalocyanine Blues*

The most important by far is Copper Phthalocyanine (XXXVI), a copper chelate of phthalocyanine (XXXVII), or Metal-Free Phthalocyanine, which is also a blue pigment, but is much less used.

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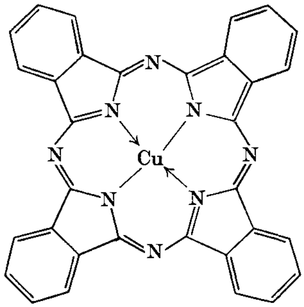
[168] CSD II, pp. 723–724.

[169] J. Lenoir, *Peintures, Pigments, Vernis* **38**, 5 (1962).



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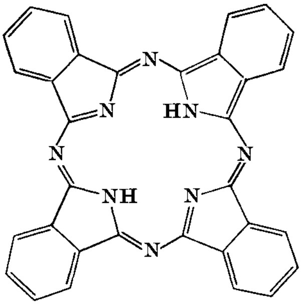

(XXXVII)

a. Polymorphic Forms. Four polymorphic modifications of Copper Phthalocyanine are known, of which two are commercial: the α form, slightly reddish blue, on the market since 1935, and the β form, a greenish blue which appeared about twenty years later. The crude copper phthalocyanine made by various methods of manufacture is the β form, but it has a hard texture which makes it unsuitable as a pigment. To make it fit for use, it must undergo pigmentary conditioning, which can be done in one of the following ways: acid pasting (dissolving in concentrated sulfuric acid followed by reprecipitation in water); acid swelling (in 70% sulfuric acid which does not dissolve the pigment); salt milling (dry ball milling with a water-soluble salt, which is then removed by washing). These three methods of conditioning convert the β form into the α form. To obtain a β-form pigment, it is necessary to carry out salt milling in the presence of an aromatic hydrocarbon or of certain solvents.

The two commercial forms of Copper Phthalocyanine are listed in *Colour Index* as CI Pigment Blue 15 (CI 74160). The α form is manufactured in many countries in considerable quantity. It is in the first rank of organic pigments, with a production which reached 4.5 million pounds in the United States in 1965, having tripled in 15 years. Production of the β form is increasing rapidly, and is now half that of the α form. The two forms are beautiful brilliant pigments of exceptional qualities: excellent fastness to light, oil, solvents, migration, heat (up to 200°), and perfect resistance to chemical reagents.

However, the α form has faults which have limited its field of application, insofar as no means have been found to remedy them. The first is crystallization, or crystal growth, which occurs slowly in the cold and rapidly when hot, in contact with aromatic hydrocarbons and many other solvents. For example, in a paint which is kept in a can and which contains such solvents, microcrystals of the pigment are slowly converted into larger crystals, with a considerable loss of tinting strength. This phenomenon is a serious drawback in uses in inks, paints, and plastics. Crystallization of the α form is a transformation into the more stable β form. Reduction of tinting strength is due to the relatively large dimensions of the slowly developed crystals of the β form; in addition, since the latter is greener, there is at the same time a change of shade.

The second defect is flocculation, which is agglomeration of particles within the liquid vehicle. Many other pigments tend to flocculate, and the β form itself is not free from this fault, but it occurs to a lesser extent than with the α form. Flocculation also entails a reduction of coloring power; this is why it has not always been clearly distinguished from crystallization. But, unlike the latter, flocculation is a reversible phenomenon. The agglomerated particles can often be redispersed by mechanical means.

Considerable research has taken place over the last twenty years on the production of noncrystallizing and nonflocculating Phthalocyanine Blues. The best means of avoiding crystallization is obviously to use the β form, which has no such tendency. With its greenish blue shade, the form fulfills certain needs perfectly (notably to act as a "cyan" component in three-color printing). It cannot, however, replace the α form when a more reddish blue is required.

It was therefore necessary to stabilize the α form. To do this, the most frequently used process is to slightly chlorinate the copper phthalocyanine. In effect, the α form of the monochlorinated derivative (CI 74250) has much less tendency to crystallize than the nonchlorinated pigment, and its shade is only very slightly more greenish. It is not even necessary that all the molecules of the phthalocyanine should be chlorinated. In industry, there are monochlorinated and "semichlorinated" Phthalocyanine Blues, more or less stabilized. Partial chlorination can be carried out by various means, at different stages of manufacture.[170]

Other methods of stabilization consist in introducing into the preparation of the pigment a little *N*-hydroxyphenylphthalimide,[171] phenylacetonitrile,[172] pyromellitic anhydride,[173] 4-benzoylphthalic anhydride,[174] or pyridine-2,3-dicarboxylic anhydride.[174a] According to certain

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[170] BASF, *FP* 1,078,277; 1,116,429; Fran, *FP* 1,094,451; G, *USP* 2,873,279; DuP, *USP* 2,833,784; 2,933,505; *FP* 1,091,466.

[171] CCC, *USP* 2,761,868.

[172] DuP, *USP* 3,014,917; 3,057,872.

[173] HSH, *USP* 3,028,392.

[174] BASF, *DBP* 1,250,404.

[174a] CIBA, *SP* 439,541.

patents, the α form can be stabilized by treatment with acid chlorides.[175] These chemical modifications have little effect on the shade.

There are commercial brands which are both noncrystallizing and nonflocculating, in which the α form copper phthalocyanine is stabilized by mixing with a few percent of another metal phthalocyanine, notably tin phthalocyanine.[176] Several patents concern similar mixtures with phthalocyanines of aluminum, magnesium, manganese, iron, cobalt, titanium, and vanadium.[177]

To prevent flocculation alone, the pigment can be incorporated with aluminum benzoate,[178] or with aluminum *tert*-butylbenzoate, which causes less reduction of coloring power.[179] Sulfophthalocyanines can also be used.[180] Treatment with paraformaldehyde[181] or with glyoxal[182] is also effective against flocculation. Finally, according to several patents, a good remedy consists in introducing into the molecule of phthalocyanine groups such as $-CH_2NMe_2$, or $-CH_2OCH_2CH_2NMe_2$.[183]

Because of the great variety of stabilizing treatments and special compositions for various uses, brands of Copper Phthalocyanine Blues are extremely numerous.

b. Metal-Free Phthalocyanine. The metal-free phthalocyanine (XXXVII), CI Pigment Blue 16 (CI 74100), is much less important. It is a greenish blue sometimes called Phthalocyanine Peacock Blue. It was used especially in inks for three-color printing, but it is now almost entirely supplanted by the β form of Copper Phthalocyanine, which is less costly and more brilliant in shade.

c. Lakes and Toners. Lakes and toners which are also greenish blue are made with a sulfonated copper phthalocyanine (CI Pigment Blue 17). Contrary to what is shown in *Colour Index*, they are more often prepared with the disulfonated (CI 74180) than with the trisulfonated (CI 74200) copper phthalocyanine.

2. *Phthalocyanine Greens*

The principal phthalocyanine green is CI Pigment Green 7 (CI 74260), which is theoretically hexadecachloro copper phthalocyanine. In fact,

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[175] CIBA, *BP* 855,098; *SP* 352,436.

[176] DuP, *FP* 967,452.

[177] Gy, *FP* 1,145,176; 1,152,882; BASF, *BP* 861,494; CIBA, *USP* 3,081,188; 3,081,189; *FP* 1,297,620.

[178] HAR, *USP* 2,327,472.

[179] SUC, *USP* 2,965,511.

[180] IC, *USP* 2,526,345; DuP, *USP* 2,799,594; G, *BP* 804,031.

[181] G, *USP* 3,117,974.

[182] S, *USP* 3,051,719.

[183] BASF, *DBP* 1,239,270; ICI, *FP* 1,353,759; *BP* 1,058,226.

the commercial product contains 14 to 15 atoms of chlorine. It has the same excellent fastness as the copper phthalocyanine from which it is derived, and it is by far the most important green pigment. Its production in the United States, which has doubled in the last five years, now exceeds 4 million pounds, which places it in the second rank, after CI Pigment Blue 15.

CI Pigment Green 7 has no tendency to crystallize, but it may flocculate; nonflocculant brands have been made. There are very many brands of this pigment in industry; differences in shade between them are relatively slight, since there is no polymorphism. Attempts have been made to produce this pigment in a little yellower form.[184]

CI Pigment Green 37 (CI 74255) is octachloro copper phthalocyanine, prepared from dichlorophthalic acid. This very bluish green is not widely distributed on the market.

The demand for yellowish greens is now satisfied primarily by the mixed bromochloro copper phthalocyanines, the first of which, Heliogen Viridine Y (G),[185] appeared on the market in 1959. Various products of this type are today manufactured in several countries; they are listed in *Colour Index* under CI Pigment Green 36, 38, 41, 43, and 44. Although formula 74265 given for CI Pigment Green 36 is that of a hexabromodecachloro copper phthalocyanine, commercial products contain only 14 to 15 atoms of halogen, of which 4 to 5 atoms are bromine in the less yellowish brands, and 11 to 12 in the more yellowish ones. Polybromo copper phthalocyanine, with 14 to 16 atoms of bromine, was patented by S; it is yellow-green.[185a]

Another yellowish green which has been known for a long time, is polychlorinated metal-free phthalocyanine (CI 74120). It appears to be made only by BASF, under the brand name Heliogen Green 5G.

There are also in industry yellowish greens which are mixtures of a phthalocyanine and another pigment. For textile printing, mixtures of CI Pigment Greens 7 and 10 are used. Other mixtures are prepared by precipitating sulfo copper phthalocyanine on an inorganic yellow pigment, which is Titanium Yellow in CI Pigment Green 25. The most important mixture is CI Pigment Green 13, the first brand of which to appear on the market was Chromastral Green (ICI). There are now many brands of CI Pigment Green 13, which are prepared by coprecipitation of sulfo copper phthalocyanine and Chrome Yellow. The proportions of the components vary from one brand to another, but the Chrome Yellow

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[184] G, *FP* 1,219,881.

[185] *Am. Ink Maker* **37**, No. 8, 26 (1959).

[185a] S, *FP* 1,544,363. Hexadecafluoro copper phthalocyanine is also known; it is blue: Imperial Smelting Corp., *USP* 3,414,583.

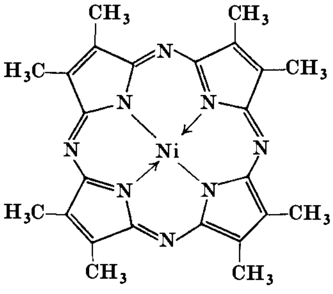
is always preponderant, since its coloring power is lower than that of the phthalocyanine.

3. *Related Pigments*

Great efforts have been made to enlarge the range of phthalocyanine pigments, but experience has shown that this class can only provide blues and greens. However, pigments of other shades which belong to chemically similar classes have been obtained.

Phthalocyanine (XXXVII) is tetrabenzoporphyrazine. Porphyrazines have been prepared without benzene rings, for example, octamethylporphyrazine, which can be obtained from dimethylmaleic anhydride. The nickel chelate of this dye is the purple pigment (XXXVIII).[186]

The possibilities of an extension in the shade range are better in the hemiporphyrazine series. These are macrocyclic compounds of a similar type to the porphyrazines, but containing only two pyrrole rings in place of four. Hemiporphyrazines can be prepared by reacting phthalodinitrile, or better 1,3-diiminoisoindoline, with a diamine; the indoline compound is known as a "phthalocyanine precursor." With this compound and 2,6-diaminopyridine, Elvidge and Linstead[187] prepared the orange-red dye (XXXIX). Metal chelates of this dye are described in a DuP patent[188]; they are more or less brownish orange to green pigments. In the same patent, and in a patent by FBy,[189] similar pigments are described in the preparation of which the diaminopyridine is replaced by 3,5-diamino-1,2,4-triazole, or by 3,5-diamino-1-phenyl-1,2,4-triazole.



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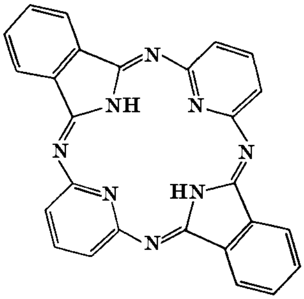

(XXXIX)

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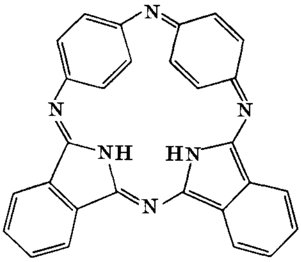
[186] ICI, *FP* 1,031,833.

[187] J. A. Alvidge and R. P. Linstead, *J. Chem. Soc.* p. 5008 (1952).

[188] DuP, *USP* 2,765,308.

[189] FBy, *DBP* 1,080,243.

Aromatic diamines were also used to make hemiporphyrazines, which could not be converted into metallic chelates since they lacked two electron donor atoms of nitrogen for this. Linstead prepared such hemiporphyrazines with *m*-phenylenediamine, or with 2,7-diaminonaphthalene, used in equimolecular proportions with 1,3-diiminoisoindoline.[190] According to a patent by FBy, macrocyclic pigments are also obtained by reacting a single mole of a diamine with 2 moles of phthalodinitrile.[191] If the diamine is, for example, 4,4′-diaminodiphenylamine, pigment (XL), brownish corinth in shade, is obtained.



(XL)

No pigment in this series appears to have been commercialized. Red pigments of high quality, for which there was a need, were finally found in other chemical classes.

I. ANTHRAQUINONE, INDIGOID, AND RELATED PIGMENTS

The oldest pigments in this class are polyhydroxyanthraquinone lakes, but the most important today are the "vat pigments." These oddly named products are vat dyes specially prepared for use as pigments. They include not only derivatives of anthraquinone and anthrone, but also derivatives of perylene, perinones, and indigoid dyes.[192]

1. *Anthraquinone Lakes*

Several dihydroxyanthraquinones or other polyhydroxyanthraquinones (mordant dyes) have been used for making lakes. Sulfonic acid derivatives of these compounds (acid dyes) have also been used. Some of these lakes still remain in use today, and these are summarized in Table XIV. They are essentially aluminum lakes. However, CI

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[190] R. P. Linstead, *J. Chem. Soc.* p. 2873 (1953).

[191] FBy, *DBP* 945,782.

[192] J. Lenoir, *Peintures, Pigments, Vernis* **38**, 384 (1962).

Pigment Red 83 (Madder lake) is an alizarin–aluminum–calcium complex.[193] This lake has lost much of the importance which it had twenty years ago. At present, the most important is CI Pigment Violet 5. One particular lake, formed by combination of an acid dye and a basic dye, is CI Pigment Blue 52, Helio Fast Navy RLW (FBy).

TABLE XIV

ANTHRAQUINONE LAKES

CI Pigment	*CI*	*Parent dye*
Red 83	58000	Alizarin
Red 84	58210	3-Sulfopurpurin
Violet 5	58055	2-Sulfoquinizarin
Violet 6	58060	6-Sulfoquinizarin
Violet 7	58065	2,6-Disulfoquinizarin
Violet 12	58050	Quinizarin
Violet 20	58225	2-(*p*-Sulfo)phenoxy-3-sulfoquinizarin
Blue 52	63010 52015	Alizarin Saphirol B Methylene Blue

2. *Anthraquinone Pigment Dyestuffs*

This group includes some old pigments which are benzamidoanthraquinones. These classical pigments are shown in Table XV; they have become of little importance. CI 60515 is still used for mass coloration of viscose rayon (Luxanthol Yellow FG, BASF). Pigment Yellow 23 is almost obsolete. It is interesting to note, however, that 1-(3,5-dichloro)-salicylaminoanthraquinone was patented in 1956 as a faster golden yellow pigment.[194]

TABLE XV

CLASSICAL ANTHRAQUINONE PIGMENT DYESTUFFS

CI	*CI*	*Anthraquinone derivative*
—	60515	1-Benzamidoanthraquinone
Vat Yellow 3	61725	1,5-Bis(benzamido)anthraquinone
Pigment Yellow 23	60520	1-Salicylaminoanthraquinone
Pigment Red 85	63350	1,5-Bis(benzamido)-4-hydroxyanthraquinone
Pigment Red 89	60745	1-Benzamido-4-hydroxyanthraquinone

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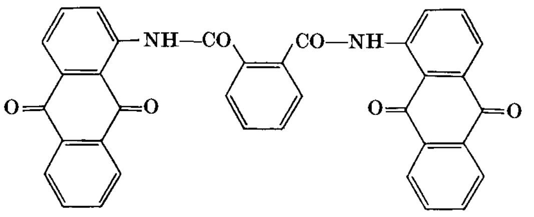
[193] See CSD II, pp. 820–821.

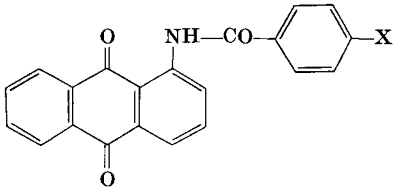
[194] CCC, *USP* 2,833,789.

Considerable research has taken place in the last fifteen years in the field of acylaminoanthraquinones to try to get pigments with better qualities than the foregoing. The phthalamide derivative of 1-aminoanthraquinone (XLI), known as Acylamino Yellow, has been put on the market. This pigment is particularly suitable for textile applications (Textile Yellow Toner Y-5776, HAR). Many patents relate to compound (XLI) and its substituted derivatives, from yellow to red.[195] According to other patents, similar pigments can be prepared which are diamides of other diacids.[196]

Acylation of 1-aminoanthraquinone by 2-chloroformyl-1-aminoanthraquinone gives a red pigment which is fast to light and migration.[197] Many patents make claims for pigments which also have such fastness, although they contain only a single anthraquinone ring. Some are obtained by acylating 1-aminoanthraquinone with 4-phthalimidobenzoyl chloride,[198] or with 4-chloroformylphthalimide.[199] Others correspond to the general formula (XLII), in which X is –CONHR, –COOC$_6$H$_4$NHCOR, or –NHCOR.[200] A red pigment arises from acylation of 2-aminofluorenone by 2-chloroformyl-1-aminoanthraquinone.[200a] Several patents deal with diaminoanthraquinones diacylated with halogenobenzoyl chlorides,[201] or with 2-chloroformylfluorenone.[202] Yellow to violet pigments are described, the shade depending on the position of the acylamino groups and other substituents present.



(XLI)



(XLII)

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[195] IC, *USP* 2,727,044; 2,848,461; *BP* 895,618; FBy, *DBP* 1,235,473; Toms River, *BP* 920,858.

[196] IC, *USP* 2,925,421; S, *USP* 2,870,172; *SP* 358,183; CIBA, *FP* 1,326,825; BASF *FP* 1,462,105; 1,471,709; *BeP* 710,460; DIC, *JP* 21,159('66); *CA* **66**, 76929t.

[197] CIBA, *BP* 887,729.

[198] S, *SP* 440,507.

[199] BASF, *FP* 1,428,199.

[200] CIBA, *FP* 1,353,749; S, *FP* 1,469,992; 1,407,958; Add 88,611.

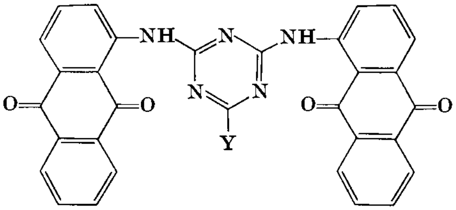
[200a] BASF, *DBP* 1,278,046.

[201] CIBA, *FP* 1,310,218; 1,375,315; *DP* 65,03825; DuP, *USP* 3,344,154; see also FBy, *BP* 1,132,818.

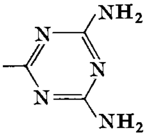
[202] CFM, *DBP* 1,141,038.

The value of amide linkages in pigments, already seen in other chemical classes, is again encountered, therefore, in the preceding patents. In the same way, other patents refer to the use as pigments (notably in plastics) of cyanuric derivatives of aminoanthraquinones. Some of these products were already known, while others are new. Most of them correspond to the general formula (XLIII), in which the anthraquinone rings may carry other substituents. Y may be NH_2 or NHR[203]; Ph, possibly substituted[204]; or OPh.[205] In this series, yellow to blue pigments are described. Ciba has also described orange to violet pigments, very fast to light and solvents, which are aminoanthraquinones *N*-substituted with a diaminotriazinyl group (XLIV).[206]

Red pigments are obtained by condensing 2 moles of an 1-aminoanthraquinone with a 2,4-dichloroquinazoline[206a]; or 1,5-diaminoanthraquinone with 2 moles of *o*-nitrochlorobenzene.[206b]



(XLIII)



(XLIV)

3. *Vat Pigments: Anthraquinone and Anthrone Derivatives*

Although the foregoing pigments are capable of being vatted, most of them would be of no use for vat dyeing textiles. The name "vat pigments" is more particularly applied to vat dyes which have been used for a long time for dyeing textiles and are now used also as pigments. Before the 1950s, only a few (indigo, indanthrone, flavanthrone) had been used, to a slight extent, as such. In spite of their excellent fastness, vat dyes in general were not envisaged for pigment applications because their price was too high and they lacked tinctorial strength. In fact, insofar as they were manufactured for dyeing textiles, they had neither the purity nor the physical form necessary for pigments.

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[203] CIBA, *SP* 348,547; *BP* 972,957.

[204] CIBA, *BP* 953,155; *FP* 1,519,103; CCC, *USP* 2,719,154.

[205] CFM, *BP* 1,029,444; 1,063,159.

[206] CIBA, *BP* 897,488; H. Gaertner, *J. Oil Colour Chemists' Assoc.* **46**, 24 (1963).

[206a] BASF, *DBP* 1,278,635.

[206b] FBy, *FP* 1,535,993.

With the opening up of new outlets (automotive finishes, coloration of plastics) for pigments of high quality, considerable work of selection among vat dyes, and of improvement of those which were selected, was undertaken about fifteen years ago. These researches were pursued with particular energy in the United States, notably by Harmon Colors, whose work has been summarized in two interesting publications by Vesce.[207]

The transformation of vat dyes into valid pigments can be achieved by the well-known pigmentary conditioning methods, such as salt milling and acid pasting. However, special methods of conditioning have been patented. One such method consists in spraying the alkaline solution of the leuco compound into an oxidizing solution, in which the pigment is precipitated in a finely divided state.[208] According to other patents, ball milling can be carried out with isopropyl alcohol,[209] or attrition milling with a solid organic compound, such as hexachloroethane.[210] Acid pasting can be followed by reprecipitation in a saturated solution of iron, copper, or zinc sulfate.[211] Hot treatments with organic liquids, such as *o*-dichlorobenzene, have also been patented.[212]

A certain number of classical vat dyes are now on the market as pigments, but they are not yet all listed as such in *Colour Index*. About 20 of them are derivatives of anthraquinone or anthrone; the principal ones are listed in Table XVI, with an indication, in brackets, of the name under which they are mentioned in *CSD*, Vol. II, and the page on which their constitution is shown.

Among the Pigments in Table XVI, the most important are the following, which have excellent fastness to light even in pale shades. Indanthrone Blue and Flavanthrone Yellow, now manufactured in very high pigment quality, also have perfect resistance to solvents and migration; they are suitable for all applications and their uses are only limited by their price. Anthrapyrimidine Yellow (XLV) is of interest on account of its attractive greenish yellow shade; it is used for automotive finishes, though it bleeds very slightly in solvents. Dibromoanthranthrone (Pigment Red 168) is in fact a brilliant red orange, which unfortunately has poor resistance to migration. The chlorinated isoviolanthrones (Pigment Violet 31) have the same defect; several brands are in existence, differing in the degree of chlorination. The chlorinated indanthrones, which also

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[207] V. C. Vesce, *Offic. Dig., J. Paint. Technol. Eng.* **28**, No. 377, Part 2 (1956); **31**, No. 419, Part 2 (1959).

[208] HAR, *USP* 2,893,994.

[209] CIBA, *FP* 1,181,045.

[210] CIBA, *FP* 1,271,325.

[211] Valik, *EGP* 23,854.

[212] FH, *DBP* 1,115,711.

differ in the degree of chlorination, are blue pigments used in stoving enamels. They are more or less confused in *Colour Index.* The greenish brands are CI 69810 and the reddish brands are CI 69825.

New products derived from anthraquinone or anthrone have been patented as pigments, but do not seem to have appeared on the market.

TABLE XVI

ANTHRAQUINONE AND ANTHRONE VAT PIGMENTS

CI	*CI*	*Names*	*CSD II, page*
Vat Yellow 1	70600	Flavanthrone	988
Vat Yellow 20	68420	Anthrapyrimidine Yellow (Formula XLV)	—
Pigment Orange 40	59700	Pyranthrone (Indanthrene Golden Orange G)	951
Vat Orange 2	59705	Dibromopyranthrone (Indanth. Orange RRT)	953
Vat Orange 4	59710	Tribromopyranthrone (Indanth. Orange 4R)	953
Vat Orange 15	69025	Anthrimide Orange (Indanth. Golden Orange 3G)	902
Vat Brown 3	69015	Anthrimide Brown (Indanth. Brown FFR)	905
Pigment Red 168	59300	Dibromoanthanthrone (Indanth. Brill. Orange RK)	956
Vat Red 10	67000	Oxazole Red (Indanthrene Red FBB)	912
Vat Red 13	70320	Bis-ethylpyrazolanthrone (Indanth. Rubine R)	994
Vat Red 35	68000	Acridone Red (Indanth. Red RK)	923
Pigment Violet 31	60010	Chlorinated Isoviolanthrone	977
Vat Violet 9	60005	Brominated Isoviolanthrone	977
Pigment Blue 21	69835	Chlorinated Indanthrones	939
Pigment Blue 22	69810		
Vat Blue 6	69825		
Pigment Blue 60	69800	Indanthrone	933
Vat Green 1	59825	Dimethoxyviolanthrone (Caledon Jade Green)	969

Among these, yellow, orange, and red derivatives of thiazolanthrone (XLVI) are particularly numerous.[213] It is interesting also to mention: trianthrimide bordeaux,[214] naphthaliminotriazinoanthraquinone blue,[215] anthrapyrimidine orange,[216] anthrapyridone violets and reds,[217]

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[213] S, *BP* 733,460; 733,461; CIBA, *DBP* 1,109,359; BASF, *DBP* 1,162,015; 1,164,002; *FP* 1,321,150; 1,333,261, 1,365,840; 1,366,437; HAR, *USP* 3,245,995.

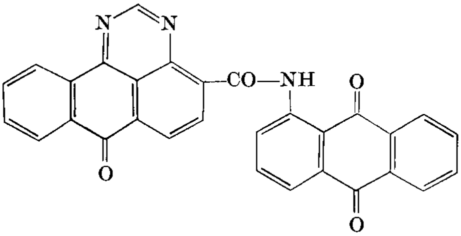
[214] CIBA, *DBP* 1,100,943.

[215] CCC, *USP* 2,967,861.

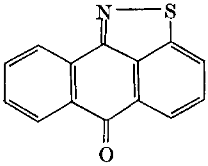
[216] BASF, *FP* 1,367,834.

[217] ICI, *BP* 964,602; 1,047,089.

phthaloylcarbazole yellows, orange, and reds,[218] phthaloyldibenzothiophene yellows and reds,[219] diphthaloylphenothiazine violets,[220] anthraquinone-acridone yellow,[221] anthraquinone-bis-thiochromone reds,[222] and dianthrone-ethylene blues.[223]



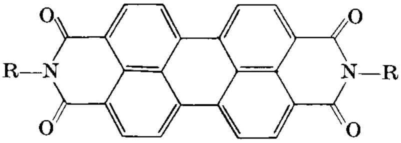
(XLV)



(XLVI)

4. *Perylene Derivatives*

This series includes red pigments which are diimides of perylene-3,4,9,10-tetracarboxylic acid. Their general formula is (XLVII). There are several vat dyes of this type,[224] and two of these have taken their place among the Perylene pigments, along with new products.



(XLVII)

One of the most important of the series is CI Vat Red 29 (CI 71140; original name: Indanthrene Scarlet R), in which R = *p*-methoxyphenyl. It is a beautiful brilliant scarlet pigment. Another newer scarlet, chemically very similar, is its homolog with R = *p*-ethoxyphenyl, which is CI Pigment Red 123.[224a] An important red in which R = 3,5-dimethylphenyl was patented by FH in 1956.[225] It is Pigment Red 149.

[218] FH, *DBP* 1,227,174; 1,227,175.

[219] FH, *DBP* 1,227,176.

[220] S, *FP* 1,436,965.

[221] FH, *BeP* 649,151.

[222] ICI, *FP* 1,328,610; 1,329,788.

[223] CFM, *BP* 978,286; *DBP* 1,217,526.

[224] CSD, II, p. 1190.

[224a] Formula CI 71145, *CI Add. & Am.*, April 1969.

[225] FH, *DBP* 1,067,157.

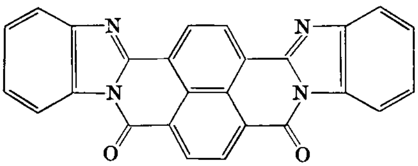
CI Vat Red 23 (CI 71130), in which R = Me, and which is known as Indanthrene Red GG, is now used as a maroon pigment.[226] The perylimide (R = H), which was not envisaged for use as a vat dyestuff, is now used as a bordeaux pigment. Its pigmentary conditioning was the subject of patents by FH.[227]

These pigments, especially the last three mentioned, are distinguished by excellent fastness to light. All of them have perfect resistance to migration, so that they are particularly useful for coloring PVC, in spite of their high price. Moreover, they have exceptional stability to heat, which makes them suitable for coloration of polyamides which are molten at 280°.

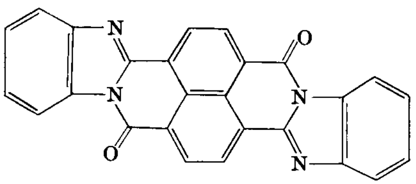
The interest which these remarkable pigments hold has been responsible for considerable research in this series. Many other reds have been obtained by condensing perylenetetracarboxylic acid with various aromatic amines,[228] with aliphatic amines,[229] with aminopyridines,[230] with aminophenols,[231] with aminoazo benzenes,[232] and with hydrazines, hydrazides, and semicarbazides.[232a]

5. *Perinone Pigments*

This series is represented on the market essentially by two pigments: Perinone Orange, which is *trans*-1,4,5,8-naphthoylenebis(benzimidazole) (XLVIII), and its cis isomer, Perinone Red (XLIX). These two products are derived from naphthalene-1,4,5,8-tetracarboxylic acid by condensation with *o*-phenylenediamine; they have been known for a long time as textile vat dyes.[233]



(XLIX)



(XLVIII)

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[226] BASF, *BP* 923,721.

[227] FH, *DBP* 1,115,711; 1,142,339.

[228] FH, *DBP* 1,055,156; 1,067,548; 1,067,951; 1,069,797; 1,070,317; 1,105,085; *BP* 852,202; *USP* 2,905,686; *FP* 1,169,426; BASF, *DBP* 1,094,897; 1,141,740; S, *BP* 901,694; NSK, *JP* 809('68); 7023('68); *CA* **68**, 106075x; **69**, 37119w.

[229] CIBA, *FP* 1,234,534; FH, *BP* 967,178.

[230] BASF, *DBP* 1,132,272; HAC, *USP* 3,357,983; *BP* 1,120,287.

[231] CIBA, *BP* 887,971.

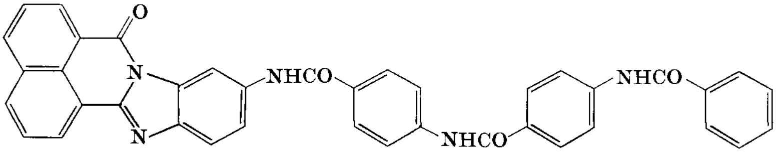
[232] BASF, *DBP* 1,213,555; 1,257,096.

[232a] FBy, *DP* 68,12399; 68,12400; 68,12401.

[233] CSD II, p. 1191.

The most important is Perinone Orange, a pigment which is very fast to heat, solvents, and migration, and is used in PVC, emulsion paints, and in textile printing. Its lightfastness is very good, except in very pale tints. Perinone Red, which bleeds in solvents, is of less interest.

Among the numerous other perinones which have been patented as pigments in less than 15 years, mention can be made of the nitro derivatives of the above products: *trans* yellow and *cis* orange,[234] and similar asymmetric compounds.[235] Condensation of perylenetetracarboxylic acid with *ortho*- or *peri*-diamines gives violet or blue perinone pigments.[236] Perinone pigments derived from naphthalic acid have acquired particular interest.[237] Among those patented by S, the yellow (L) can be mentioned. Iminophthaloperines have also been patented,[238] as well as derivatives of perimidine-6,7-dicarboxylic acid or 4,5-diaminonaphthalic acid.[239]



(L)

Generally speaking, these Perinone pigments are as resistant to heat as the Perylene Reds. Most patents mention their use for mass coloration of textile polyamides spun in a molten condition.

6. *Indigoid and Thioindigoid Pigments*

Indigo itself (CI Vat Blue 1, CI 73000) has a certain amount of interest as a pigment because of its insolubility in most solvents and its very good fastness to light and heat (in spite of its tendency to sublimation). That is why it is still used, notably in rubber and for mass coloration of rayon in a navy blue shade, although it has the drawback of being sensitive to the reducing action of viscose.

Halogenated derivatives of indigo have also been used as blue pigments, but today they are obsolete. On the contrary, several halogenated

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[234] FH, *DBP* 1,104,093.

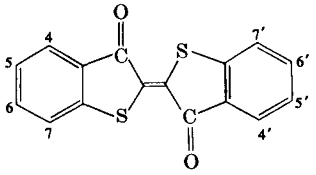
[235] FH, *FP* 1,386,979.

[236] S, *BP* 859,288; IC, *BP* 925,409; BASF, *DBP* 1,213,554.

[237] FH, *DBP* 1,121,750; BASF, *DBP* 1,159,115; 1,278,641; 1,278,643; S, *FP* 1,469,894; 1,473,448.

[238] ICI, *FP* 1,165,422; 1,165,423.

[239] BASF, *BeP* 654,385; 654,636.



(LI)

derivatives of thioindigo (LI) have been recognized as valuable pigments. They are reds and violets, three of which are also textile vat dyes of importance.[240] These pigments are shown in Table XVII.

TABLE XVII

THIOINDIGO PIGMENTS

CI	*CI*	*Thioindigo derivative*
Pigment Red 86	73375	6,6′-Dibromo-4,4′-dimethyl
Pigment Red 87	73310	7,7′-Dichloro
Pigment Red 88	—	4,4′,7,7′-Tetrachloro
Vat Red 1	73360	6,6′-Dichloro-4,4′-dimethyl
	73390	7,7′-Dichloro-4,4′-dimethyl
Vat Violet 2	73385	5,5′-Dichloro-7,7′-dimethyl
Vat Violet 3	73395	5,5′-Dichloro-4,4′,7,7′-tetramethyl

These pigments are all appreciated for their brilliance of shade. The most used at the present time are Thioindigo Red Violet RH (CI Vat Violet 2) and Thioindigo Pink (CI Vat Red 1). They are not, however, the best, since they bleed slightly in solvents and have only moderate fastness to light in pale tints. The fastest are the derivatives substituted in the 4,4′,7,7′ positions: Thioindigo Red Violet Y or Maroon (CI 73390) and especially Thioindigo Red Violet B or Bordeaux (CI Pigment Red 88).[207] The latter is shown as nonmigrating and exceptionally fast to light, even in pastel shades.[241]

Apart from the interesting work of selection which has been done in this series, there are hardly any novelties worth mentioning in the indigoid class of pigments. It should be noted, however, that in 1963, BASF patented derivatives of isoindigo, e.g., a red pigment obtained by condensation of *o*-phenylenediamine with the phenylimide of dichloromaleic acid.[242]

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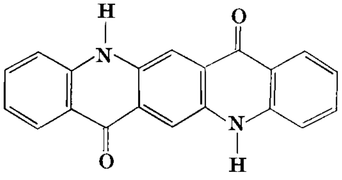
[240] CSD II, pp. 1033–1034.

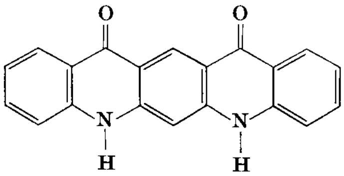
[241] H. Gaertner, *J. Oil Colour Chemists' Assoc.* **46**, 22 (1963).

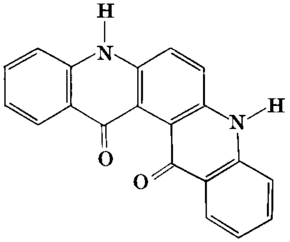
[242] BASF, *FP* 1,410,733.

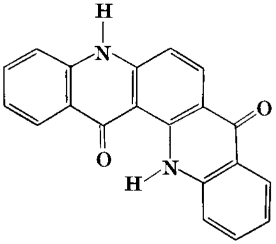
J. QUINACRIDONE PIGMENTS

Quinacridone pigments were first marketed in 1958, although quinacridones had already been known for a long time. These compounds are diketo derivatives of quinolinoacridines or quinacridines.[243] Four types of quinacridones are known, two of which are linear [(LII) and (LIII)], and two angular [(LIV) and (LV)].


(LII)


(LIII)


(LIV)


(LV)

The linear compound (LII), a red, is nowadays the principal pigment of this family. Its correct name is 7,14-dioxo-5,7,12,14-tetrahydroquinolino[2,3-*b*]acridine, or quino[2,3-*b*]acridine-5,12-dihydro-7,14-dione. It is more briefly known as linear *para-N,N'*-quinacridone, or linear *trans*-quinacridone, or even just quinacridone. Compound (LIII) is yellow and is called linear *meta-N,N'*-quinacridone, or linear *cis*-quinacridone, or more commonly isoquinacridone. The angular quinacridones (LIV) and (LV) are also yellow.

The first compound of this family was prepared by Niementowski[244] in 1896 by condensing 2 moles of anthranilic acid with 1 mole of phloroglucinol. It was a yellow hydroxy derivative of angular quinacridone (LV). In 1906 Ullmann and Maag[245] condensed 2 moles of anthranilic acid with 1 mole of *p*-dibromobenzene. After cyclization in sulfuric acid,

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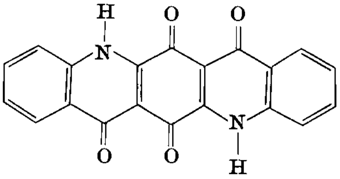
[243] J. Lenoir, *Peintures, Pigments, Vernis* **39**, 545 (1963); N. V. Shah, *J. Soc. Dyers Colourists* **83**, 221 (1967); S. S. and L. L. Labana, *Chem. Rev.* **67**, 1 (1967).

[244] S. Niementowski, *Chem. Ber.* **29**, 76 (1896).

[245] F. Ullmann and R. Maag, *Chem. Ber.* **39**, 1693 (1906).

a yellow product was obtained to which they ascribed formula (LII) and which in fact was the angular quinacridone (LIV). In 1918 Lesnianski[246] prepared the brownish yellow quinacridonequinone (LVI) by cyclizing in sulfuric acid the benzoquinone-dianthranilic acid which he had obtained through condensation of benzoquinone with 2 moles of anthranilic acid. Lesnianski was therefore the first to discover a linear *trans*-quinacridone derivative.



(LVI)

In 1921 Eckert and Seidel[247] obtained isoquinacridone (LIII) from 4,6-dianilinoisophthalic acid through successive treatments with phosphorus pentachloride and aluminum chloride. Finally between 1925 and 1935 Liebermann[248] first succeeded in preparing the linear *trans*-quinacridone, using 2,5-dianilinoterephthalic acid as starting material. Their best process consisted in fusing this product with boric acid at 320°. For her thesis (Berlin, 1934), N. Anitschkoff, a student of Liebermann, prepared many substituted derivatives of quinacridone (LII).

From then on, knowledge of the quinacridones was well advanced, but no one had thought of using these products as pigments. It was W. S. Struve (DuP) who first thought of using the red linear *trans*-quinacridone for this purpose and who worked out the industrial manufacture of this product. Above all, he discovered the polymorphism and the pigmentary conditioning methods giving rise to the different forms. The first patents (DuP) were taken out in 1955.[249] These pigments were marketed as Monastral Reds and Violet. The designation suggested that they were comparable to phthalocyanines in their outstanding fastness. For sale outside the United States the name Monastral was changed into Cinquasia. In the years that followed other manufacturers became interested in quinacridones and a great amount of research was carried out on this class of pigments. It mainly concerned the linear *trans*-quinacridone and its substituted derivatives, but patents also refer

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[246] W. S. Lesnianski, *Chem. Ber.* **51**, 701 (1918).

[247] A. Eckert and F. Seidel, *J. Prakt. Chem.* [2] **102**, 354 (1921).

[248] H. Liebermann, *Ann. Chem.* **518**, 245 (1935).

[249] DuP, *USP* 2,821,529; 2,821,530; 2,844,484; 2,844,485.

to isoquinacridone, to an angular quinacridone, and to many related compounds.

1. *Preparation of Linear* trans-*Quinacridones*

There exist several methods of preparation of quinacridones. One group of processes consists in cyclizing 2,5-diarylaminoterephthalic acids or esters, or the analogous derivatives of dihydroterephthalic acid. In the latter case, cyclization must be followed by dehydrogenation. In a second group of processes, which will be described later, a linear *trans*-quinacridonequinone is first prepared and then reduced.

Preparations of unsubstituted quinacridone through terephthalic acid derivatives are summarized in Chart 1. According to the first patents of DuP[249] 2 moles of diethyl succinate (1a) are condensed in the presence of sodium ethoxide, thus giving diethyl succinylsuccinate or 2,5-bis-(ethoxycarbonyl)cyclohexane-1,4-dione (1b). By condensing (1b) with 2 moles of aniline in the presence of aniline hydrochloride, diethyl 2,5-dianilino-3,6-dihydroterephthalate (1c) is obtained. The reaction is carried out in Dowtherm A, a mixture of biphenyl and dibenzofuran. Compound (1c) is then cyclized in this solvent by heating at 250° in a nitrogen atmosphere. The dihydroquinacridone (1d) thus formed is then separated by dilution with ethanol. Finally (1d) is oxidized with sodium *m*-nitrobenzenesulfonate by heating in ethanol or in ethylene glycol, thus giving rise to quinacridone.

Many modifications of this method have been patented. According to a one-step process,[250] (1d) can be obtained directly by condensing (1b) with aniline in polyphosphoric acid. It is also possible to obtain quinacridone directly from (1c) by cyclizing in polyphosphoric acid and oxidizing in situ with chloranil.[251] The final dehydrogenation of (1d) can also be achieved by using a polysulfide or a quinone: chloranil, anthraquinonesulfonic acid,[252] or even by air oxidation in the presence of anthraquinone as catalyst.[253] It is also possible to invert the order of the reactions by oxidizing (1c) with chloranil and cyclizing afterwards.[254]

In a second manufacturing process of quinacridone, the starting material is a 2,5-dihalogenoterephthalic acid (2a), in which X = Cl or Br. This acid or its diester is made to react with an excess of aniline in order to obtain 2,5-dianilinoterephthalic acid (2b) or its diester.[255] According

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[250] DuP, *FP* 1,264,480.

[251] ICI, *BP* 894,610.

[252] CIBA, *FP* 1,225,352.

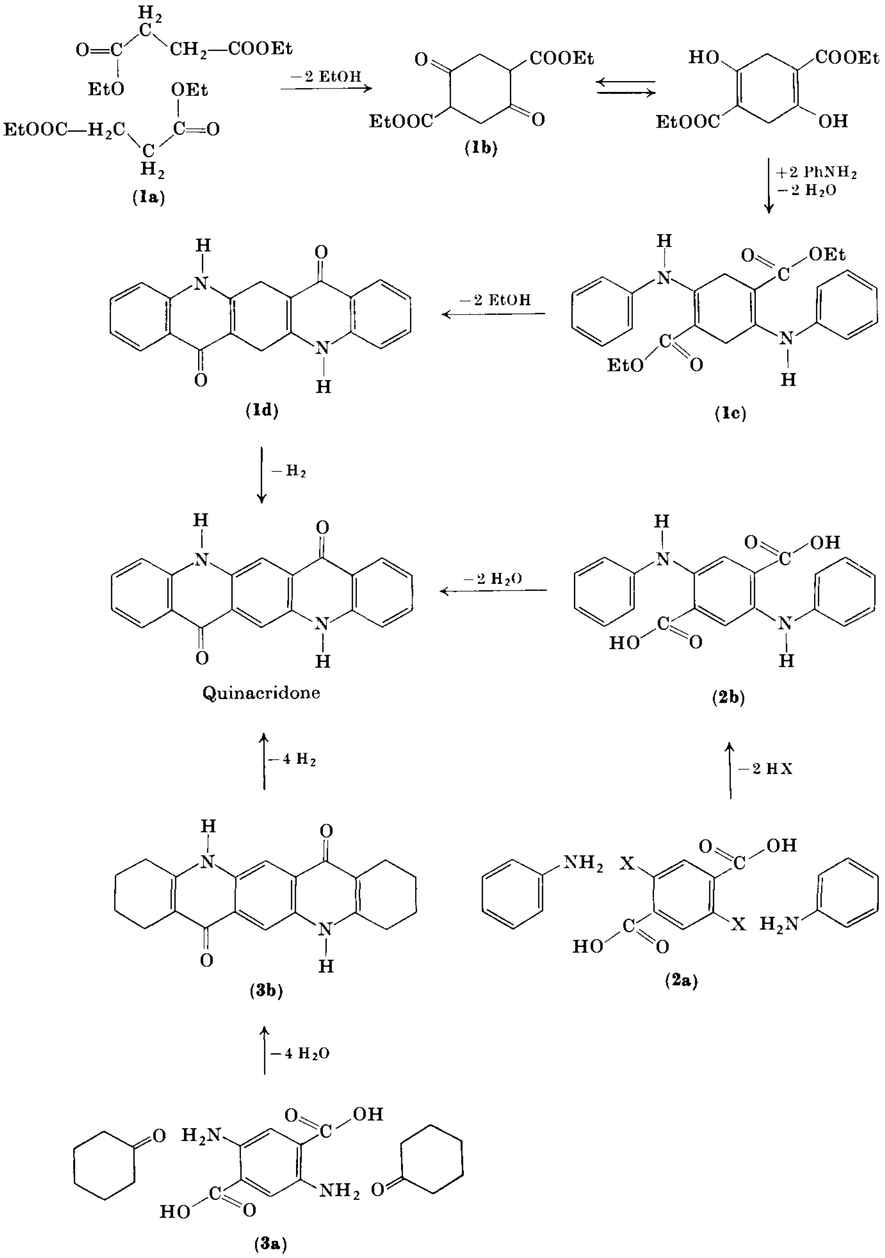
[253] CFM, *FP* 1,328,160; DuP, *FP* 1,496,960.

[254] ICI, *BP* 868,361.

[255] DuP, *FP* 1,264,157.

CHART 1

Preparation of Linear *trans*-Quinacridone



to some patents issued to S[256] (2a) is condensed with aniline in buffered aqueous ethylene glycol in the presence of copper acetate and potassium iodide. A two-step process enables the successive condensation of two different arylamines, thus leading to an asymmetrical quinacridone.

Many processes have been invented in order to transform 2,5-diarylaminoterephthalic acids (2b) or their esters into quinacridones. Cyclization is brought about by heating in a medium containing a condensing agent. The latter may be a molten mixture of aluminum chloride and sodium chloride,[257] or aluminum chloride in trichlorobenzene heated under reflux.[258] It is said that in this case the quinacridone is directly obtained in a useful pigmentary form. Such a form can also be obtained by using polyphosphoric acid, which seems to be the preferred medium and cyclizing agent.[259] Good yields are also said to be obtained by using benzoyl chloride in *o*-dichlorobenzene[260] or in nitrobenzene[261]; benzoyl chloride could be replaced by phosgene.[262] The use of phthalic anhydride[263] and that of phosphorus oxychloride in nitrobenzene[264] have also been put forward. Concentrated sulfuric acid will also act as cyclizing agent; it will, however, sulfonate the quinacridone at the same time. But desulfonation can easily be achieved by heating in dilute sulfuric acid.[265] Ring closure can also be carried out in a molten alkaline hydrogen sulfate.[266] A good yield is also said to be obtained with chloroacetic acid or ethylene glycol containing a small amount of sulfuric acid.[267] Treatment in an autoclave with hydrofluoric acid has also been suggested.[268]

A third method of preparation of quinacridone has been described in a patent issued to DuP[269] (see Chart 1). It consists in condensing 2,5-diaminoterephthalic acid (3a) with cyclohexanone in excess, in the presence of sulfuric acid, thus giving octahydroquinacridone (3b). The latter is finally dehydrogenated by pyrolysis.

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[256] S, *FP* 1,233,785; Add 78,382.

[257] CIBA, *FP* 1,277,183.

[258] HAR, *USP* 3,020,279.

[259] CIBA, *FP* 1,226,825; HAR, *FP* 1,255,770; *USP* 3,257,405; 3,342,823; FH, *DBP* 1,184,881; 1,199,906; CFM, *FP* 1,258,551; ICI, *BP* 868,360.

[260] CIBA, *SP* 392,737.

[261] BASF, *FP* 1,295,839.

[262] BASF, *FP* 1,301,053.

[263] FBy, *FP* 1,244,061.

[264] S, *SP* 404,034; 419,393; 419,396.

[265] CIBA, *BP* 896,803; *USP* 3,200,122; DuP, *USP* 3,261,836.

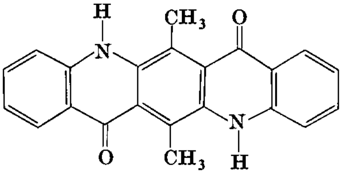
[266] DuP, *USP* 3,107,248.

[267] S, *SP* 409,192.

[268] FH, *DBP* 1,132,273; CFM, *FP* 1,294,523.

[269] DuP, *USP* 3,133,071.

There exists a special method of preparation of the 6,13-substituted linear *trans*-quinacridones.[270] 6,13-Dimethylquinacridone (LVII), for instance, is prepared by condensing 2,5-dimethyl-1,4-dibromobenzene with 2 moles of anthranilic acid. In the absence of 2,5-substituents this simple method leads to an angular quinacridone of type (LIV) similar to that obtained by Ullmann and Maag with *p*-dibromobenzene as starting material.



(LVII)

2. *Preparation of the Linear* trans-*Quinacridonequinones and Their Reduction*

The different methods of preparation of quinacridonequinone (LVI) are summarized in Chart 2. In the oldest method, that of Lesnianski, 2 moles of anthranilic acid are first condensed with 1 mole of *p*-benzoquinone (1a), thus giving 2,5-bis(*o*-carboxyanilino)-1,4-benzoquinone (1b). The reaction can be carried out under heat in ethanol or acetic acid; it is, however, an oxidative condensation requiring an excess of benzoquinone (2 moles) transformed into hydroquinone. To avoid this inconvenience, a recent patent[271] describes a condensation in aqueous methanol using sodium chlorate as oxidizing agent and vanadium pentoxide as catalyst. The ring closure of (1b) in quinacridonequinone can be carried out under heat in sulfuric acid, polyphosphoric acid,[272] or in nitrobenzene by thionyl chloride.[271]

The second method consists in cyclizing 2,5-dianilino-3,6-dicarboxy-1,4-benzoquinone (2b), R = H, or its ester, R = Et. Compared to the first, the second method represents an easier way of obtaining substituted quinacridone quinones, since in the preparation of (2b), aniline can be replaced by different arylamines; (2b) can be obtained by heating in ethanol a 2,5-dihalogeno-3,6-bis(ethoxycarbonyl)-1,4-benzoquinone (2a; X = Cl or Br) with excess aniline.[273] According to a recent patent

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[270] FBy, *DBP* 1,136,040.

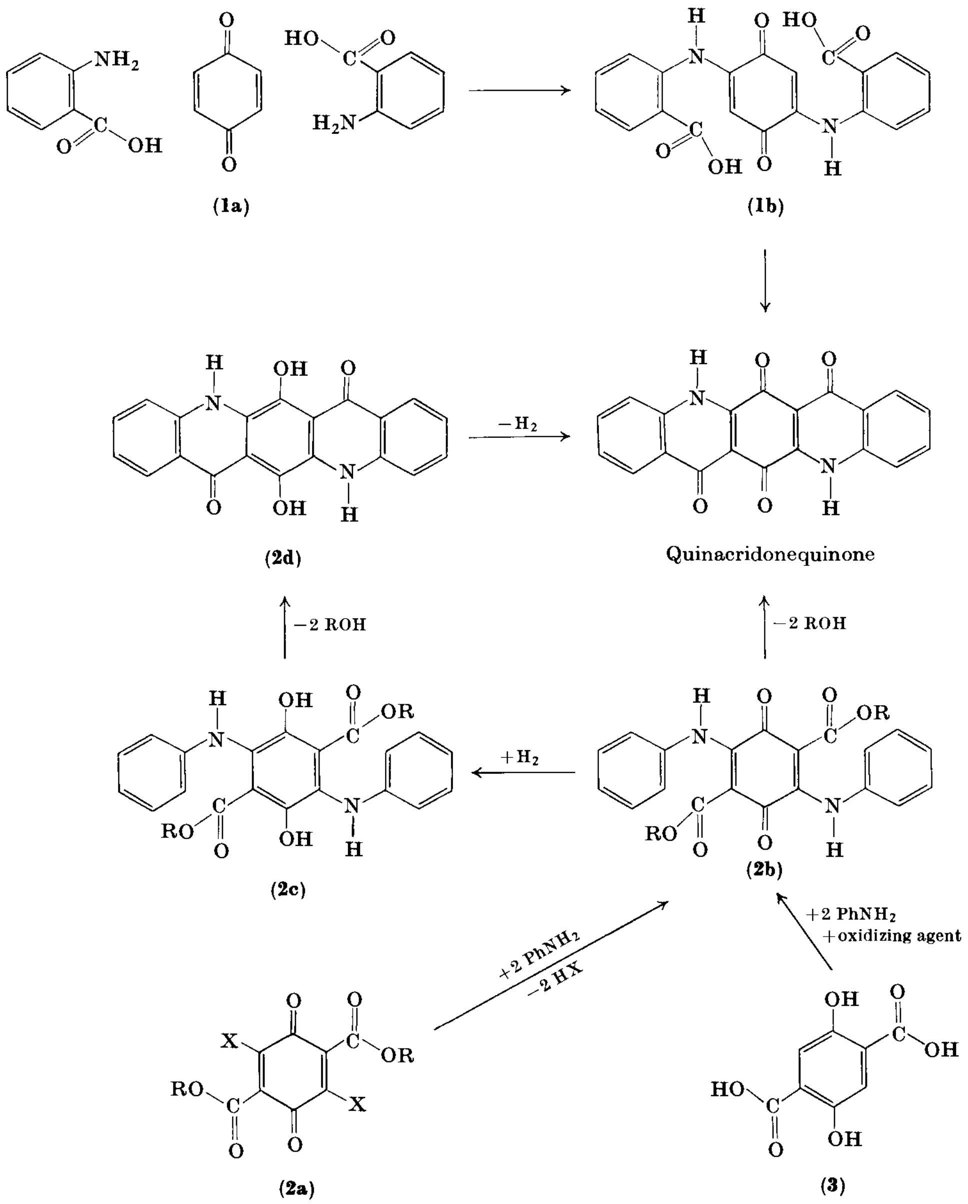
[271] BASF, *DBP* 1,254,269.

[272] BASF, *BeP* 627,375.

[273] BASF, *DBP* 1,140,300.

CHART 2

Preparation of Linear *trans*-Quinacridonequinone



(2b) is prepared in good yield through oxidative condensation of 2,5-dihydroxyterephthalic acid (3) with 2 moles of aniline, by using sodium chlorate in the presence of ammonium vanadate.[274] 2,5-Bis(ethoxycarbonyl)cyclohexane-1,4-dione (1b in Chart 1) can also be used as starting material. It is chlorinated and then anilinated.[275]

If R = Et, the cyclization of (2b) into quinacridonequinone takes place at about 250° in a solvent such as Dowtherm A. If R = H, ring closure can be obtained either by operating in concentrated sulfuric acid or by the action of thionyl chloride in nitrobenzene in the presence of pyridine.

A third method[276] consists in cyclizing diethyl 2,5-dihydroxy-3,6-dianilinoterephthalate. This compound (2c) is easily obtained by reducing (2b), R = Et, in an alcoholic medium by means of sodium dithionite (hydrosulfite). The ring closure of (2c) can be achieved by heating in chloronaphthalene at 250° in a nitrogen atmosphere. The quinacridone hydroquinone (2d) thus obtained is intensely colored. It is finally oxidized into quinacridonequinone by sodium *m*-nitrobenzenesulfonate in an alkaline aqueous alcoholic medium, for instance. This third method has the advantage of not giving rise to a side reaction which sometimes takes place in the second process on cyclization (formation of triphenodioxazine-9,10-dicarboxylate, see Section II,K,2).

It is to be noted that quinacridonequinone may also be prepared by oxidizing quinacridone or 6,13-dihydroquinacridone. Conversely, quinacridonequinone can be reduced to quinacridone, thus giving an interesting method of preparation of the latter.

The reduction can be carried out by means of finely divided metals under different conditions.[277] Zinc powder is preferred and used in a molten mixture of aluminum chloride and one of the following: sodium chloride, potassium chloride, sodium formate, urea, or acetamide. Excellent yields of quinacridone are obtained if the reduction is allowed to take place at 80° in a mixture of aluminum chloride and urea or at 45° in a mixture of aluminum chloride and acetamide. It is also possible to carry out reduction with zinc dust and caustic soda in an aqueous alcoholic medium at 200° under pressure. By this process a mixture of quinacridone and dihydroquinacridone is obtained; to reoxidize the latter a treatment with sodium *m*-nitrobenzenesulfonate is necessary. Finally the quinacridonequinone can be reduced by zinc in 70% sulfuric acid at room temperature; the reduction is then completed by heating at 100°. The yield of quinacridone is equally good.

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[274] BASF, *DBP* 1,195,425.

[275] DuP, *USP* 3,124,582.

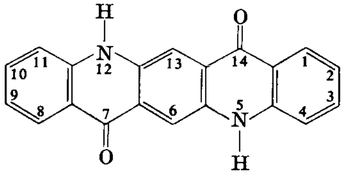
[276] Gy, *SP* 419,395; A. Pugin and J. von der Crone, *Chimia* (*Aarau*) **19**, 242 (1965).

[277] BASF, *DBP* 1,178,159; 1,184,440; 1,187,755.

It is remarkable that in the reduction by copper powder in 70% sulfuric acid at 130° different results are obtained. In that case a red-violet pigment is formed which is said to be 6,13-dihydroxy-6,13-dihydroquinacridone. Under similar conditions 6-hydroxyquinacridone, a violet-red pigment, can also be obtained.[278]

3. *Properties of Linear trans-Quinacridone Pigments*

The unsubstituted quinacridone (LVIII) possesses general properties similar to those of phthalocyanines: excellent fastness to light and to most chemical agents, insolubility in organic solvents and in all the usual dispersion media, good resistance to heat up to 165°.



(LVIII)

For such a simple and small molecule (mol. wt. 312) this stability and most of all this insolubility are rather surprising. These remarkable properties are very probably due to an intermolecular association by hydrogen bonding between $>$N—H and O=C$<$ groups. It is indeed known that 5,12-dimethylquinacridone, which has no hydrogen on its nitrogen atoms, is soluble in alcohol. Knowledge of this dimethyl derivative has another theoretical interest: It can only exist in the ketonic form and it shows a great spectral analogy with the unsubstituted quinacridone. This confirms for the latter the ketonic structure (LVIII) instead of the enolic structure that might be imagined. On the other hand, one can admit the quinacridone molecule as being planar, as shown by the molecular models.

A great number of linear *trans*-quinacridones substituted on their aromatic nuclei are known. Their gamut of shades ranges from orange to purple. They have the same general properties as the unsubstituted quinacridone, with some differences in light fastness which depend on the nature and position of the substituents. They are prepared by the methods described for unsubstituted quinacridones, namely, by using 2,5-diarylaminoterephthalic acids substituted on the arylamino nucleus, or on the terephthalic acid nucleus in the 3,6-positions.

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[278] BASF, *FP* 1,411,752.

Nonetheless, quinacridones obtained by the above-mentioned processes are not in general directly usable as pigments. They have to be submitted to special treatments. Most often the pigmentary conditioning consists in ball milling with sodium chloride in the presence of a small amount of an organic solvent. The pigment is then washed with boiling dilute acid. Other treatments giving rise to finely divided pigments have also been described. For instance, a pigment of soft texture is obtained by ball milling with acetone in the absence of salt,[279] or by wet milling with small plastic marbles in the presence of a glycol to obtain the appropriate viscosity.[280] The crude quinacridone can also be milled with anhydrous aluminum chloride, ammonium sulfate, and tetrachloroethylene; a blue complex is thus obtained which is then decomposed by a dilute acid, giving rise to a pigment of high color strength.[281]

It is to be noted that according to the nature of the conditioning the pigment can be obtained in different crystalline forms, as the quinacridones are indeed polymorphous. The polymorphism of the unsubstituted quinacridone is the best known. According to the X-ray diffraction patterns quinacridone has at least four different crystalline forms.

The crude quinacridone obtained from most manufacturing processes is in the α form. The product keeps this form after a solventless ball milling with sodium chloride; or after dissolving in concentrated sulfuric acid at 10°, followed by reprecipitation in ice-cold water.[249] The same treatments will convert other forms into the α form. The α form is bluish red, but cannot be used as a pigment because of its lack of stability to solvents. Contact with solvents tends to transform it into the γ form.

The pigmentary forms which have been commercialized are the reddish violet β form and the red γ form. They are very fast to solvents and of excellent durability. The first is Quinacridone Violet, the second Quinacridone Red. They have been listed together in *Colour Index* as CI Pigment Violet 19 (CI 46500). Two varieties of Quinacridone Red are available: one is opaque (Red Y), the other transparent (Red B). These two brands mainly differ by their particle size, the opaque being the finer. It is also known that quinacridones can be resinated, in particular with hydrogenated rosin calcium salt,[249] and resination is known to enhance transparency.

The β and γ forms can be obtained from crude quinacridone by ball milling with sodium chloride in the presence of a small amount of a suitable solvent. Xylene and *o*-dichlorobenzene lead to the β form, while dimethylformamide gives rise to the γ form.[249]

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[279] CIBA, *FP* 1,262,270.

[280] Acna, *FP* 1,374,077.

[281] DuP, *USP* 3,148,191.

Several processes giving rise to the β form consist in dissolving the crude quinacridone and reprecipitating it afterwards: dissolution in methylsulfuric acid at 20–25° and precipitation into water[282]; dissolution in concentrated sulfuric acid stirred at 65° with toluene and precipitation into boiling water.[283] It is also possible to prepare the deep blue sodium salt by dissolving the quinacridone in 2-methoxyethanol with sodium hydroxide and then precipitating the β form by a dilute mineral acid.[284] If the crude quinacridone has been dissolved in polyphosphoric acid at 75–80°, the β form can be reprecipitated at 45° by rapid addition of ethanol; otherwise, if the ethanol is added slowly the γ form is obtained.[285]

The γ form is obtained by heating the crude quinacridone or another form in an organic medium such as boiling dimethylformamide,[249] quinoline at 180°,[286] ethanol under pressure at 150°,[287] *p*-cresol at 150°,[288] or 2-pyrrolidone.[289] It can also be obtained by oxidizing dihydroquinacridone with oxygen in 2-pyrrolidone at 180°.[290]

Oxidation of normal dihydroquinacridone (α form) by sodium *m*-nitrobenzenesulfonate in aqueous methanol gives rise to quinacridone in the β form, while in aqueous ethylene glycol in the presence of pyridine the γ form is obtained.[291] In one method, the starting material is dihydroquinacridone (β form) obtained by cyclizing diethyl 2,5-dianilinodihydroterephthalate in tetramethylenesulfone at 250°. Oxidation of this product by sodium *m*-nitrobenzenesulfonate gives rise to quinacridone, γ form.[292]

Besides the normal γ form, a "modified γ form," slightly yellower and more brilliant, is also known. It differs slightly from the conventional γ form in its X-ray diffraction pattern and infrared spectrum. It is obtained by treating quinacridone in *N*-methylpyrrolidone at 200°[293] or in dimethyl sulfoxide at 150°.[294] Finally, there also exists a red δ form obtained from crude quinacridone by sublimation at 425° under vacuum.[295]

[282] Acna, *BP* 979,289.
[283] DuP, *USP* 3,326,918.
[284] FH, *DBP* 1,129,250.
[285] DuP, *USP* 3,265,699.
[286] FH, *DBP* 1,196,619.
[287] FH, *DBP* 1,268,586.
[288] Acna, *FP* 1,379,970.
[289] Tekkosha, *FP* 1,489,908.
[290] Tekkosha, *FP* 1,480,493.
[291] DuP, *USP* 3,287,457; *FP* 1,220,223.
[292] DuP, *USP* 3,007,930.
[293] BASF, *DBP* 1,183,884.
[294] Acna, *FP* 1,397,723.
[295] Eastman-Kodak, *USP* 3,272,821.

Unsubstituted β- and γ-quinacridone commercial pigments are particularly suitable for baking enamels (automotive finishes) as well as for PVC and other plastics. It has been pointed out that quinacridone increases the ductility of polypropylene, even with 5 parts per 10,000 which gives a very weak red coloration.[296]

Although lightfast, Quinacridone Red is not irreproachable in pale tint (it darkens). It can be improved by precipitating on it small amounts of nickel hydroxide, basic nickel carbonate,[297] or manganese carbonate.[298] The best protection against ultraviolet light is said to be achieved by the incorporation of 5% *N*,*N*′-diphenyl-*p*-phenylenediamine in solid solution into the pigment.[299]

On the other hand, quinacridones have a tendency to flocculate in paints. According to a recent patent[300] this fault can be overcome by the introduction of *o*-carboxybenzamidomethyl groups. To prepare the *o*-carboxybenzamidomethylquinacridone, the quinacridone is dissolved in concentrated sulfuric acid; this is followed by the addition at 35° of phthalimide and paraformaldehyde. Dilution with water will cause the modified pigment, slightly yellower than the untreated γ form, to precipitate.

Some substituted linear *trans*-quinacridones have been commercialized, in particular the bluish red 2,9-dimethylquinacridone (CI Pigment Red 122) known as Quinacridone Magenta. It has the same applications as the unsubstituted quinacridone and it is of particular interest for the mass coloration of polyamides.[301] This bluish red pigment is obtained by ring closure of 2,5-di-*p*-toluidinoterephthalic acid or ester by aluminum chloride or polyphosphoric acid. Its texture is improved by heating in ethanol at 125° under pressure.[302] On the other hand, it is well known that this pigment is polymorphic.[303] Recent patents describe two new forms.[304] A yellowish red form is obtained by cyclization in trichlorobenzene at 213° in the presence of *p*-toluenesulfonic acid or by heating the bluish form in dimethylformamide. A "super yellowish" form is obtained by shearing the other forms in a kneading trough with microatomized salt and a poly(ethylene glycol).

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[296] FH, *FP* 1,410,265.

[297] DuP, *BP* 902,630.

[298] DuP, *USP* 3,085,023.

[299] DuP, *USP* 3,341,345.

[300] DuP, *USP* 3,275,637.

[301] HAR, *FP* 1,345,244.

[302] FH, *DBP* 1,261,106.

[303] S, *SP* 405,510.

[304] CCC, *USP* 3,264,298; 3,264,299; 3,264,300.

The dichlorinated and tetrachlorinated quinacridones have been particularly studied; they are oranges and reds. There exists a commercial Quinacridone Orange, probably belonging to this series. The polymorphism of 2,9-dichloroquinacridone is known.[305] The α, β, or γ forms may be obtained according as the cyclization of 2,5-di-*p*-chloroanilinoterephthalic acid takes place in more or less concentrated sulfuric acid, or in polyphosphoric acid. Different treatments will convert one form into the other. Halogenated quinacridones have mainly been prepared from 2,5-dianilinoterephthalic acids halogenated on the aniline nucleus. One should also mention the 6,13-dichloroquinacridone, a brilliant bluish red pigment prepared from 2,5-dianilino-3,6-dichloroterephthalic acid[306] or from quinacridonequinone.[307] On the other hand, chlorination of quinacridone by sulfur chloride in the presence of aluminum chloride gives rise to yellow to red octa- and decachloroquinacridones.[308] Direct bromination in sulfuric acid gives rise to violet polybromoquinacridones.[309]

A violet-red 3,10-bis(trifluoromethyl)quinacridone has been patented.[310] Many other substituted quinacridones have been described in patents, notably some red and orange dimethoxy derivatives,[310a] some red to red-violet dinitro derivatives, the orange-brown 3,4,10,11-dibenzoquinacridone [obtained from 2,5-bis(naphthylamino)terephthalic acid], etc. Very few asymmetric derivatives have been prepared, and among the symmetric ones the best known are the 2,9; 3,10; and 4,11-disubstituted quinacridones. It has been pointed out that the 4,11-disubstituted derivatives are less fast to light than those substituted in the 2,9-positions.[299] On the other hand, azoquinacridones of high color strength have recently been patented.[311]

The quinacridonequinone (LVI), the preparation of which has been described (see Chart 2), is a brownish yellow pigment. Its fastness to heat makes it an interesting pigment for plastics. However, its lightfastness in pale tints is weak. It can be very much improved by incorporation of *N*,*N*′-diphenyl-*p*-phenylenediamine.[299] On the other hand, quinacridonequinone can be transformed into metallic chelates by heating in dimethylformamide with nickel, copper, or zinc acetate. Chelates are

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[305] BASF, *BP* 923,069; S, *SP* 405,560.

[306] S, *FP* 1,233,785.

[307] Yoshio Nagai, *JP* 9274('64); *CA* **61**, 16208b.

[308] DuP, *USP* 3,272,822.

[309] *RP* 140,134; 166,795; *Chem. Zentra.* No. 3, p. 2520 (1965); No. 9, p. 3013 (1967).

[310] S, *SP* 408,944.

[310a] A red violet β form of 2,9-dimethoxyquinacridone was recently patented by DuP, *USP* 3,317,539.

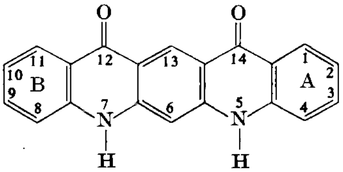
[311] BASF, *DBP* 1,236,696.

red, olive, and yellow pigments of much greater lightfastness. The chelation is said to be intermolecular, the metal being linked to the nitrogen atoms of two molecules by covalency and to the quinone oxygen atoms by coordination.[312]

Quinacridones are capable of forming between themselves solid solutions, as has been claimed in many patents.[313] These solutions can, for example, be obtained by heating a mixture of quinacridones in boiling dimethylformamide, or by ball milling the mixture with salt, followed by a treatment in cold dimethylformamide. The shades of these solid solutions are different from those of simple physical mixtures of the components; they may be more brilliant and faster to light. They are formed of mixed crystals and their X-ray diffraction pattern differs from the sum of those of the components. Solid solutions of this type have been put on the market. Quinacridone Scarlet is said to be formed of unsubstituted quinacridone and of a dichloroquinacridone; Quinacridone Maroon is a solid solution of unsubstituted quinacridone and quinacridonequinone. This last solid solution can also be obtained by the simultaneous preparation of its components through suitable oxidation of dihydroquinacridone.[314] Finally, similar mixed pigments prepared from chemically identical quinacridones but differing physically, for instance, the α and β forms of 2,9-dimethoxyquinacridone, are also claimed to be of interest.[315]

4. *Other Quinacridones*

The linear *cis*-quinacridone, or isoquinacridone (LIX), and its derivatives substituted on rings A and B, are yellow pigments. They have been the subject of claims in some patents. They are prepared from 4,6-diarylaminoisophthalic acids, esters, or chlorides. Cyclization can be carried out by heating in polyphosphoric acid, in chloroacetic acid containing some sulfuric acid,[316] by benzoyl chloride in nitrobenzene,[317]



(LIX)

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[312] DuP, *USP* 3,121,718.

[313] ICI, *BP* 896,916; *FP* Add 83,976; DuP, *USP* 3,160,510; 3,298,847.

[314] DuP, *USP* 3,148,075.

[315] CIBA, *FP* 1,395,204.

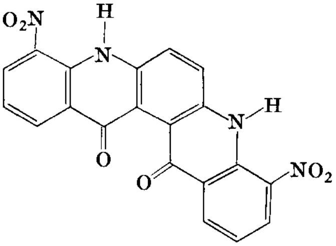
[316] S, *USP* 3,124,581.

[317] FBy, *FP* 1,254,084.

or in a molten alkaline hydrogen sulfate.[266] Another process consists in condensing cyclohexanone with 4,6-diaminoisophthalic acid in sulfuric acid followed by dehydrogenation of the resulting octahydroisoquinacridone (analogous to 36 in Chart 1).[269]

Three crystalline forms of isoquinacridone, α, β, and γ, are known.[318] Only the β and the γ forms are useful as yellow pigments. Fastness to light, however, is insufficient; it can be improved by incorporating *N*,*N'*-diphenyl-*p*-phenylenediamine.[299] It is claimed that the substituted derivatives, e.g., 2,9-dimethylisoquinacridone, are faster and conspicuous by their overspray fastness and migration resistance.[316] None of these pigments, however, seems to have been marketed.

The angular dinitroquinacridone (LX) was patented by DuP in 1956[319]; it is an orange-yellow pigment. The method of preparation consists in condensing *p*-phenylenediamine with 2 moles of 2-bromo-3-nitrobenzoic acid in ethylene glycol at 125° in the presence of copper acetate and anhydrous potassium carbonate. The condensation product is finally cyclized in phosphorus oxychloride.



(LX)

5. *Related Pigments*

The success obtained by quinacridones revived the study of similar pigments in which both –NH– linkages of the heterocycles (or only one) are replaced by –O– or –S– linkages. Some compounds of this type were prepared in 1921 by Eckert and Seidel[247] and in 1934 by Liebermann.[320]

Research was particularly aimed at linear *trans* compounds of general formula (LXI). Chromonoxanthone (X=Y=O) known as "dixanthone" is a yellow pigment. According to a patent issued to Sandoz[321] in which some of its substituted derivatives are also described, it is prepared by cyclizing 2,5-diphenoxyterephthalic acid in polyphosphoric acid. The

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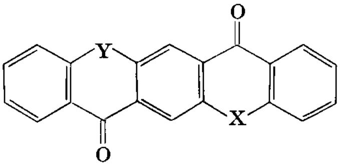
[318] BASF, *BeP* 625,666.

[319] DuP, *USP* 2,830,990.

[320] H. Liebermann, *Ann. Chem.* **513**, 156 (1934).

[321] S, *SP* 386,029.

intermediate product is prepared by condensing 2,5-dibromoterephthalic acid with potassium phenate.



(LXI)

Thiochromonothioxanthone (X=Y=S), also known as "dithioquinacridone" or "benzo-bis-thiachromone," is a bright golden yellow pigment. It is obtained by condensing 2,5-dichloro- (or dibromo)-terephthalic acid with potassium thiophenate, followed by cyclization and pigmentary conditioning.[322] ICI patents describe many yellow, orange, and red pigments of this family obtained by replacing thiophenol by its substituted derivatives.

Thiochromonoacridone (X = NH, Y = S) is a bright orange pigment obtained by cyclizing 2-anilino-5-phenylthioterephthalic acid in polyphosphoric acid. The intermediate product is prepared from 2-chloro-5-nitroterephthalic acid by condensation with thiophenol, followed by the replacement of the $-NO_2$ group by a chlorine atom (reduction, diazotization, Sandmeyer reaction), and finally by condensation with aniline. Many substituted thiochromonoacridones are described in a patent issued to ICI.[323] They constitute a wide gamut ranging from yellow to purple. These pigments must undergo a conditioning similar to those used for quinacridones. Their fastness to light can also be improved by precipitating on them nickel hydroxide or basic nickel carbonate.[324] Between themselves or with quinacridones they can form interesting solid solutions.[325]

In 1959, BASF patented[326] polychlorinated derivatives of 6,13-dihydroxychromonoxanthone. The bright red pigment (LXII) is prepared from diethyl 2,5-dichloro-1,4-benzoquinone-3,6-dicarboxylate, by condensation with 2,4-dichlorophenol, followed by reduction of the quinone compound and ring closure. The same patent also claims red and more bluish analogous thio compounds.

[322] CIBA, *SP* 367,586; ICI, *BP* 851,571; *FP* 1,235,709.

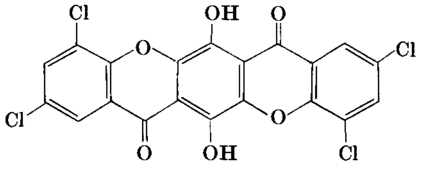
[323] ICI, *BP* 911,206.

[324] ICI, *BP* 1,064,416.

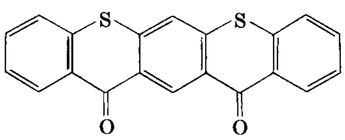
[325] ICI, *BP* 968,473; 968,474.

[326] BASF, *FP* 1,269,435.

cis-Thiochromonothioxanthones were patented in 1961 by S.[327] The unsubstituted product (LXIII) is a yellow pigment obtained by cyclization of 4,6-bis(phenylthio)isophthalic acid.



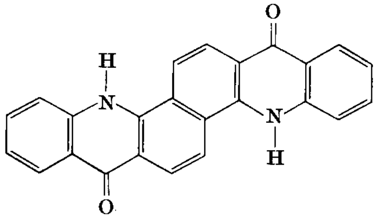
(LXII)



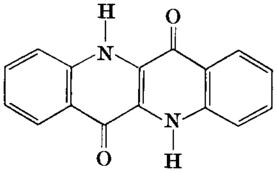
(LXIII)

Compounds similar to quinacridones, with the same two heterocycles, but in which the middle ring is naphthalene instead of benzene, were described in 1962 in a BASF patent.[328] They are yellow to orange acridonoacridone derivatives. The unsubstituted compound (LXIV) is prepared from 1,5-bis(*o*-carboxyanilino)naphthalene dimethyl ester; cyclization occurs in nitrobenzene at 150° by treatment with benzoyl chloride. After being acid-pasted, the greenish yellow pigment obtained should be suitable for use in printing inks and in plastics.

A recent patent issued to DuP[329] claims quinolonoquinolones (epindolidiones), compounds having one ring less than quinacridones. The simplest (LXV) is described as an intense yellow pigment of excellent durability. It is obtained by condensing dimethyl dihydroxyfumarate with 2 moles of aniline in boiling methanol in the presence of aniline hydrochloride. The condensation product is then cyclized in Dowtherm A at 250° or in polyphosphoric acid at 150°.



(LXIV)



(LXV)

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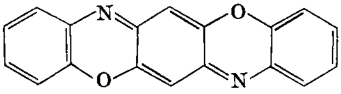
[327] S, *SP* 422,200.

[328] BASF, *DBP* 1,188,551.

[329] DuP, *USP* 3,334,102; see also E. E. Jaffe and H. Matrick, *J. Org. Chem.* **33**, 4004 (1968).

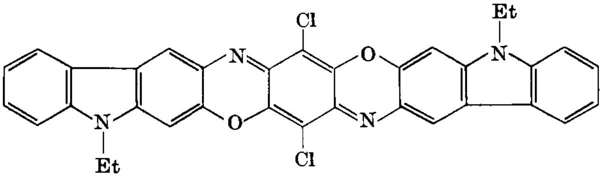
K. DIOXAZINE PIGMENTS

These pigments are derived from triphenodioxazine (LXVI). This compound, by itself, is of no interest, but it has some excellent derivatives, which have been known since 1928.[330] The first to be used were dyes for cotton; several direct dyes of this family are listed in *Colour Index*.[331]



(LXVI)

These direct cotton dyes are described in *CSD II*, pp. 786–791. The preparation of Sirius Supra Blue FFRL (CI Direct Blue 108) is described in detail (*CSD II*, Chart 1, p. 787). It starts by condensing 2 moles of 3-amino-*N*-ethylcarbazole with 1 mole of chloranil, followed by cyclization of the intermediate diimine to the dioxazine (LXVII). By sulfonating the latter, the direct cotton blue is obtained.



(LXVII)

The insoluble dioxazine intermediate (LXVII) was called "Pigment Fast Violet R Base." In fact, it is violet, and IG had envisaged selling it as a pigment under the name Pigment Fast Violet R. However, its actual introduction, commercially, was delayed for some time owing to difficulties encountered in presenting this product in a suitable pigmentary form. In 1952, FH patented a method of improving the pigment, which consisted in treating it with nitrobenzene and *m*-nitrobenzenesulfonic acid.[332] Shortly afterwards, there appeared on the market Permanent Violet RL (FH).

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[330] IG, *DBP* 517,194.

[331] CI Direct Blues 106, 107, 108, 109; CI Direct Violet 54; Formulae CI 51300, 51305, 51310, 51315, 51320, 51325.

[332] FH, *DBP* 946,560.

Today, this pigment, which is commonly called Carbazole Dioxazine Violet, is made by many manufacturers throughout the world. *Colour Index* has listed it under CI Pigment Violet 23, but gave its exact formula, CI 51319, only in 1965.[333]

The excellent properties of this pigment have stimulated interest among research workers. Several methods of pigmentary conditioning have been patented, not only for carbazole violet, but also for other pigments already known as intermediates for direct dyes, such as pyrene violet, an intermediate for Sirius Light Blue F3GL (CI Direct Blue 109). Research workers have particularly aimed at creating entirely new dioxazine pigments. Already in 1949 ICI had patented a violet prepared from chloranil and 4-aminobiphenyl.[334] The most important discovery was that of a new method of preparation of dioxazines. It consists in cyclizing 2,5-di(*o*-alkoxyanilino)-1,4-benzoquinones. Very many pigments prepared by this method have been patented since 1955. Most of them are also violets, but the range of dioxazines now known extends from orange to blue.

1. *General Methods of Preparation of Dioxazines*

Synthesis of a dioxazine is done in two stages. In the first general method, a 2,5-diarylamino-1,4-benzoquinone, free from a substituent in an ortho position of the arylamine, is first prepared. Oxidizing cyclization then produces the dioxazine. It is known that 2,5-dianilino-1,4-benzoquinone, (1b) in Chart 3, with X = H, can be obtained simply by heating 1,4-benzoquinone with aniline, for example, in alcohol. But the yield is low because of side reactions. In practice, 2 moles of an arylamine with a free ortho position (but having other substituents in its W ring) are condensed with 1 mole of a 2,5-dichloro- or 2,5-dibromo-1,4-benzoquinone, (1a) in Chart 3. Chloranil (X = Cl) is generally used, but quinones with other X substituents can be used. It is agreed that cyclization of 2,5-diarylamino-1,4-benzoquinone (1b) occurs by passing through its tautomeric form (1c). It was by this general method that the first dioxazine pigments such as Carbazole Dioxazine Violet (Pigment Fast Violet R Base) were prepared, as indicated in *CSD II.*

In the new method of preparation of dioxazines, the starting material is an arylamine with an –OR group (alkoxy or aryloxy) in the ortho position to its $-NH_2$, and possibly having in addition other substituents in its W ring. Two moles of this amine, (2a) in Chart 3, are condensed with 1 mole of chloranil or of a 2,5-dihalogeno-1,4-benzoquinone disubstituted in the 3,6-positions by X, which can be, for example, an acylamino or an

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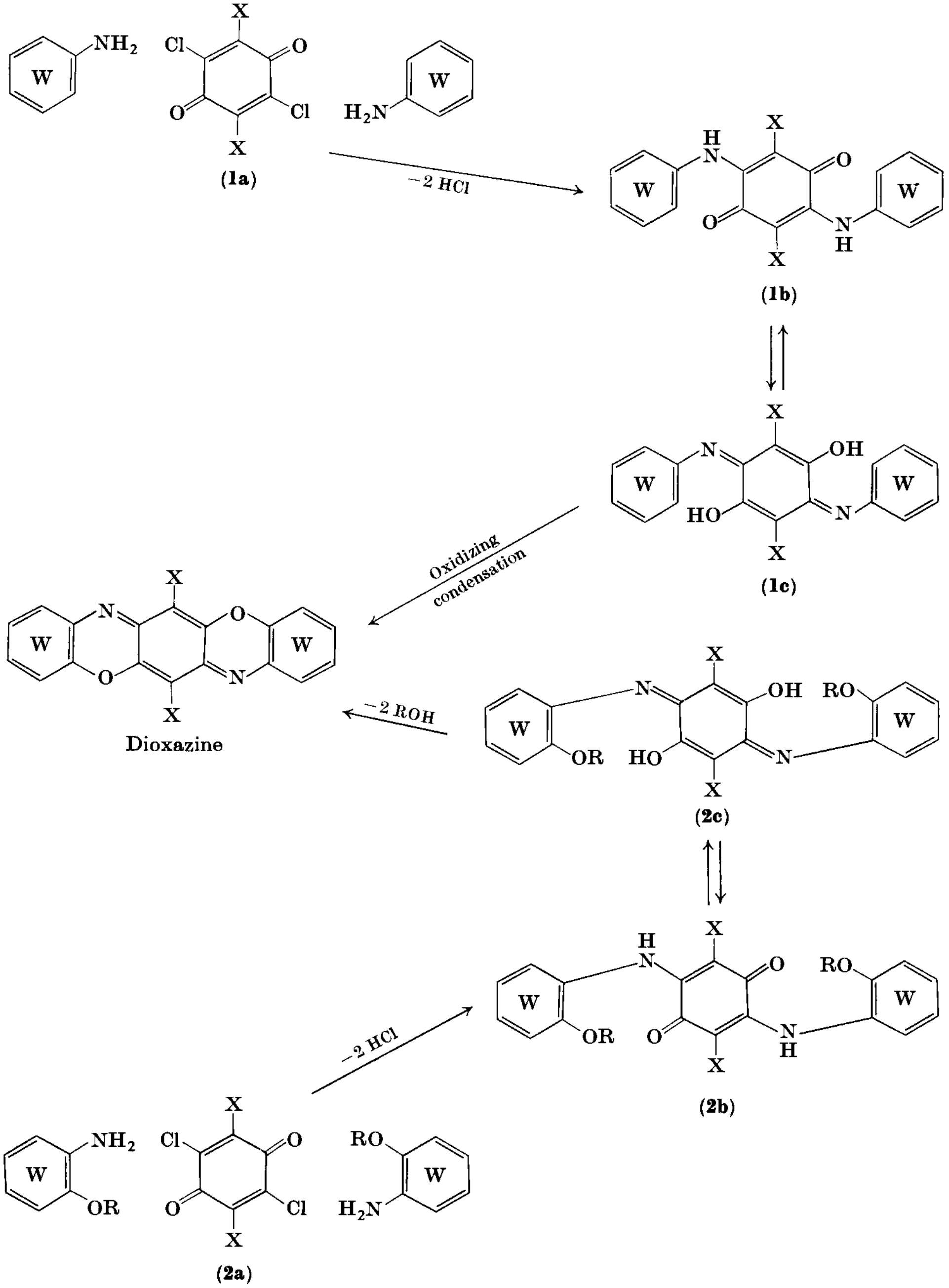
[333] *CI Add. & Amend.*, July 1965.

[334] ICI, *FP* 985,779.

CHART 3

Preparation of Dioxazines



ethoxycarbonyl group. Compound (2b) is obtained, which is then cyclized by heating in a solvent, if required in the presence of a catalyst. Ring formation into the dioxazine takes place readily, probably on the tautomeric form (2c). ROH (alcohol or phenol) is removed during the reaction.

The question arises as to whether the oxygen atom of the liberated ROH comes from the –OR group or from the quinone. Pugin[335] has shown that very probably it comes from the –OR group, while the oxygen of the quinone remains in the dioxazine. In fact, by using an amine ortho-substituted with –SPh instead of –OR, he obtained a dioxazine with the elimination of thiophenol, and not a dithiazine with the removal of phenol.

2. *Conditions of Preparation and Cyclization of 2,5-Diarylamino-1,4-benzoquinones*

Condensation of 2 moles of arylamine with 1 mole of chloranil is always carried out in virtually the same way, whether or not the arylamine is substituted with an –OR group in the ortho position. It is done in a solvent, which is most frequently ethanol at the boil, though it can also be *o*-dichlorobenzene or nitrobenzene at temperatures below 100°. The presence of an acid binding agent is necessary; this may be anhydrous sodium acetate or magnesium oxide. After cooling, the diarylaminobenzoquinone is separated by filtration and washed with alcohol. It is, in fact, exceptional for this product to be cyclized in the same medium which it was prepared.

The method of condensation is still generally the same, whether a 2,5-dichloro-3,6-diacylamino-1,4-benzoquinone or a 2,5-dibromo-3,6-bis(ethoxycarbonyl)-1,4-benzoquinone is used in place of chloranil. It seems, however, that more drastic conditions are necessary for condensing 2,5-dibromo-3,6-dicarbanilino-1,4-benzoquinone with 2,5-dimethoxyaniline, for example. According to a Gy patent,[336] it can be done at 200–210° in 1-chloronaphthalene in the presence of anhydrous sodium acetate; in this way, the dioxazine is obtained directly.

The methods of cyclization of diarylaminobenzoquinones are more varied. For compounds which are not substituted in the ortho position by an –OR group, it is necessary to heat for a long time at a high temperature (180–260°, depending on the case), for example in 1-chloronaphthalene, and in the presence of catalysts (benzenesulfonyl chloride, *p*-toluenesulfonyl chloride, *m*-nitrobenzenesulfonyl chloride).

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[335] A. Pugin, *Chimia* (*Aarau*) **19**, 242 (1965).

[336] Gy, *FP* 1,374,546.

Cyclization of 2,5-di(*o*-alkoxyarylamino)-1,4-benzoquinones is generally done under milder conditions, and especially, more rapidly. According to most patents, the compounds (2b) in Chart 3 are heated in *o*-dichlorobenzene at 170–175° in the presence of benzoyl chloride as a catalyst. The time of heating varies from one case to another, between 1 and 10 hours. In certain cases, the medium of cyclization is trichlorobenzene or nitrobenzene, and the temperature is taken to 180–190°. The catalyst is sometimes thionyl chloride, which is added little by little during heating to 145–150°, in *o*-dichlorobenzene.[337] One patent mentions benzenesulfonyl chloride as a catalyst, this being added directly to the medium of formation (nitrobenzene) of the diarylaminobenzoquinone, and heating being done for 4 hours at 180°.[338] Anhydrous aluminum chloride can also be used, working in pyridine. According to one patent, the absence of a catalyst is preferable in some cases: by heating to the boil in *o*-dichlorobenzene and gradually distilling off the alcohol liberated by cyclization, the yield obtained is better than with benzoyl chloride.[339] Different methods have also been described: cyclization in concentrated sulfuric acid,[340] cyclization by heating to 250–260° while stirring with anhydrous sodium sulfate or calcium chloride.[341]

In the most usual method, which consists of heating in an organic solvent, the purpose of the catalyst is to lower the temperature at which ring formation becomes possible in a sufficiently short time. The temperature necessary is generally below 200°; it is, however, sometimes higher, being influenced by the substituents present in the W ring. In general, conditions of cyclization are not greatly influenced by the X substituents present in the 3,6-positions in the quinone ring, whether these substituents are Cl or NHCOMe, NHCOPh, COOR, CONHR, etc.

There is, however, one case in which cyclization may give a product other than a dioxazine. It is that of the 2,5-diarylamino-1,4-benzoquinone-3,6-dicarboxylic esters (LXVIII). These esters can be cyclized either into dioxazine (LXX) or into quinacridonequinone (LXIX).

As Pugin[335] has shown, these two types of ring formation usually occur at different temperatures. The formation of quinacridonequinone requires a temperature above 200° and is better between 230 and 270°; the presence of a catalyst does not help to bring about this cyclization at a lower temperature. Cyclization into dioxazine is, on the other hand, more often possible below 200°, so that it can be done without producing

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[337] CIBA, *DBP* 1,142,212.

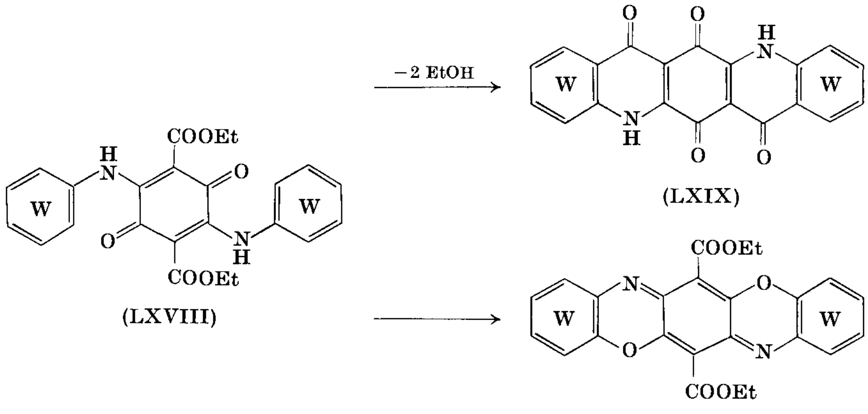
[338] Gy, *USP* 3,009,913.

[339] CIBA, *FP* Add 80,889.

[340] BASF, *DBP* 1,034,294.

[341] Gy, *SP* 412,156.

quinacridonequinone. However, when certain substituents are present, cyclization into dioxazine can only be done at a temperature at which quinacridonequinone may also be formed. This is what happens, for example, if the W ring has a phenoxy group in the ortho position to the –NH–. In such cases, mixtures of (LXIX) and (LXX) are obtained. It is



(LXVIII) (LXIX) (LXX)

to get around this difficulty that a suggestion was made to reduce (LXVIII) to the corresponding hydroquinone when the product desired is quinacridonequinone.[342] The former can only cyclize into quinacridonehydroquinone, oxidation of which will give quinacridonequinone.

Dioxazines of the type (LXX), when they can be prepared without a side reaction, are useful as intermediates for the preparation of 9,10-bis(carbanilino)triphenodioxazines. According to a Gy patent,[343] (LXX) is hydrolyzed in 80% sulfuric acid; the diacid obtained is separated by dilution with water. It is then treated with thionyl chloride in *o*-dichlorobenzene, which gives the bis carboxychloride. Finally, the latter is condensed with an arylamine.

3. *Properties of Dioxazine Pigments*

In the condition in which they are obtained after cyclization, filtration, and washing, the dioxazines are not yet suitable for use as pigments. It is essential to submit them to conditioning treatments similar to those applied to pigments of other classes.

The pigmentary conditioning which is most often mentioned in patents is ball milling with a mineral salt harder than the pigment and a

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[342] See Section II,J,2.

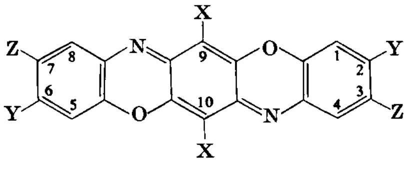
[343] Gy, *SP* 440,508.

small quantity of an organic liquid.[344] The mineral salt should be soluble in water, so that it can be removed by washing (NaCl, $CaCl_2$, Na_2SO_4). The organic liquid may be an aromatic hydrocarbon, a petrol hydrocarbon, a glycol, dimethylformamide, or dimethyl sulfoxide. Ball milling may be replaced by kneading, also with a salt and an organic liquid,[345] or with an aromatic sulfonic acid.[346] According to a patent by Ciba, a soft texture pigment can be obtained by damp grinding with isopropyl alcohol.[347]

The principal commercial pigment from dioxazine is still, today, Carbazole Dioxazine Violet (LXVII), or CI Pigment Violet 23. It is appreciated for its beautiful bright shade, its excellent fastness to light, even in pale tints, and to heat (up to 200°), and its good resistance to chemicals and to many solvents. Only its fastness to certain solvents and plasticizers does not meet maximum requirements. Nevertheless, since its properties are similar enough to those of the phthalocyanines, it is widely used for shading the greenish phthalocyanine blues. That is its principal use, the others being limited by its high price. However, one unexpected use has been patented: the incorporation of this pigment with lubricating greases, to make them more consistent.[348]

Other violets from dioxazines have been put on the market by Gy and by Ciba: Irgazine Violets BLT, and 6RLT,[349] and Cromophtal Violet B.[349a] From the immense amount of research work which has gone into the dioxazines, we may expect the appearance of other pigments of this class, and perhaps in shades other than violet.

Almost all the pigments given as examples in patents are symmetrical dioxazines, unsubstituted in positions 1,4,5,8. They can be represented by the general formula (LXXI).



(LXXI)

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[344] Gy, *FP* 1,196,878; 1,361,268; 1,374,546; *SP* 393,600; CIBA, *FP* 1,260,402.

[345] G, *USP* 2,918,465.

[346] G, *USP* 3,022,299; *DBP* 1,237,530.

[347] CIBA, *SP* 367,917.

[348] Texaco, *USP* 3,010,904.

[349] It should be noted that other Irgazine pigments are azomethines derived from tetrachloroisoindolinone, see Section II,L,2.

[349a] CI Pigment Violet 37, *CI Add. & Am.*, January 1969.

During the research, it was noticed that the influence of substituents on the shade is sometimes different from what had been expected. Pugin explained these anomalies, which are due to the polymorphism of these pigments.[350] He has shown that certain dioxazines have distinct crystalline forms, differing in their X-ray diffraction pattern and having very different shades.

The dioxazine in which X = Cl, Y = *p*-chlorophenyl, and Z = H is a reddish violet, very fast to light, which has the defect of flocculating when used in mixture with phthalocyanines. This can be avoided by incorporating a small percentage of the aluminum salt of the analogous dioxazine in which Y = *p*-carboxyphenyl.[351]

Several patents refer to violet to blue dioxazines, very fast to light, in which X = Cl, Y = NHBz or NHAc, and Z = alkoxy.[352] In particular, the dioxazine in which Y = NHBz, Z = OEt is a blue-violet of very strong coloring power; it is prepared by cyclization of the condensation product of chloranil with Fast Blue BB Base (2 moles). According to H. Gaertner,[353] the dioxazine in which Y = NHBz and Z = isopropoxy is a reddish violet which is faster to solvents than Carbazole Dioxazine Violet, thanks to its two acylamino groups. The dioxazine in which X is no longer Cl, but NHAc, with Y = NHBz and Z = OEt, is a bluish violet, completely nonmigrating and nonbleeding, due to its four acylamino groups. This last pigment is described in two patents by Ciba,[354] the more recent of which concerns the preparation of its β violet form. A patent by Gy concerns the analogous dioxazine with X = CONHPh; it also is an intense and very fast bluish violet.[355] In some violet to blue pigments patented by Ciba X is NHCOR and R a heterocyclic radical.[355a]

A patent by Gy[356] describes diaminotriphenodioxazines, for example, X = Cl, Y = NH_2, and Z = OEt, which is a pure blue pigment. It is shown as very fast to light, and even to acids, which is exceptional for a pigment containing amino groups. Pigments of this type are obtained from corresponding acylamino or nitrocompounds, by deacylation or by reduction.

There are some bordeaux pigments among the dioxazines having

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[350] A. Pugin, *Off. Dig., J. Paint Technol. Eng.* **37**, 782 (1965); *Chimia* (*Aarau*) Suppl., p.54 (1968).

[351] DuP, *USP* 2,843,498.

[352] BASF, *DBP* 1,034,294; CIBA, *SP* 360,149; *BP* 869,357; Gy, *USP* 3,009,913; *SP* 412,156.

[353] H. Gaertner, *J. Oil Colour Chemists' Assoc.* **46**, 28 (1963).

[354] CIBA, *FP* 1,269,107; 1,496,356.

[355] Gy, *USP* 3,130,195.

[355a] CIBA, *BP* 1,114,012.

[356] Gy, *FP* 1,280,449.

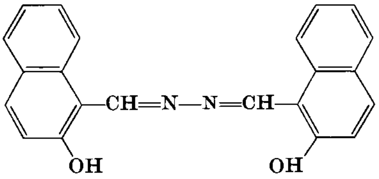
$X = Cl$, if $Z = Cl$ and $Y = NHAc$ or OPh.[357] If $Y = H$, with $Z = Cl$, the pigment is also bordeaux, but if $Z = NO_2$ it is yellowish brown.[358] Dioxazines with $X = Cl$, $Y = H$, and $Z = COPh$, possibly with the Ph being substituted, are red or orange.[359] With $Z = CONHCH_2Ph$, an orange also results.[360]

Bordeaux, reds, oranges, and browns are also known among the dioxazines having $X = NHAc$,[361] $X = NHBz$,[362] $X = CONH_2$,[363] and $X = CONHPh$.[364] Finally, according to a Japanese patent,[365] a polyoxazine blue-black is produced from dianisidine and chloranil, and polyoxazines of other shades can result from other diamines.

L. Azamethine Pigments

Until recently, the azamethine dyes, in which the chromophore is $>C{=}N-$ (Schiff's bases), were hardly represented at all commercially. Only two are mentioned in *Colour Index*, in which they are shown as obsolete and are listed among the methine dyes.[366] However, in 1940 IG put on the market two dyes which are fluorescent in ultraviolet radiation and which are diazamethines: salicylaldazine (Lumogen L Yellow Orange) and 2,2′-dihydroxy-1,1′-naphthaldazine (Lumogen L Light Yellow). The latter (LXXII) had even been envisaged as a yellow pigment for mass coloration of viscose rayon.

In the last twenty years, important studies have been undertaken in the field of azamethines, and some very interesting pigments have been found. They are for the most part diazamethines, and they can be



(LXXII)

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[357] Gy, *FP* 1,361,268; 1,400,086.

[358] CIBA, *DBP* 1,142,212.

[359] Gy, *SP* 393,600.

[360] S, *BP* 892,384.

[361] CIBA, *BP* 892,092.

[362] Gy, *FP* 1,374,546.

[363] Gy, *SP* 408,248.

[364] Gy, *FP* 1,424,131.

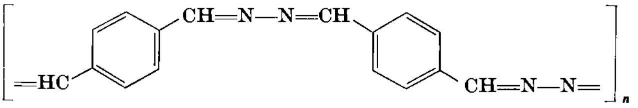
[365] Daito Chem. Ind., *JP* 17,150 ('66); *CA* **66**, 47326p.

[366] CI 48045, solvent dye, and CI 48050, disperse dye, both chromium chelates.

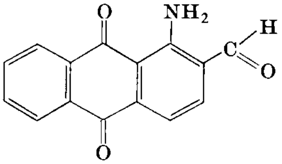
classified into two main groups: (a) isoindoline derivatives; (b) *o*-hydroxyaldehyde derivatives.

In addition to these two groups, of which details will be given, there are a few other azamethines worth mentioning. In 1950, the Calico Printers' Association patented polyterephthalaldazine (LXXIII), which results from polycondensation of terephthalaldehyde with hydrazine.[367] It is a lemon yellow pigment which can be formed in situ on textiles. When prepared in *substance*, it could be used in paints and for pigment printing, since it has good fastness to solvents and to heat.

According to patents by NSK, 2-formyl-1-aminoanthraquinone (LXXIV) is condensed with *o*-phenylenediamine or with ethylenediamine. The resulting azamethines are transformed into copper chelates, which are violet-gray to greenish gray pigments.[368]



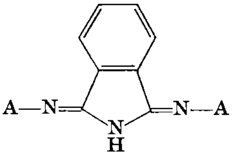
(LXXIII)



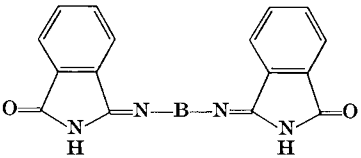
(LXXIV)

1. *Isoindoline Derivatives*

Among the derivatives of isoindoline, a distinction should be drawn between the two categories of diazamethine pigments, which can be represented by the general formulas (LXXV) and (LXXVI), A and B being aromatic or heterocyclic residues, A monovalent and B divalent.



(LXXV)



(LXXVI)

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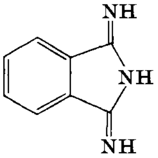
[367] Calico Printers' Assoc., *BP* 694,451.

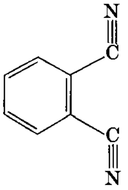
[368] NSK, *JP* 1275 and 1276 ('65); *CA* **63**, 11744–11745.

These pigments have in particular the structural feature that the carbon atom of the azamethine linkage forms part of a heterocycle in which it is attached to a second atom of nitrogen. These compounds can therefore be regarded as special amidines. It should be noted that azamethine groups of the same nature exist in the molecules of the phthalocyanines.

The first pigments of type (LXXV) were described in 1953 by Clark, Elvidge, and Linstead.[369] These authors prepared them by condensing 2 moles of a primary amine with 1 mole of 1,3-diiminoisoindoline (LXXVII). This last compound, well known as a phthalocyanine precursor, was also used, as has been mentioned previously,[370] for preparing hemiporphyrazines by condensation with diamines. Yellow diazamethines have been obtained by heating in ethanol 1 mole of (LXXVII) with 2 moles of aniline, β-naphthylamine, or 3-aminopyridine, respectively. This reaction occurs, of course, with the liberation of 2 moles of ammonia. The same result can be obtained by using phthalodinitrile (LXXVIII), in place of (LXXVII); in this case, the reaction releases a single mole of ammonia.



(LXXVII)



(LXXVIII)

In 1953, BASF patented red pigments resulting from the condensation of phthalodinitrile with substituted 2-aminobenzothiazoles, such as 2-amino-6-methoxybenzothiazole.[371] In the same way, BASF prepared a yellow pigment with 2-aminobenzimidazole.[372] According to a patent by S,[373] the yellow pigment (LXXIX) is prepared by heating, under reflux in trichlorobenzene, 1 mole of phthalodinitrile with 2 moles of 2-aminobenzoxazole. A red, fast to light and to migration in PVC, is obtained from 4,5-dichlorophthalodinitrile and 2-amino-5-methylsulfonylbenzoxazole. The same patent also describes an orange tetrazamethine pigment resulting from condensation of 2,3,6,7-tetracyanonaphthalene (1 mole) with 2-aminobenzoxazole (4 moles).

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[369] P. F. Clark, J. A. Elvidge, and R. P. Linstead, *J. Chem. Soc.* p. 3593 (1953).

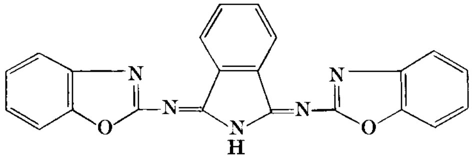
[370] See Section II,H,3.

[371] BASF, *DBP* 955,178.

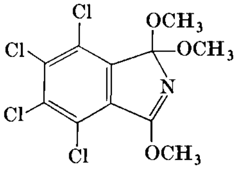
[372] BASF, Patent-Anmeldung B 32144.

[373] S, *BP* 379,670.

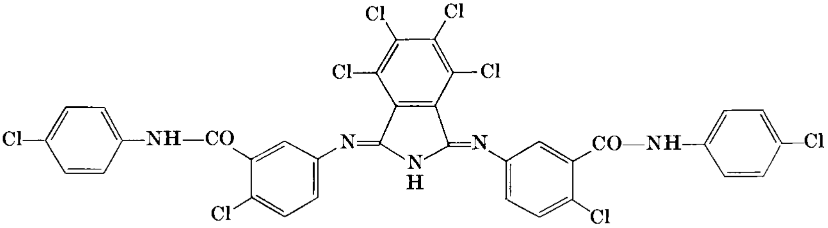
In 1964, Gy patented pigments of type (LXXV), in which the benzene ring of the isoindoline is tetrachlorinated, and the residues A are aromatic with carboxamide or sulfonamide groups and halogen atoms.[374] These pigments are superior in coloring power and in fastness (to light, migration, and overspraying) to those derived from nonchlorinated isoindoline and heterocyclic amines. This patent includes more than 100 examples, most of which are yellow pigments. The intermediate product most commonly used for preparing them is 1,3,3-trimethoxy-4,5,6,7-tetrachloroisoindolenine (LXXX), accessible from 1,3,3,4,5,6,7-heptachloroisoindolenine by reaction with sodium methoxide. Condensation of (LXXX) with 2 moles of amine is easily realized in glacial acetic acid at the boil (3 moles of methanol are liberated). If the amine used is 5-amino-2,4′-dichlorobenzanilide, the greenish yellow pigment (LXXXI) is obtained. Yellow pigments are also obtained with amines such as 3-(*p*-chlorobenzoyl)aminoaniline and 2-chloro-5-sulfamoylaniline.



(LXXIX)



(LXXX)



(LXXXI)

The first representatives of the second type (LXXVI) of diazamethine derivatives of isoindolines were products patented by ICI in 1946, such as the yellow pigment (LXXXII) obtained by condensing 1 mole of dianisidine with 2 moles of iminophthalimidine.[375]

Iminophthalimidine (LXXXIII), better named 3-imino-1-oxoisoindoline, was also used by Clark, Elvidge, and Linstead[369] to prepare

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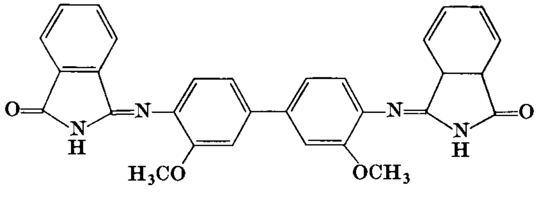
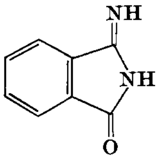
[374] Gy, *FP* 1,434,590.

[375] ICI, *USP* 2,537,352.

yellow pigments with 2,7-diaminonaphthalene, 3,5-diaminopyridine, and 2,4-diaminopyrimidine. A patent by DuP describes a yellow dye prepared in the same way with 2,2′-diamino-4,4′-bis(thiazole).[376]



(LXXXII)



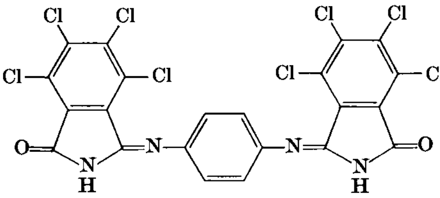
(LXXXIII)

None of these products had the properties to justify their commercial exploitation. But pigments of the same type were discovered which are much more interesting; these are derivatives of 4,5,6,7-tetrachloro-1-oxoisoindoline, or tetrachloroisoindolinone.

2. *Tetrachloroisoindolinone Derivatives*

This particular group of isoindoline diazamethines was patented by Gy in 1956.[377] In 1964, the inventors Pugin and von der Crone gave a detailed lecture on the chemistry and properties of these new pigments, some of which had just been put on the market.[378]

One of the principal representatives of this series is the reddish yellow pigment (LXXXIV) which results from condensation of 1 mole of *p*-phenylenediamine with 2 moles of 3,3,4,5,6,7-hexachloroisoindolinone (LXXXV), with the liberation of 4 moles of hydrogen chloride.



(LXXXIV)

Numerous pigments obtained in the same way with other diamines have been described. For example, the derivative of benzidine is a reddish orange, that of dianisidine is a red. Yellows which are more greenish

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[376] DuP, *USP* 2,692,267.

[377] Gy, *SP* 346,218.

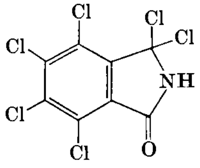
[378] A Pugin and J. von der Crone, *8th Congr. FATIPEC*, p. 61 (1964); *Offic. Dig., J. Paint Technol. Eng.* **37**, 1071 (1965).

than (LXXXIV) are obtained with *m*-diamines such as 2,6-diaminotoluene, or, according to a more recent patent, with 2,2′-diaminobiphenyl.[379]

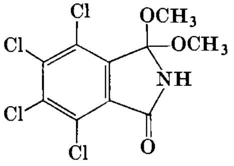
The range of these pigments extends from greenish yellow to bluish red and to brown. Those which Gy has commercialized are Irgazine Yellow 2GLT, Irgazine Yellow 3RLT, Irgazine Orange RLT, and Irgazine Red 2BLT.[380] These pigments are distinguished by excellent fastness to light, migration, and overspraying. They meet the most exacting requirements in paints and plastics.

Yellow (LXXXIV), for example, is prepared by heating, at 160–170°, a mixture of solutions of hexachloroisoindolinone and *p*-phenylenediamine in *o*-dichlorobenzene. The insoluble pigment which is formed is filtered hot, then washed with alcohol and acetone; the yield is quantitative.

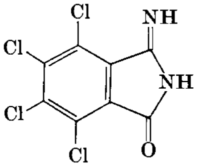
3,3,4,5,6,7-Hexachloroisoindolinone (LXXXV) is prepared from 4,5,6,7-tetrachlorophthalimide by reaction with 1 mole of phosphorus pentachloride. Compound (LXXXV) is the most reactive of the derivatives of isoindolinone suitable for the manufacture of the pigments; others can also be used which have, in position 3, substituents which are easily exchangeable and more mobile than the oxygen atom in position 1. The other principal intermediates which are possible are 3,3-dimethoxy-4,5,6,7-tetrachloroisoindolinone (LXXXVI) and 3-imino-4,5,6,7-tetrachloroisoindolinone (LXXXVII). These products can be obtained from (LXXXV) by reaction with sodium methoxide and with ammonia; they can be obtained in the same way from methyl 3,4,5,6-tetrachloro-2-cyanobenzoate.[381]



(LXXXV)



(LXXXVI)



(LXXXVII)

In the pigments of this family, the four chlorine atoms present in the benzene ring of the isoindolinone play an essential part. They enhance the differences in shade due to the diamine, and they have a decisive

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[379] Gy, *BP* 1,093,669.

[380] The Irgazine brand name is not reserved exclusively for this series: Irgazine Red GLT is an azoic, Irgazine Violets BLT and 6RLT are dioxazines.

[381] Gy, *SP* 348,496; 363,980.

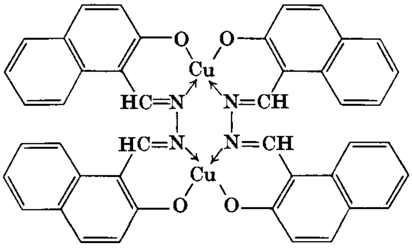
effect on the fastness of the pigment, which without them would be very inferior. The fastness remains mediocre if the molecule is unsymmetrical, with one ring tetrachlorinated and the other not chlorinated. Monoazomethines obtained with primary aromatic monoamines are slightly colored and notably soluble.

The presence of the hydrogen atom in the imide group is also essential. Methylation of this group gives dyes with no fastness and pale yellow in shade, whatever the diamine.

For pigments of type (LXXXIV), atomic models suggest the possibility of a cis–trans isomerism, which has not yet been established. On the other hand, they show that the three rings of the molecule cannot be coplanar, but that the outside rings can be in the same perpendicular plane as that of the middle ring. In apparent contradiction to this, spectral study of the pigments in solution in dimethylformamide seems to prove a conjugation of π electrons along the length of the molecule. Pugin concludes the probable existence of intermolecular associations as a result of the formation of a complex between electron donor and electron acceptor groups (the residue of the diamine of one molecule and the iminotetrachloroisoindolinone residue of another).

3. o-*Hydroxyaldehyde Derivatives*

In these compounds, the azamethine linkage comes from condensation of a formyl group and an amino group, with the liberation of one molecule of water. The oldest diazamethine pigment of this type is 2,2′-dihydroxy-1,1′-naphthaldazine (LXXII), already mentioned, a fluorescent yellow resulting from the condensation of hydrazine (1 mole) with 2-hydroxy-1-naphthaldehyde (2 moles). The copper chelate of this compound (LXXXVIII) was patented in 1956 by CCC[382] and described as a chocolate brown pigment suitable for stoving enamels.



(LXXXVIII)

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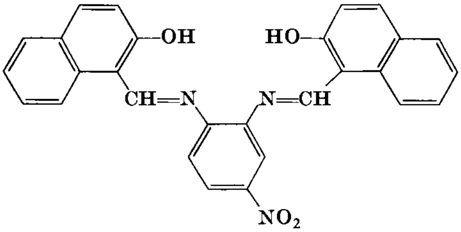
[382] CCC, *USP* 2,877,252.

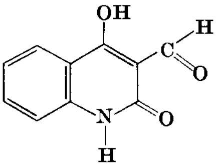
As early as 1939, IG had patented metal complexes of another type, yellow to red and brown.[383] These were zinc, nickel, chromium, iron, and manganese chelates of azamethines formed by condensation, with monoamines or diamines, of 3-formylsalicylic acids (3-carboxy-2-hydroxybenzaldehyde, possibly substituted). In 1966 BASF patented yellow metal complexes of azamethines produced by condensing salicylaldehyde with 4-phenyl-2-aminophenol.[383a]

Several patents have described metal complexes of diazamethines derived from *o*-phenylenediamine condensed with 2 moles of an *o*-hydroxyaldehyde. If the latter is 2-hydroxy-1-naphthaldehyde, a nickel chelate which is a red pigment is obtained.[384] Another red pigment, also a nickel complex, is obtained in the same way from 3,5-dichloro-2-hydroxybenzaldehyde.[385] A patent by BASF describes zinc and cadmium chelates of diazamethines derived from nitro-*o*-phenylenediamine (1,2-diamino-4-nitrobenzene) and various *o*-hydroxyaldehydes, principally 2-hydroxy-1-naphthaldehyde.[386] With zinc, diazamethine (LXXXIX) forms a yellowish red chelate, and with cadmium an orange chelate. These pigments are obtained by heating the components in solution in *N*-methylpyrrolidone, in the presence of the metal acetate.

In 1961, DuP patented nickel, zinc, and copper complexes of diazamethines derived from 3-formyl-4-hydroxycarbostyril (XC).[387] This compound can be made from 2,4-dihydroxyquinoline by the Reimer-Tiemann reaction. According to the patent, this aldehyde is condensed with *p*-phenylenediamine in boiling butanol. Metallization is then carried out by heating the diazamethine with nickel acetate in dimethyl-



(LXXXIX)



(XC)

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[383] IG, *DBP* 745,337.

[383a] BASF, *BP* 1,122,938; 1,123,859.

[384] IC, *USP* 2,993,065.

[385] HCC, *JP* 16,432('61); *CA* **57**, 3596b.

[386] BASF, *FP* 1,416,293; see also similar tetrakisazomethine chelates: BASF, *FP* 1,520,020; *BeP* 720,305.

[387] DuP, *USP* 3,132,140.

formamide under reflux. The resulting chelate is a brilliant yellow pigment. With *o*-phenylenediamine, a reddish yellow pigment is obtained in the same way.

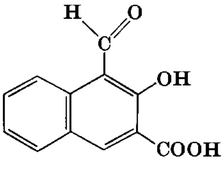
Two patents by IC[388] refer to the copper chelates of azamethines derived from benzoguanamine (2,4-diamino-6-phenyl-1,3,5-triazine) by condensation either with salicylaldehyde or with 2-hydroxy-1-naphthaldehyde. The complexes are, respectively, maroon and brownish yellow pigments.

All the above derivatives of *o*-hydroxyaldehydes are metal complexes. Mention must now be made of metal-free diazamethines, which are pigments of high quality. They are derivatives of 2-hydroxy-3-carboxy-1-naphthaldehyde.

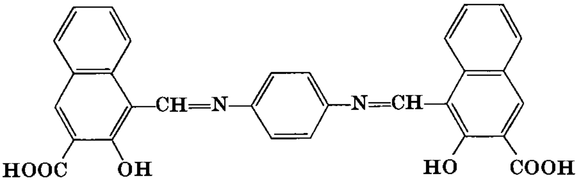
4. *2-Hydroxy-3-carboxy-1-naphthaldehyde Derivatives*

In 1965 and 1966, diazamethines resulting from condensation of this aldehyde with various primary diamines were the subject of several patents by Fran.[389] Although it can be made from 2-hydroxy-3-naphthoic acid by reaction with chloroform in the presence of sodium hydroxide (Reimer-Tiemann reaction) and is easy to purify, 2-hydroxy-3-carboxy-1-naphthaldehyde (XCI) was formerly not well known. Whereas its actual melting point is 227°, this compound was described in 1897 as melting at 170°,[390] and in 1955 as melting at 280° with decomposition.[391]

Depending on the nature of the diamine condensed with 2 moles of aldehyde (XCI), the shades of diazamethines vary from yellow to violet and brown. The yellow pigments are those in which the sequence of conjugated double bonds is interrupted (e.g., the derivative of 4,4′-diaminodiphenylmethane). The pigments which are most interesting for their intense coloring power and for their fastness are the reds



(XCI)



(XCII)

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[388] IC, *USP* 3,290,299; 3,297,691.

[389] J. Lenoir, J. Ligot, and Fran, *FP* 1,449,666; 1,462,234; 1,479,348; 1,505,360; Add 89,692.

[390] Gy, *DBP* 98,466.

[391] FBy, *DBP* 952,629.

derived from 1,4-diaminobenzenes and from 4,4′-diaminobiphenyls. The derivatives of *p*-phenylenediamine (XCII) and of benzidine are bordeaux, those of tolidine and 3,3′-dichlorobenzidine are yellowish scarlets, that of dianisidine a corinth red, and those of 2,5-diethoxy-1,4-diaminobenzene and of 1,4-diaminonaphthalene are violets.

These pigments can be obtained in at least two forms, α and β, differing in their fastness to light and in their shade (the shades shown above are those of the β forms). If condensation is carried out in hot alcoholic medium, the α form is obtained. This can also be prepared in aqueous acid medium, by introducing a solution of the diamine (hydrochloride or sulfate) into a hot suspension of the aldehyde (XCI) reprecipitated by acidification of its aqueous alkaline solution in the presence of a surfactant. The α form is converted into the β form by heating at 150° in a strongly polar solvent such as dimethylformamide or dimethyl sulfoxide. The β form can also be obtained directly by condensation in certain hot solvents or aqueous emulsions of solvents. In all cases, the components are used in stoichiometric proportions and the yield is quantitative.

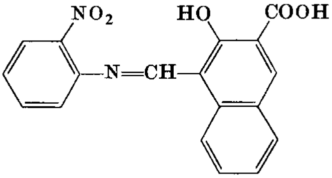
The two forms of the pigments are completely insoluble in almost all solvents and have only an extremely slight solubility in dimethylformamide. Their resistance to migration is perfect in PVC plasticized with dioctyl phthalate. Their fastness to overspraying is also perfect under the most severe conditions of temperature. On the other hand, the α forms, which are in most cases a little yellower than the β forms, have only moderate lightfastness in pale tints, while the β forms have excellent fastness to light, even in the palest tints. Because of their exceptional qualities, the β forms are perfectly adapted for coloration of plastics and stoving enamels.

The carboxyl group in position 3 plays an essential part in these pigments, which are much faster than the corresponding derivatives of 2-hydroxy-1-naphthaldehyde; it has, moreover, a very marked bathochromic effect: the diazamethine corresponding to (XCII) without carboxyl is an orange which migrates in PVC. The presence of a carboxyl as a free acid group is a peculiarity of these pigments, which lose their remarkable properties if the carboxyl is esterified, and also if the hydroxyl group in position 2 is methylated. It is probable that the carboxyl forms a chelate ring with the oxygen atom of the hydroxyl, and that there is also a hydrogen bond between the hydroxyl and the nitrogen atom.

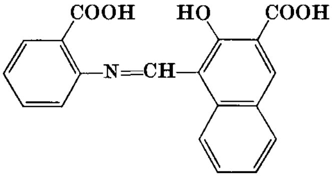
It is remarkable that the diazamethine derivatives of *p*-diamines are easily formed at the expense of other azamethines, such as the yellow anil of aldehyde (XCI) and the diazamethines formed by (XCI) with *m*-phenylenediamine (yellow brown) or *o*-phenylenediamine (orange). If these compounds are heated in alcohol with *p*-phenylenediamine, the bluish red pigment (XCII) is formed, with the liberation, respectively, of aniline, *m*- or *o*-phenylenediamine. On the other hand, a monoazamethine can be formed with 1 mole of (XCI) and 1 mole of *p*-phenylenediamine, by condensing in alcohol at low temperature (0–20°) and in the absence of acid. This monoazamethine is easily transformed into pigment (XCII) with the removal of one-half a mole of diamine, by heating in acid medium.

In general, the monoazamethines of 2-hydroxy-3-carboxyl-1-naphthaldehyde are too soluble and insufficiently fast to light to be of use as pigments. There are, however, some which are valuable pigments, such as the derivative of *o*-nitroaniline (XCIII), an orange-red pigment patented by Fran in 1966, which has excellent lightfastness.[392]

Finally, condensation of 2-hydroxy-3-carboxy-1-naphthaldehyde with anthranilic acid and its ring-substituted derivatives gives azamethines such as (XCIV), which are of no interest by themselves, but are capable of being transformed into pigmentary metal complexes. These pigments, patented by Fran in 1966, have very good fastness to overspraying, migration, and light[393] For example, with copper, zinc, and manganese, azamethine (XCIV) forms complexes which are, respectively, yellow-green, reddish yellow, and orange.



(XCIII)



(XCIV)

M. Fluorubine Pigments

Fluorubine is 6,13-dihydropyrazino[2,3-*b*;5,6-*b*′]diquinoxaline, or 6,13-dihydro-5,6,7,12,13,14-hexaazapentacene (XCV). It is a yellow coloring matter, discovered in 1903 by Hinsberg and Schwantes,[394] who gave it this strange name of fluorubine because of its intense fluorescence and the ruby red color of its solution in concentrated sulfuric acid.

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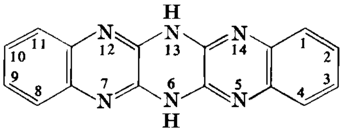
[392] J. Lenoir, M. Maigrot, and Fran, *FP* 1,503,786.

[393] J. Lenoir, R. Lanzarone, and Fran, *FP* 1,469,573.

[394] O. Hinsberg and E. Schwantes, *Chem. Ber.* **36**, 4048 (1903).

It was only in 1959, by BASF,[395] and in 1960, by Ciba,[396] that the exploitation of fluorubine as a pigment was envisaged. However, some years earlier, Switzer had patented the use, in fluorescent pigments, of quaternary salts of fluorubine.[397]



(XCV)

The BASF and Ciba patents concerned not only fluorubine and its substituted derivatives, but also many related pigments. However, it was fluorubine itself which was most closely investigated with a view to pigmentary applications.

1. *Preparation and Properties of Fluorubine*

All syntheses of fluorubine are based on the use, as an intermediate, of 2,3-dichloroquinoxaline, (1b) in Chart 4. To prepare this compound, the first step is to condense *o*-phenylenediamine with oxalic acid, which gives 2,3-dihydroxyquinoxaline (1a) This is then transformed into 2,3-dichloroquinoxaline (1b) by treatment with phosphorus pentachloride.

A second intermediate product used by Hinsberg was 2,3-diaminoquinoxaline, (2a) in Chart 4, which he obtained by reacting cyanogen with *o*-phenylenediamine in solution in methanol. According to the most recent methods, 2,3-diaminoquinoxaline is obtained by treating 2,3-dichloroquinoxaline either with ammonia in a saturated alcoholic solution under pressure at 150°,[398] or with anhydrous ammonia at 90° under 65 atm.[399] In the latter case, the yield attains 98%. On the other hand, if ammonia gas is passed into a solution of 2,3-dichloroquinoxaline in *N*-methylpyrrolidone at 140°, a single atom of chlorine is substituted by NH_2.[400] The product then obtained with a yield of 89% is 2-amino-3-chloroquinoxaline, (2b) in Chart 4, which can also be used for synthesizing fluorubine.

The classical method for preparing fluorubine consists in condensing 2,3-dichloroquinoxaline with 2,3-diaminoquinoxaline. Hinsberg and

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[395] BASF, *FP* 1,278,293.

[396] CIBA, *FP* 1,290,568.

[397] Switzer, *USP* 2,495,202.

[398] A. H. Gowenlock, G. T. Newbold, and F. S. Spring, *J. Chem. Soc.* p. 622 (1945).

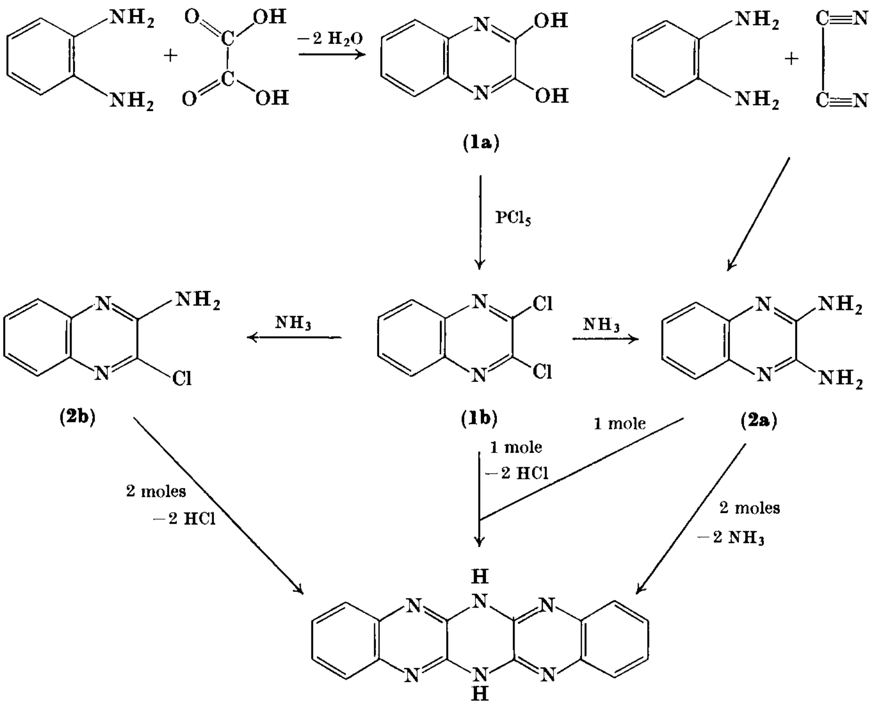
[399] BASF, *DBP* 1,149,477.

[400] BASF, *DBP* 1,135,471.

Schwantes brought about this condensation by melting the two products together at about 270°. The large excess of dichloroquinoxaline used as a flux was then removed by extraction with chloroform. According to the first BASF patent,[395] fluorubine is obtained in a purer state and with better yield if the two components are reacted in equimolecular proportions in boiling dimethylformamide, in the presence of anhydrous sodium carbonate as an acid binding agent. However, further purification is still necessary, and the yield is not very satisfactory

CHART 4

Preparation of Fluorubine



Fluorubine

A new method,[401] patented by BASF in 1960, has an advantage over the foregoing in that it only depends on the purity of a single raw material. It consists, in effect, in condensing with itself 2-amino-3-chloroquinoxaline (2b), 2 moles of which provide 1 mole of fluorubine.

[401] BASF, *DBP* 1,142,981.

This condensation can be carried out by heating for 5 hours at 180° in *N*-methylpyrrolidone. It can also be done in dimethylformamide in the presence of anhydrous sodium carbonate, or in trichlorobenzene at the boil.

A third method was patented by BASF in 1960[399] and by Ciba in 1961.[402] This also used a single raw material: 2,3-diaminoquinoxaline, which is condensed with itself with the liberation of ammonia. It is interesting that the liberated gas does not raise problems of corrosion of the plant, as in the two previous methods. Condensation can be done in different ways. According to the BASF patent, diaminoquinoxaline is heated for 65 hours at 205° in *N*-methylpyrrolidone under an atmosphere of nitrogen. The fluorubine formed is filtered after cooling to 100° and washed with methanol. According to the Ciba patent, condensation can be achieved simply by heating the molten diaminoquinoxaline at high temperature. It is, however, preferable to mix the diaminoquinoxaline with a substance which lowers the melting point and the temperature at which ammonia is liberated. With benzoic acid, the reaction is completed in half an hour at 230°; zinc chloride can also be used. Depending on the nature of the product added, the mass is finally washed with an alcohol, or with water, etc.

Whatever the method of preparation, the crude fluorubine obtained must undergo pigmentary conditioning. The method which is most often shown in patents is acid pasting. The fluorubine is dissolved in concentrated sulfuric acid below 30°; but it is not sufficient, in order to reprecipitate it, to dilute it with water. In fact, if this is done, the precipitate is fluorubine sulfate, which is not hydrolyzed. To obtain free fluorubine, it is necessary to do the precipitation in a solution of ammonia. An additional treatment with boiling dimethylformamide can be useful. Fluorubine has only a very slight solubility in this solvent, and it should be noted that the fluorescence of the solution is green.

On the other hand, acid solutions of fluorubine (notably that in glacial acetic acid with a little hydrochloric acid) have an orange-red fluorescence. Along with its basic properties, fluorubine also has acid properties: it can be solubilized by sodium hydroxide, slightly so in water, but readily in alcoholic medium.

Fluorubine is a bright greenish yellow pigment with excellent fastness to light, solvents, and plasticizers, which is particularly outstanding for its exceptional stability to heat (crystalline structure is unchanged at 400°). It is especially suitable for mass coloration of synthetic fibers which are melt-spun. In spite of its remarkable properties, this beautiful

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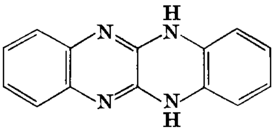
[402] CIBA, *BP* 935,630.

pigment has apparently not been put on the market. Its cost is still too high, even after the improvements which have been made in the methods of preparing it.

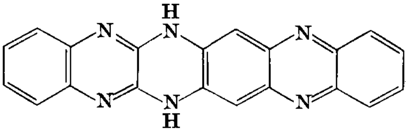
A certain number of derivatives of fluorubine, substituted in its outer rings, symmetrical or unsymmetrical, have been described in patents. They are prepared by using quinoxalines which have chlorine atoms or methyl or methoxy groups in their benzene ring. In general, these pigments are yellow—a little redder than unsubstituted fluorubine—and have no advantage over the latter.

2. *Related Pigments*

Along with fluorubine, other heterocyclic derivatives of quinoxalines are mentioned in patents. They are almost all new products. However, the simplest, which is fluoflavine (XCVI), was prepared in 1896 by Hinsberg and Pollak by condensing *o*-phenylenediamine with 2,3-dichloroquinoxaline.[403] Fluoflavine is also a greenish yellow pigment. Although its fastness properties are very good, it is apparently less interesting than fluorubine. The introduction of substituents into the benzene ring of fluoflavine has little effect on the shade—slightly redder. On the other hand, annellation of a quinoxaline ring gives an orange pigment (XCVII).



(XCVI)



(XCVII)

All the quinoxalodihydropyrazines can be prepared, like fluorubine, by the general method of condensing a 2,3-dichloroquinoxaline with an *o*-diamine. If, in this preparation, the *o*-diamine is replaced by an *o*-aminophenol or by an *o*-aminothiophenol, there are produced, respectively, a quinoxalobenzoxazine or a quinoxalobenzothiazine. The simplest compounds in this series are yellows of low coloring power; but quinoxalophenazinoxazine of formula (XCVIII) is an intense greenish yellow. Quinoxaloanthraquinonoxazine of formula (XCIX) is a red pigment of remarkable lightfastness.[395]

Particular interest attaches to pigments which have four heterocycles in their molecule. The golden yellow (C) is mentioned in a patent by

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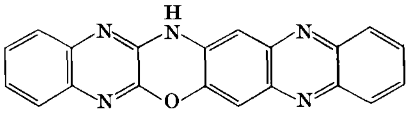
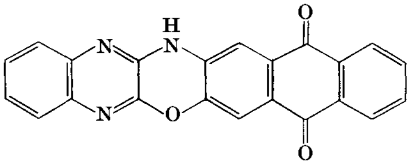
[403] O. Hinsberg and J. Pollak, *Chem. Ber.* **29**, 784 (1896).



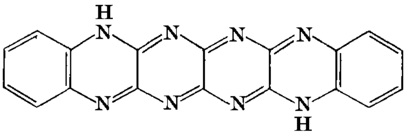
(XCVIII)



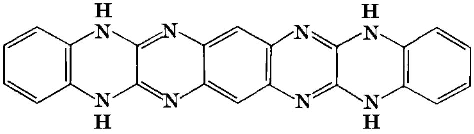
(XCIX)

Ciba.[396] The red (CI) was the subject, with a series of analogous pigments, of a patent by BASF.[404]

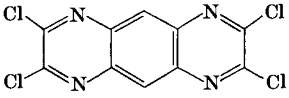
The red pigment (CI) is prepared by condensing 2 moles of *o*-phenylenediamine with 1 mole of 2,3,7,8-tetrachloropyrazino[2,3-*g*]quinoxaline (CII). This intermediate is obtained from 1,2,4,5-tetraminobenzene by a method which is similar in every way to that described for preparing 2,3-dichloroquinoxaline from *o*-phenylenediamine.



(C)

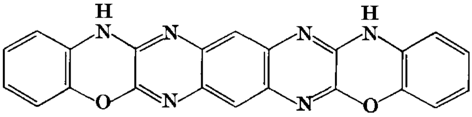


(CI)



(CII)

If the intermediate (CII) is condensed with 2 moles of *o*-aminophenol or *o*-aminothiophenol, there are produced, respectively, the yellow pigment (CIII) or the bluish red pigment (CIV). These pigments are described in the same patent,[404] as well as several of their derivatives. They are of interest for their brilliance of shade, high coloring power, and excellent fastness properties.



(CIII)

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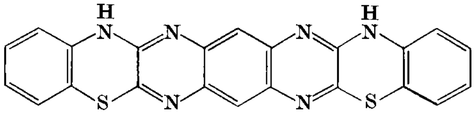
[404] BASF, *DBP* 1,228,356.



(CIV)

N. NAPHTHINDOLIZINEDIONE PIGMENTS

These pigments are derived essentially from naphtho[2,3-*b*]indolizine-6,11-dione, which is also called 2,3-phthaloylpyrrocoline and has the general formula (CV), with R = H. Certain pigments of this family have as a base compound a homolog of the above product: benzo[*g*]naphtho-[2,3-*b*]indolizine-8,13-dione, formula (CVI), with R = H.

All these pigments belong to a new class of coloring matters, which has been closely studied since the work of Pratt *et al.* in 1954 and 1957,[405] and that of Acharya, Suryanarayana, and Tilak in 1955.[406] These quinone coloring matters are vat dyes which can be used for dyeing textiles. Their chemistry is treated in detail in Chapter I. We shall only deal here with pigments from naphthindolizinedione which have been described in patents. Although the range extends from orange-yellow to blue-violet, these pigments are mainly reds which are of interest for their bright shade and their outstanding fastness properties. However, no representative of this family seems to have appeared as yet on the market.

1. *Intermediate Products of the Pigments*

The principal intermediate for the preparation of these pigments is 12-ethoxycarbonylnaphthindolizine-6,11-dione (CV; R = COOEt). This ester is obtained by reacting 2,3-dichloro-1,4-naphthoquinone with pyridine and ethyl acetoacetate.[405] The analogous ester, (CVI; R = COOEt), is obtained by a very similar reaction, in which isoquinoline is used in place of pyridine. E. F. Pratt has shown that this last preparation can be carried out with a crude mixture of quinoline and isoquinoline, since the quinoline does not react.

These preparations of esters have the defect of not giving very good yields: 45% for (CV) and 64% for (CVI). According to a Ciba patent,[407] the same products are obtained with yields above 80% if, in the preceding preparations, ethyl acetoacetate is replaced by ethyl chloroacetate, and if the reaction is carried out in a solvent at the boil.

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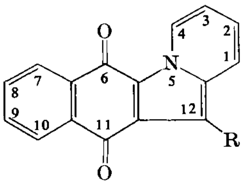
[405] E. F. Pratt, R. W. Luckenbaugh, and R. L. Erickson, *J. Org. Chem.* **19**, 176 (1954); E. F. Pratt, R. G. Rice, and R. W. Luckenbaugh, *J. Am. Chem. Soc.* **79**, 1212 (1957).

[406] R. V. Acharya, B. Suryanarayana, and B. D. Tilak, *J. Sci. Ind. (India) Res.* **14B**, 394 (1955).

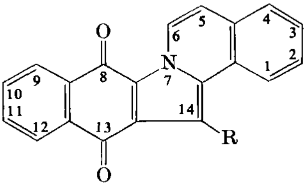
[407] CIBA, *BP* 1,046,648.

The acids of formulas (CV) and (CVI), with R = COOH, are prepared from these esters by hydrolysis; and by treating these acids with thionyl chloride, the acid chlorides, R = COCl, are produced. It is by means of these acid chlorides that most of the pigments are prepared.

However, certain pigments require the use of intermediates prepared from the naphthoindolizinediones themselves. These compounds are easily obtained from the acids (R = COOH), decarboxylation being effected, for instance, at the boil in a mixture of acetic and hydrochloric acid. By nitration, naphthindolizinedione provides 12-nitronaphthindolizinedione (R = NO_2), which can be reduced with sodium sulfide to 12-aminonaphthindolizinedione (R = NH_2). The nitrated derivative can also be obtained by nitration of 12-acetylnaphthindolizinedione (R = $COCH_3$). As Pratt has shown, the last compound is accessible by the reaction of 2,3-dichloronaphthoquinone with pyridine and acetylacetone. Preparations of these intermediates are described in patents by Gy.[408]



(CV)



(CVI)

On the other hand, it should be noted that, in the preparation of intermediates, substituted derivatives of the basic materials can be used, to finish up with pigments carrying various substituents. According to a Gy patent,[409] 3-hydroxy or 3-aminopyridine is used. 2,3-Dichloro-1,4-naphthoquinone can carry at least one additional halogen atom, or an alkyl, alkoxy, nitro, or other group.

2. *Monoamides of Naphthindolizinedione Carboxylic Acids*

In 1957, CCC[410] patented pigments obtained by condensing the acid chloride of type (CV) with a nitroarylamine in *o*-dichlorobenzene at 140–145°. For example, with 2-chloro-4-nitroaniline, a red pigment (CVII) is obtained. A considerable number of pigments stemming from the same acid chloride, or its type (CVI) homolog, and a wide variety of aromatic monoamines, are described in several patents taken out by Gy since 1963.[411] It is also mentioned that these pigments can be obtained

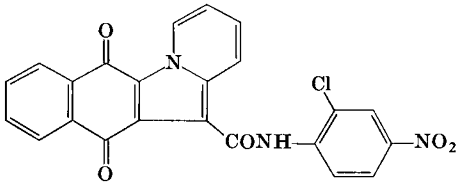
[408] Gy, *BP* 1,087,221; 1,087,222; 1,090,633; 1,090,635.

[409] Gy, *BP* 1,034,047.

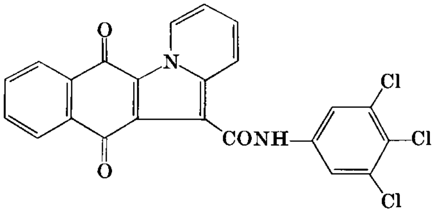
[410] CCC, *USP* 2,877,230.

[411] Gy, *FP* 1,419,702; 1,432,323; 1,442,370; 1,462,494; 1,462,495; *BP* 1,066,250; 1,076,482; 1,078,366; 1,082,045.

directly from the acid (R = COOH), by using phosphorus trichloride as a condensing agent; and that they can even be prepared by reacting together 2,3-dichloro-1,4-naphthoquinone, pyridine, or isoquinoline, and the corresponding acetoacetarylide.

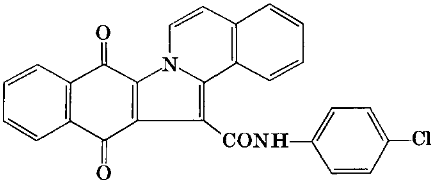


(CVII)

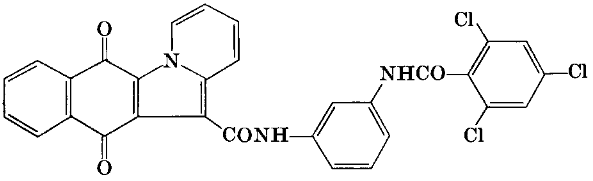


(CVIII)

It is interesting to note the choice of amines condensed with acid chlorides. In particular, 3,4,5-trichloroaniline gives the red pigment (CVIII), which is said to have exceptional fastness to light, heat and migration. Among the pigments of type (CVI), the orange of formula (CIX), derived from *p*-chloroaniline, is suitable for baking enamels, being very fast to heat and light. There are, moreover, many examples in Gy patents of pigments of types (CV) and (CVI) derived from aminobenzanilides or chlorinated benzoylphenylenediamines, such as the violet-red of formula (CX).



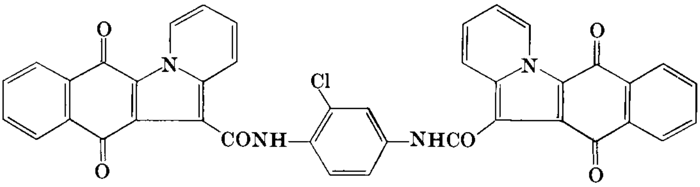
(CIX)



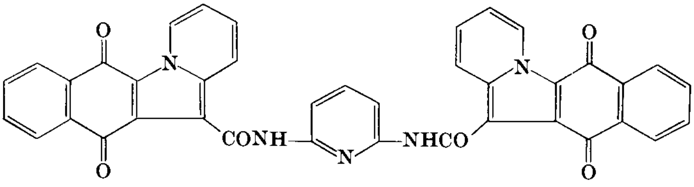
(CX)

3. *Bis(naphthindolizinedionecarboxamides)*

Pigments from "bis-phthaloylpyrrocoline" have also been envisaged. They result from condensation of 2 moles of acid chloride of type (CV) with 1 mole of a primary aromatic diamine. Several patents taken out by Ciba in 1959 described a large number of pigments of this kind, obtained from a wide variety of diamines.[412] Most often, condensation is carried out in *o*-dichlorobenzene at 140–145° in the presence of a little pyridine as an acid binding agent. The shade of the pigment formed varies from yellowish red to blue-violet, depending on the nature of the diamine used. Among the pigments described mention may be made of the bluish red (CXI) derived from 1,4-diamino-2-chlorobenzene. With 3,3′-dichlorobenzidine a yellowish red is obtained; with 3,3′-diaminodiphenylmethane, a ruby; and with 1,5-diaminonaphthalene, a violet. In general, these pigments have remarkable fastness to light and heat, and they do not migrate in PVC. The same applies to the red pigment (CXII), produced from 2,6-diaminopyridine and patented by Gy in 1962.[413]



(CXI)



(CXII)

4. *Other Naphthindolizinedione Pigments*

In 1963, Ciba[414] patented pigments containing also two naphthindolizine rings, but these nuclei are linked by one or two atoms of sulfur. If

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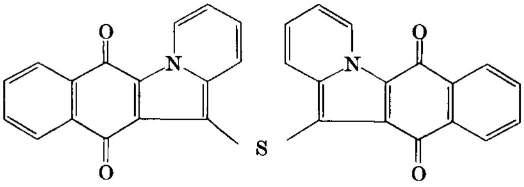
[412] CIBA, *FP* 1,274,843; 1,276,869; 1,278,216; 1,278,809.

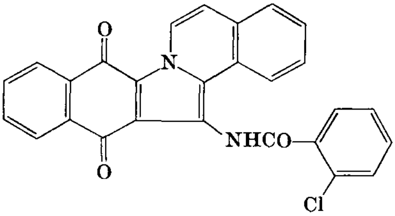
[413] Gy, *BP* 696,309.

[414] CIBA, *FP* 1,390,110.

naphthindolizinedione (CV; R = H), is treated between 90 and 120° with thionyl chloride in *o*-dichlorobenzene, in the presence of dimethylformamide, pigment (CXIII) is obtained, which colors PVC ruby. The same patent describes a red pigment prepared by treating benzonaphthindolizinedione (CVI; R = H) with sulfur chloride in *o*-dichlorobenzene at 85–100°. In this case, there is an –S—S– linkage between the two rings.



(CXIII)



(CXIV)

Acylaminonaphthindolizinedione pigments are described in a Gy patent of 1965.[415] They are obtained by acylation of compounds of formulas (CV) and (CVI) in which R = NH_2. For example, the type (CVI) aminonaphthindolizinedione is condensed with *o*-chlorobenzoyl chloride in *o*-dichlorobenzene under reflux. After salt milling, the red pigment (CXIV) can be used for stoving enamels and in synthetic polymers. An orange-yellow pigment was patented by Xerox Corp.[415a] Its formula is (CVI; R = CN) with a nitro group in the 12 position.

5. *Related Pigments: Dinaphthofurandiones*

In 1961, a series of pigments which show some analogy with those from naphthindolizinedione was the subject of a patent by Ciba.[416] They were derivatives of dinaphtho[2,1-*b*:2′,3′-*d*]furan-8,13-dione (CXV),

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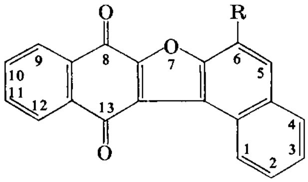
[415] Gy, *BP* 1,090,634.

[415a] Xerox Corp., *USP* 3,402,177.

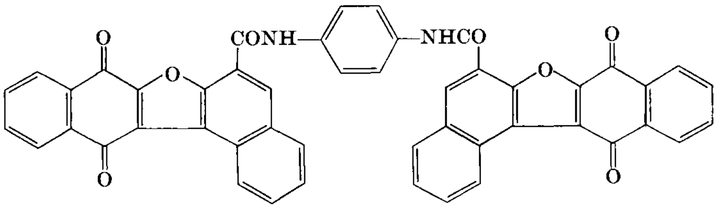
[416] CIBA, *BP* 959,147.

in which R = H. These pigments, which are also vat dyes, are diamides resulting from condensation of a diamine with 2 moles of 6-chloroformyldinaphthofuran-8,13-dione (CXV; R = COCl). This acid chloride is prepared by the following sequence of reactions: 2,3-Dichloro-1,4-naphthoquinone is condensed with ethyl 2-hydroxy-3-naphthoate by heating under reflux in pyridine, which produces 6-ethoxycarbonyldinaphthofuran-8,13-dione (CXV; R = COOEt). This ester is then hydrolyzed into the acid (CXV; R = COOH), and the acid is transformed into the chloride by treatment with hot thionyl chloride in *o*-dichlorobenzene.

The Ciba patent mentions a certain number of yellow, orange-brown, and red pigments obtained by condensing the acid chloride with various diamines. For example, the orange pigment (CXVI), fast to light and migration, is obtained with *p*-phenylenediamine.



(CXV)



(CXVI)

O. MISCELLANEOUS PIGMENTS

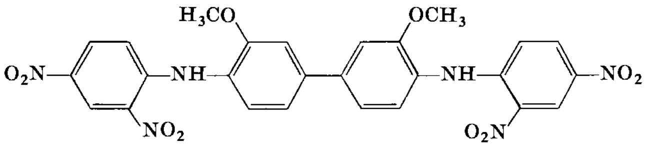
There are some pigments which cannot be classified in any of the foregoing sections, and which, from a chemical point of view, are unique of their type or belong to a series which is of too little importance to constitute an actual class. Some of these pigments are old and are still found in industry; others, on the contrary, are of recent discovery and it is not certain whether they will appear on the market.

1. *Nitro Pigments*

Compounds which have a nitro group as the sole chromophore are even more rare among pigments than among textile dyes. The oldest is the barium lake of 2,4-dinitro-1-naphthol-7-sulfonic acid, CI Acid Yellow 1, well known under the name of Naphthol Yellow S.[417] This lake is hardly used at all now, although it is faster to light than the dyed textiles.

At the beginning of this century, several yellow pigment dyestuffs were in use which were the products of condensation of nitroanilines with formaldehyde.[418] The most important was bis(4-chloro-2-nitrophenylamino)methane, CI Pigment Yellow 11, or Lithol Fast Yellow GG. It was still available on the market a few years ago, but is now obsolete.

It is, however, interesting to note that several nitro pigments have been patented by Ciba since 1959.[419] A reddish brown suitable for mass coloration of rayons has been put on the market: It is the product of condensation of dianisidine with 2 moles of 2,4-dinitrochlorobenzene (CXVII).[419a] Among other pigments, patents describe an orange obtained by condensation of dianisidine with 2 moles of 3-nitro-4-chlorobenzophenone, and a yellow which is the product of condensation of 2,5-diethoxy-1,4-diaminobenzene with 2 moles of 4-chloroformyl-2-nitro-4′-bromodiphenylamine.



(CXVII)

2. *Metal Chelates of Nitroso Dyes*

The principal representative of this series is the ferrous complex of 1-nitroso-2-naphthol, well known under the name of Pigment Green B.[420] It is CI Pigment Green 8, and it is still of commercial importance, although its production has greatly diminished (in the United States,

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[417] CSD I, p. 405.

[418] CSD I, p. 408.

[419] CIBA, *DBP* 1,143,483; *SP* 423,051; 428,045.

[419a] It is probably CI Pigment Brown 22.

[420] CSD I, pp. 402–403; J. Lenoir, *Peintures, Pigments, Vernis* **39**, 537 (1963).

810,000 pounds in 1951; 184,000 in 1965). This cheap pigment is of interest because of its very good fastness to light, alkalis, and most solvents. Long experience in its manufacture, which is delicate, has brought about an improvement in its shade. However, it is not very bright in comparison with the Phthalocyanine Greens, which tend to replace it in many applications.

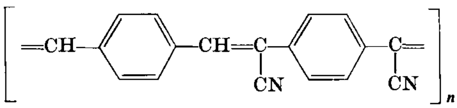
Other metal complexes of 1-nitroso-2-naphthol are known, but only the chrome complex is used, as a brown pigment. The yellow-brown nickel chelate was considered to be insufficiently fast to light. A new crystalline form of this pigment, which is fast to light, was discovered in 1964. Its preparation has been described in two patents by IMP.[421]

Some use is still made of CI Pigment Green 12, which is the barium lake of Naphthol Green (CI Acid Green 1), the ferrous complex of 1-nitroso-2-naphthol-6-sulfonic acid.

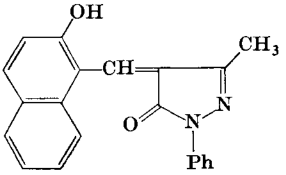
Metal chelates of 1-nitroso-2-hydroxy-3-naphtharylides and of isonitrosoacetoacetarylides are known,[422] but these products do not appear to have been exploited. Attention should, however, be drawn to a recent patent[423] which refers to the nickel complex of 2,3-dihydroxyiminobutyranilide (isonitrosoacetoacetanilide oxime).

3. *Methine Pigments*

No pigment of this series appears to have been put on the market, but some of them have been described in patents. An orange-red pigment of probable formula (CXVIII) is obtained by polycondensation of terephthalaldehyde with *p*-phenylenediacetonitrile; it is said to be very fast to heat and light.[424]



(CXVIII)



(CXIX)

According to a patent by G,[425] condensation of 2-hydroxy-1-naphthaldehyde with 1-phenyl-3-methyl-5-pyrazolone gives the reddish

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[421] IMP, *USP* 3,338,937; 3,338,938.

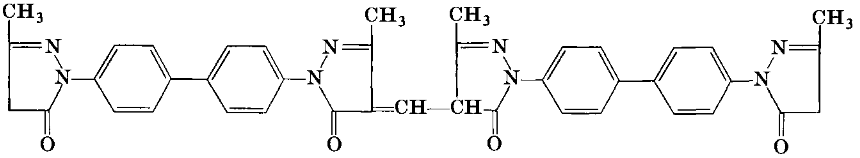
[422] CSD I, p. 404.

[423] BASF, *DBP* 1,252,341.

[424] Forschungsinstitut für Pigmente und Lacke, *DBP* 1,088,637.

[425] G, *USP* 2,739,963.

yellow pigment (CXIX). Other patents from the same source refer to yellow pigments of polypyrazolones.[426] For example, the pigment of formula (CXX) is prepared from the bis-pyrazolone derivative of benzidine. Treatment with formamide or with ethyl orthoformate provides a methine group which links two molecules of bis-pyrazolone.

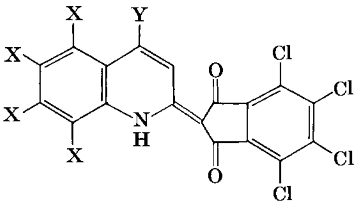


(CXX)

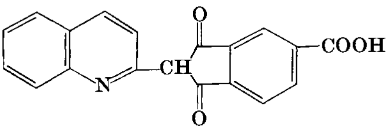
4. *Quinophthalones*

The barium lakes of Quinoline Yellows[427] have been appreciated for their brightness of shade. Today, CI Acid Yellow 3 (CI 47005) still figures among the ranges of dyes for lakes, but only for limited usage in this respect. However, the quinophthalone family, though few in number, has not been overlooked by research workers, as indicated by several patents concerning pigment dyestuffs.

A patent by Gy[428] refers to yellow to orange pigments of general formula (CXXI), which are fast to solvents, light, and heat. These are prepared by condensation of tetrachlorophthalic anhydride with substituted quinaldines, in which X may be halogen atoms, and Y = H, Ph, Me, or $CONH_2$. Red pigments which are bis-quinophthalone derivatives of pyromellitic acid were recently patented by S.[428a]



(CXXI)



(CXXII)

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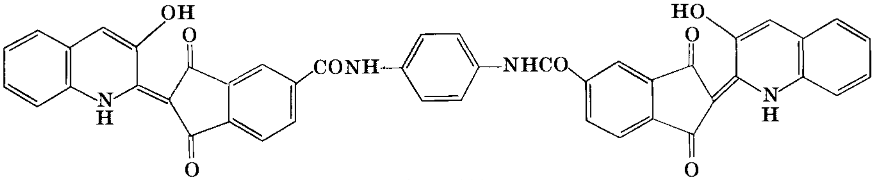
[426] G, *USP* 2,903,451; 2,903,452; 2,903,461; 2,903,462.

[427] CSD II, p. 1198.

[428] Gy, *FP* 1,523,982.

[428a] S, *SP* 463,667.

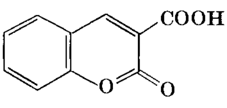
For mass coloration of polyester fibers, ICI patented[429] carboxyquinophthalone (CXXII), a greenish yellow pigment resulting from the condensation of quinaldine with trimellitic anhydride. According to a Ciba patent,[430] an analogous carboxyquinophthalone, but derived from 3-hydroxyquinaldine, is treated with thionyl chloride, then the resulting acid chloride (2 moles) is condensed in solvent medium with 1 mole of a diamine. For example, if the latter is *p*-phenylenediamine, the orange-yellow pigment (CXXIII) is produced, which is suitable for coloration of plastics and of synthetic fibers in the mass.



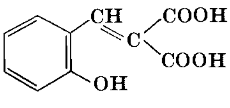
(CXXIII)

5. *Condensation Pigments*

The preceding patent shows the general method by which Ciba prepared several azo condensation pigments belonging to Classes A and E. Apart from these classes, it is also interesting to mention some derivatives of coumarin-3-carboxylic acid (CXXIV). This compound is transformed by alkaline hydrolysis into 2-hydroxy-α-carboxycinnamic acid (CXXV), which can be coupled, for instance, with diazotized 4-chloro-2-aminotoluene. After coupling, the lactone is reformed by heating with a strong acid. Finally, the resultant monoazo compound is converted into the acid chloride, 2 moles of which are condensed with a diamine to obtain a pigment fast to migration, the orange of formula (CXXVI).[431]



(CXXIV)



(CXXV)

According to another Ciba patent,[432] condensation pigments of a different type are obtained by reacting a diisocyanate with 2 moles of

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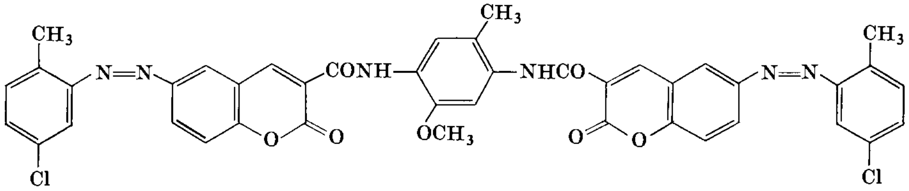
[429] ICI, *BeP* 678,479.

[430] CIBA, *SP* 438,542.

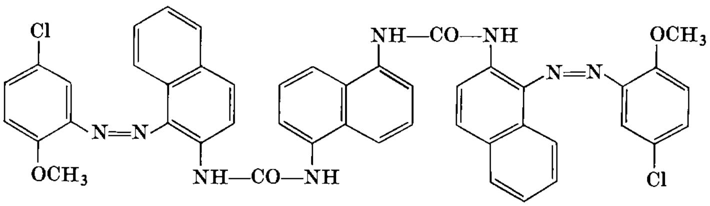
[431] CIBA, *USP* 3,127,390.

[432] CIBA, *USP* 2,988,544; see also condensation of similar aminoazo dyes with terephthaloyl chloride, Toyo Ink Man. & Daito Chem. Ind., *JP* 17,306('68); *CA* **69**, 97700p.



(CXXVI)

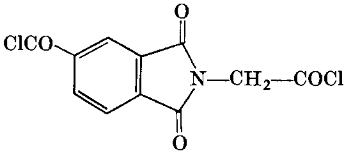
an aminoazo compound. For example, the reddish yellow pigment (CXXVII), fast to light and to migration in PVC, is obtained from the azo compound 4-chloro-2-amino-anisole → β-naphthylamine, by reaction with naphthalene-1,5-diisocyanate.



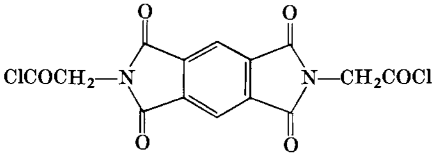
(CXXVII)

A recent patent by FBy mentions other pigments formed by condensation of a di- or triisocyanate with hydroxyazoic dyes or hydroxyanthraquinones.[433]

Some very general patents by BASF concern condensation pigments which contain trimellitamide or pyromellitamide groups.[434] These pigments are obtained by condensing 2 moles of an aminoanthraquinone or of an aminoazo compound with 1 mole of a biscarboxychloride such as (CXXVIII) or (CXXIX). For example, with 2 moles of 1-amino-5-benzamidoanthraquinone, (CXXIX) gives a reddish yellow pigment. In the same way, (CXXIX) gives a yellow pigment with 1-amino-anthraquinone.



(CXXVIII)



(CXXIX)

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[433] FBy, *DP* 67,15442; *BP* 1,141,654.

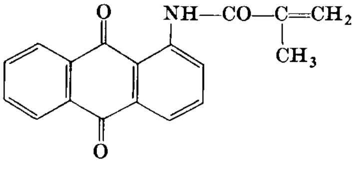
[434] BASF, *BP* 1,092,580; *FP* 1,462,105.

6. *Macromolecular Pigments*

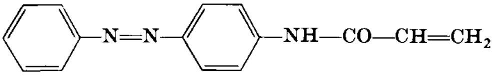
Condensation pigments have excellent fastness properties, which they owe partly to the amide linkages formed by condensation, but also to the fact that their molecules are larger than those of the classical pigments. The idea of making macromolecular pigments arose as a logical consequence of efforts directed at producing pigments of higher and higher molecular weight.

The first macromolecular azo compounds described in patents[435] were obtained by diazotizing a styrene copolymer, after amination by nitration followed by reduction, or more simply an aminostyrene polymer, and coupling, for instance, with resorcinol or salicylic acid. More recently, red azoic pigments have been prepared by using macromolecular coupling components with simple diazonium salts. For example, diazotized anthranilic acid is coupled with a novolak, then the azo compound formed is reticulated by reaction with formaldehyde.[436] According to a BASF patent, diazotized naphthionic acid is coupled with a copolymer formed from acrylic monomers, one of which is *m*-acryloylaminophenol.[437] Another patent uses the diazonium salt of 3-amino-4-methoxybenzamide, and a copolymer of acrylamide and 3-(2-hydroxy-3-naphthoyl)aminomethacrylanilide.[438]

Macromolecular pigments can also be obtained from polymerizable dye monomers. Thus, a yellow pigment is obtained by polymerization of 1-methacryloylaminoanthraquinone (CXXX).[439] It would seem to be more interesting, however, to copolymerize a dye monomer with a colorless monomer in preponderant amount. This is done, according to BASF patents, with azoic or anthraquinonoid monomers. For example, copolymerization of 4-acryloylaminoazobenzene (CXXXI) with methyl



(CXXX)



(CXXXI)

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[435] Kodak-Pathé, *FP* 864,407; Norsk Hydro-Elektrisk, *BP* 622,935.

[436] Continental Can, *USP* 3,267,064.

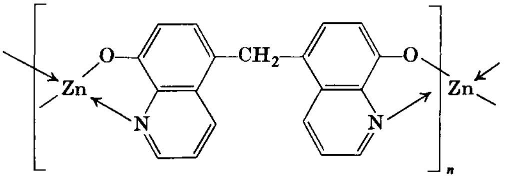
[437] BASF, *FP* 1,458,306.

[438] Dainichiseika Col. & Chem. Co., *BeP* 698,813.

[439] Tanabe Seiyaku Co., *BP* 1,036,700.

methacrylate gives a yellow pigment.[440] The copolymer can be reticulated if the dye monomer contains groups which are capable of condensation (e.g., hydroxymethyl groups).[441]

Metal-bearing macromolecular pigments have also been prepared. Some of them are copolymers analogous to the foregoing, in which the dye monomer has groups which are capable of forming complexes.[442] Thus, the dye 4-sulfamoyl-2-aminophenol → *N*-acryloyl-J-acid, after copolymerization and metallization with cobalt, gives a red pigment. Organometallic polymers of a very different type have been described; they are prepared from ligands derived from 8-hydroxyquinoline.[443] For example, the zinc complex of bis(8-hydroxy-5-quinolinyl)methane is a yellow linear polymer (CXXXII) of extraordinary stability to heat. On the other hand, green copper polyphthalocyanines have been prepared from pyromellitic anhydride.[444] Their stability is even superior to that of copper phthalocyanine; they have been suggested as semiconductors.



(CXXXII)

Copolymers of ill-defined composition, which can be used in inks as brown or black pigments, are obtained from mixtures of hydrocarbons, including olefins, dienes, cyclodienes, and aromatic hydrocarbons.[445] Polymerization is carried out under pressure at high temperature in the presence of a Friedel-Crafts catalyst and a dehydrogenating substance.

Macromolecular pigments can also be produced by polycondensation.[446] Certain patents concern dyes which are intended to be polycondensed with the components of polyester or polyamide fibers, in particular, tetracarboxyphthalocyanines.[447]

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[440] BASF, *BP* 877,402.

[441] BASF, *FP* 1,295,638.

[442] BASF, *FP* 1,410,229.

[443] E. Horowitz, *Mod. Plastics*, 146 (1967).

[444] Monsanto, *BP* 883,552; W. Drinkard and J. Bailar, *J. Am. Chem. Soc.* **81**, 4795 (1959).

[445] BASF, *BP* 1,020,839.

[446] See also Section II,L, formula (LXXIII); and Section II,O,3, formula (CXVIII).

[447] Alpine Chem. A.G., *FP* 1,492,938; ICI, *DP* 67,15541; 67,15542.

In 1963, FBy patented pigments which are very fast to solvents and heat, obtained by mixing with the components of an aminoplast or a phenoplast, water-soluble dyes which contain groups capable of reacting with formaldehyde.[448] These pigments are formed by condensing in an acid medium. Analogous pigments were patented by Ciba in 1959; they are made with dyes containing a diaminotriazinyl group, which are condensed with the components of a melamine resin or another aminoplast.[449]

Ciba also patented the use of water-soluble dyes containing a chlorotriazinyl group, which are condensed with an aminoplast in alkaline medium.[450] In effect, in this last case, it is a question of dyeing a colorless macromolecular compound with a reactive dye. A similar case is that of pigments formed by fixation of acid or basic dyes on ion-exchanging resins of opposite polarity.[451] Numerous other pigments in which only the substrate is macromolecular have been the subject of patents. These cannot properly be called macromolecular pigments, but lakes with an organic substrate. It is known that the fluorescent pigments of industry are lakes of this type.

7. *Miscellaneous Heterocyclic Pigments*

It remains to mention a certain number of pigments which do not in any way constitute a homogeneous group, having nothing in common except that they are heterocyclic. The oldest of these pigments is CI Pigment Black 1 (CI 50440), which is aniline black specially prepared in substance for pigmentary use.[452] It is known that this pigment is a complex azine whose structure is not perfectly understood. Since it is prepared by oxidation of aniline in acid solution with the help of dichromate in the presence of copper sulfate, it contains partly combined chromium and copper. It is difficult to get rid of these metals completely; they are nonetheless removed to a large extent by treatment with dilute sulfuric acid. Aniline black demetallized in this way (Pigment Black Conc.) has a much higher coloring power than the nondemetallized brands. However, the latter are more widespread on the market. There are also brands prepared from mixtures of aniline and *o*-toluidine or xylidine. In spite of their excellent fastness, the aniline blacks, which are practically the only black organic pigments, are much less used than Carbon Blacks.

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[448] FBy, *DBP* 1,271,856.

[449] CIBA, *FP* 1,257,930.

[450] CIBA, *DBP* 1,088,707.

[451] E. Redding, *USP* 3,216,948.

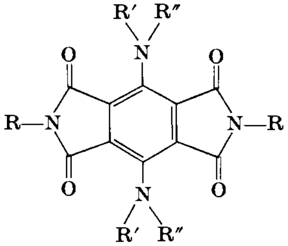
[452] CSD II, pp. 776–778.

CI Pigment Green 9, Hansa Green GS, now obsolete, was an iron complex of an ill-defined azinic compound, prepared from 1,2-diaminonaphthalene-5-sulfonic acid.[453]

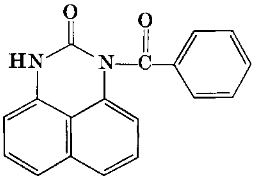
Azine pigments patented by HAR in 1966 are prepared by condensing 2 moles of 9,10-phenanthrenequinone with 1,2,4,5-tetraminobenzene (brick red) or with 2,3,7,8-tetraminophenazine (dark purple).[453a]

Other heterocyclic pigments worth mentioning are recently patented products, none of which appear to have been put on the market, at least up to now.

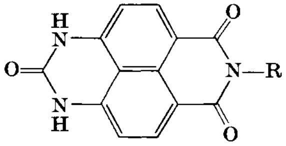
Blue and violet pigments patented by S in 1961 correspond to the general formula (CXXXIII), in which R, R′, and R″ are H, alkyl, or aryl.[454] These derivatives of 3,6-diaminopyromellitic acid are diimides, like the Perylene Reds,[455] but their molecules are much smaller. They would nevertheless be suitable for coloring PVC.



(CXXXIII)



(CXXXIV)



(CXXXV)

A greenish yellow pigment, very fast to light and presenting a certain analogy with the perinones,[456] is *N*-benzoylperimidone (CXXXIV). Its pigmentary conditioning, by salt milling and treatment with dimethylformamide, is described in a patent by BASF.[457] Other yellow pigments

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[453] CSD II, p. 1195.

[453a] HAR, *USP* 3,403,154.

[454] S, *SP* 419,166; 421,987.

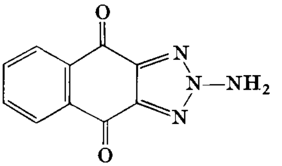
[455] See Section II,I,4.

[456] See Section II,I,5.

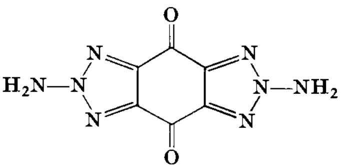
[457] BASF, *DBP* 1,164,977.

are the imides of perimidone-6,7-dicarboxylic acid. Their general formula is (CXXXV), with R = H, alkyl, or aryl. According to the BASF patent,[458] they are prepared from 4,5-diaminonaphthalic anhydride. Treatment with phosgene in solution in nitrobenzene gives perimidone-6,7-dicarboxylic anhydride, and this is finally converted into the imide by reaction with ammonia or an amine.

In 1963, CCC patented pigments which can be used in plastics: aminotriazolo-1,4-naphthoquinone yellow (CXXXVI) and bis(aminotriazolo)-1,4-benzoquinone orange (CXXXVII).[459] The second is prepared from chloranil by reaction with sodium azide in dimethylformamide, which gives 2,3,5,6-tetraazidobenzoquinone. By reaction with triphenylphosphine in methylene chloride, the latter forms a compound which hydrolyzes to give the pigment.

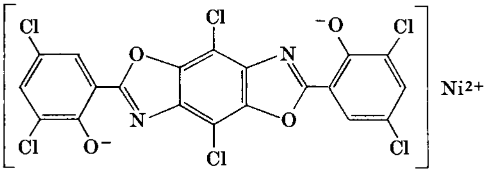


(CXXXVI)



(CXXXVII)

Metal complexes of bis-oxazoles, which can be used as yellow to red pigments, are described in a BASF patent.[460] For example, the yellow pigment (CXXXVIII) is obtained by condensing in solvent medium at 190°, 2,5-diamino-3,6-dichlorobenzoquinone with 2 moles of 3,5-dichlorosalicylaldehyde, and then metallizing with nickel acetate in dimethylformamide at 120°.



(CXXXVIII)

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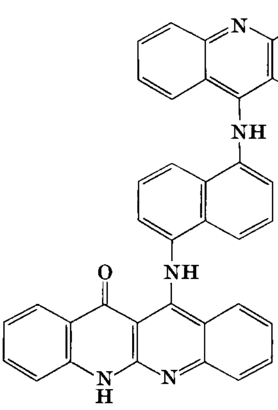
[458] BASF, *FP* 1,371,102; see also similar pigments: BASF, *DBP* 1,278,642; HAR *USP* 3,371,092.

[459] CCC, *USP* 3,198,795; 3,198,796.

[460] BASF, *FP* 1,464,325.

Another BASF patent concerns yellow to orange pigments, stable at high temperature, which are formed by condensation of a diamine with 2 moles of 11-chloro-12-hydroxydibenzonaphthyridine.[461] If, for instance, the diamine used is 1,5-diaminonaphthalene, then the yellow pigment (CXXXIX) is obtained; this does not migrate in PVC.



(CXXXIX)

III. Evaluation of Pigments

The evaluation of pigments includes a large number of tests the object of which is to determine the physical and technological properties of the pigments, and to assess their suitability for a specific application. These tests are necessary for the manufacturer and the user, and they have a special importance for the chemist who is looking for new pigments which are capable of meeting as yet unfulfilled requirements.

The tests may be divided into two categories:

(A) *Tests carried out directly on the pigments.* These are mainly physical tests of general interest, and their number is relatively limited. They are useful, but not in themselves sufficient, since the value of a pigment depends above all on its properties when it is incorporated in the various media in which it may be used.

(B) *Tests carried out on materials colored with pigments.* Some of these tests also involve physical measurements; most of them are tests of formulation in which the technological properties are checked. There is a very large—almost unlimited—number of these tests, because of the extraordinary variety of applications of pigments. New methods of

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[461] BASF, *DBP* 1,246,912.

application constantly invoke the need for new tests. It is not possible, therefore, to mention here all the tests carried out on pigmented materials. The most important concern shade, coloring power, dispersibility, and lightfastness—all qualities which cannot be ascertained on the pigments themselves.

A certain number of tests in both categories have been standardized in several countries (ASTM, DIN, BS, AFNOR, CEI, ISO). There are, indeed, special standards for certain pigments, this is the case for most mineral pigments, but only for the following few organic pigments: Copper Phthalocyanine Blue (ASTM D 963-65) and Toluidine Red and Para Reds (ASTM D 656-49, D 970-65T, D 475-49, D 475-50T).

A. TESTS ON THE PIGMENTS

The appearance of a pigment in lumps as it emerges from the drier, or in powder as it comes from the grinder, already provides the manufacturer with a certain amount of information regarding the success of his product. The friability of the pigment can be estimated by the "finger test," which consists in placing a little of the pigment on a paper and rubbing it with the fingertip, applying more or less pressure. An experienced operator can assess slight differences in texture (softness or hardness) and can even get a rough idea of the shade and brilliance of the pigment. Such observations can, however, only give rough indications as to whether manufacture, washing, and drying have been properly carried out. The tests which follow are more exact.

1. *Test for Fineness*

The state of division of the pigment is of paramount importance. Its effects on shade, coloring power, and hiding power, in particular, are well known. The particles of the pigment are not of uniform size, and it is sometimes of interest to determine the particle size distribution. However, the commonest test is screening, which provides little information on this point.

a. Screening. By screening it is at least possible to detect the presence of coarse particles and to determine their proportion in the pigment. These coarse particles are generally agglomerates resulting from insufficient grinding, and their presence is particularly harmful if the pigment has a hard texture. Sieves of varying degrees of fineness may be used, depending on requirements. Screening can be done dry, by rubbing lightly with a soft brush until no more pigment passes through. It is far preferable, however, to sieve under running water, as given in ASTM D 185-45 and AFNOR T 30-024 standards. According to ASTM, a 10-g sample of pigment is used in a 3-inch No. 325 sieve, under a tap which delivers 300 to 500 ml of water per minute. The operation is carried on, brushing lightly all the time, until the water is perfectly clear. Finally, the residue on the sieve is dried and weighed.

b. Particle size distribution. In practice, there is no sieve fine enough to carry out a complete particle size analysis, the actual particles of pigments having diameters below 10 and often even 1 μ. A recommended practice for reporting particle size characteristics of pigments is given by ASTM D 1366-65. The following characteristics are defined: specific surface diameter (average particle size by surface mean); coarseness parameter (diameter below which 99.5% of the pigment falls); dispersion parameter, calculated from the distribution curve. The principal methods of determination are by microscopy and by sedimentation.

The optical microscope has insufficient magnification for a complete size analysis of organic pigments. In principle, the electron microscope gives valid measurements, but the sample under observation is so small that it is hardly representative of the actual size distribution. Moreover, appreciation of the coalescence of the particles is difficult on the photographs which this instrument provides.

Analysis by gravitational sedimentation relies on Andreasen's method. A suspension of the pigment flows through a pipette; the samples of liquid are evaporated to dryness and weighed.[462] The drawback of this method is that it is virtually useless for particles below 2 μ.

A recently developed method is best suited for organic pigments: this is centrifugal sedimentation.[463] In particular, the ICI-Joyce Loebl disk centrifuge gives a size analysis for pigments of very fine particle size, ranging from 0.04 to 1 μ.[464] Casta's Microgranulometer[464a] applies to particles of 0.8 to 40 μ.

2. *Crystalline Form*

The crystalline form of pigments can be usefully examined by the electron microscope. As has been said, the possibilities of the optical microscope are limited. However, it is sometimes possible to check the form and color of the microcrystals of a pigment during its manufacture by using this instrument.

A useful additional method in evaluating polymorphous pigments is provided by an examination of their X-ray diffraction patterns. Thus,

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[462] H. Kittel, "Pigmente," p. 141. Wiss. Verlagsges., Stuttgart, 1960.

[463] D. Patterson, "Pigments, An Introduction to their Physical Chemistry," p. 105. Elsevier, Amsterdam, 1967.

[464] J. Beresford, *J. Oil Colour Chemists' Assoc.* **50**, 594 (1967).

[464a] L. Casta, *Rev. Geogr. Phys. Geol. Dynamique* **11**, 141 (1969). Casta's Microgranulometer is supplied by Soc. Brewer-Houlier, Paris.

with a Copper Phthalocyanine Blue containing both α and β forms, it is possible to estimate the proportion of each form.

3. *Specific Gravity*

Knowledge of the specific gravity is useful for establishing a formulation which involves a suspension of the pigment in a liquid vehicle. It is also useful in determining particle size, specific surface, and compactness. The specific gravity is determined by the well-known pycnometer method. The method of carrying out this test is described in detail in ASTM D 153-54. The immersion liquid used is kerosine, and it is essential that air occluded in the pigment should be carefully eliminated. This is done by evacuating, and the higher the degree of precision required, the greater must be the vacuum.

4. *Bulking Value*

The bulk density (sometimes called the apparent density) is the weight of pigment which can be lodged in a container of fixed capacity. It is generally expressed in kilograms per liter, or in pounds per gallon. Conversely, the bulking volume is the volume in liters occupied by 1 kg of pigment when filled normally. It can also be expressed in gallons per pound. Measurement is carried out by completely filling with the pigment a cylindrical container of known volume (e.g., 100 ml), without tamping down. The bulking value is calculated from the increase in weight of the container.

Knowledge of the bulking volume is useful for formulations. On the other hand, a high bulking volume (e.g., 4 liters/kg) is generally a good indication of the fineness and texture of the pigment. It has, however, the drawback that it requires bulky packaging. The bulking volume can be appreciably diminished, without impairing the quality of the pigment, by deaerating under vacuum.

It should be noted that, in addition to the bulking volume as defined above (German *Schüttvolumen*), the volume, obviously smaller, obtained after tamping down the pigment in the container, is sometimes determined (German *Stampfvolumen*, DIN 53194).

The compactness is the ratio, expressed in percent, of the bulk density to the specific gravity.

5. *Moisture Test*

A very small water content can profoundly modify the behavior of a pigment (dispersion, coloring power) in certain media. It is useful, therefore, first, to check the dryness of the pigment, and second, to determine the moisture uptake when it is exposed to a humid atmosphere.

According to ASTM D 1208-65, the water content is determine by placing 50 g of the pigment in 100 ml of toluene and distilling the mixture. The condensate is collected in a graduated receiving trap, where the water separates from the toluene; distillation is continued until there is no further increase in the volume of condensed water. From this volume, the water content of the pigment can easily be deduced.

According to ASTM D 280-33, the hygroscopic moisture is measured by the loss in weight of the pigment when held for 2 hours at 105–110°.

6. *Water-Soluble Matter*

Water-soluble materials which a pigment may contain are generally mineral salts (NaCl, Na_2SO_4) resulting from manufacture, the presence of which is an indication of insufficient washing. These salts have an adverse effect on the properties of the pigment, notably its texture. Other soluble matter may also be present: rosin or fatty acid soaps, surfactants, excess of raw materials, etc. The pigment rarely contains a water-soluble dye, which would show up in the water bleed. It should be noted, however, that on contact with water, lakes have a tendency to hydrolyze and bleed.

Soluble matter is determined by extraction with water, followed by evaporation to dryness. According to ASTM D 1208-65, extraction is done on 10 g of pigment in 100 ml of water at the boil for 5 minutes. The extract is diluted to 250 ml and filtered; 100 ml of the filtrate is evaporated to dryness in an oven at 125°. The water-soluble content is calculated from the weight of the residue.

7. *Ash*

Normally, pigment dyestuffs have a very low ash content, consisting of salts arising during manufacture. Metal complexes, toners, and especially lakes obviously contain more ash. Determination of the ash content is particularly useful in assessing the amount of extender in a pigment reduced with an inorganic extender.

The ash content is determined by calcining, e.g., 2 g of pigment, in a crucible and weighing the residue (ASTM D 970-65T, 1208-65).

8. *Bleeding Tests*

It is important to assess, by means of bleeding tests, the fastness of pigments to water, oil, solvents, and plasticizers, i.e., to determine whether they are insoluble or more or less soluble in these liquids (or if they contain a soluble colored impurity).

Routine tests, which are not standardized, consist in vigorously shaking a small quantity of the pigment with the liquid in a test tube, then allowing it to rest. When the pigment has completely settled out, the coloration of the liquid is assessed, and the fastness of the pigment is rated from 1 to 5 (1 = heavy bleeding; 5 = no coloration). If the pigment does not settle, or does so slowly, centrifuging is necessary. Some operators prefer to filter.

a. Water Bleed. The test is carried out either by shaking with water at room temperature, or by boiling for, say, 5 minutes. If filtration is to be done through a paper, this must be repeated several times until there are no longer any particles of pigment suspended in the filtrate. It should be noted that a pigment rendered very hydrophilic by the presence of a surfactant may give an appearance of heavy bleeding.

b. Solvent Bleed. This also is done at room temperature, or by heating to 100°, or to the boiling point of the solvent. If desirable, filtration can be carried out as in the above case. The solvents generally used for this test are ethanol, *n*-butanol, acetone or methyl ethyl ketone, *n*-butyl acetate, toluene or xylene, white spirit, solvent naphtha, trichloroethylene, Cellosolve, diethylene glycol, and NC solvents (mixtures commonly used for dissolving nitrocellulose, e.g., acetone + butyl acetate + Cellosolve + toluene).

c. Oil and Plasticizer Bleed. With these liquids, the tests cannot be carried out in the same way as for the preceding ones. With a spatula the pigment is rubbed on a glass plate with a small amount of the liquid to give a thick paste. This is then diluted with the same liquid to make it sufficiently fluid, and it is then spotted onto absorbent paper. The coloration of the oil (or plasticizer) halo is rated from 1 to 5 when compared with a spot of the same liquid alone. Extremely fine pigments may diffuse into the halo and make an evaluation difficult.

This test is mainly carried out with linseed oil, but it is also done with castor oil and oleic acid. For plasticizers, dioctyl phthalate, dibutyl phthalate, and tritolyl phosphate are used.

9. *pH Value*

A knowledge of the pH of a pigment (in actual fact, that of its aqueous extract) is useful for certain applications (paints, inks). The pH is particularly important for flushing, which is easier if the pH is above 6. In determining this property, the pigment/water ratio should not be too high, since the water extract is practically not buffered. The ratio generally adopted is 1/10.

ASTM D 1208-65 recommends an electrometric measurement, using freshly boiled distilled water (to remove carbon dioxide); 5 g of the pigment is shaken with 50 g of this water, and the pH is measured with a glass electrode at 25°. A colorimetric method, using a suitable indicator, is less to be recommended.

10. *Fastness to Acids and Alkalis*

These fastness properties are assessed by suspending at room temperature a certain quantity of the pigment in a dilute acid or alkaline solution. After standing for a sufficient time, say 2 hours, the change in shade and eventual bleeding are noted, and compared with a suspension in distilled water. The change and bleeding are rated from 1 to 5 (5 = no bleeding, no change). For the acid test, a 5% solution of hydrochloric acid is generally used. The alkaline solution is most frequently 1% caustic soda, though *Colour Index* indicates the use of a solution of 5% sodium carbonate, which is a less severe test. On the other hand, ASTM 970-65T indicates more severe conditions for tests on Para Red and Toluidine Red (3:5 HNO_3; 1:1 HCl; 100 g/liter NaOH).

In certain cases (pigments intended for lime paints), the fastness to lime is determined as follows: A dry ground mixture of the pigment with slaked lime is made into a suspension with water. The change in appearance of the pigment is assessed by comparison with a similar suspension in which the lime is replaced by natural barium sulfate.

11. *Oil Absorption*

Oil absorption is the minimum amount of oil necessary to wet out all the particles of a given weight of pigment, and so produce a stiff paste. It is generally expressed as grams of linseed oil required for 100 g of the pigment (BS 3483, 1962); or, pounds of oil for 100 lbs of pigment (ASTM D 281-31). It can also be expressed as milliliters of oil per 100 g of pigment (AFNOR T 30-022).

Oil absorption is an important characteristic of pigments, because of its relationship with particle size and wettability with organic liquids (organophilic properties). By its determination, an approximate idea can be obtained of the critical pigment volume concentration of a paint or an ink. If the oil uptake is too high, it may lead to excessive viscosity of the ink prepared from that pigment.

The most usual method of measuring the oil absorption is described in ASTM D 281-31. It is done by placing 1 g of dry pigment on a glass plate, and raw linseed oil (acid value 1 to 3) is run onto it, drop by drop, from a graduated burette. Each drop of oil is incorporated in the pigment by rubbing with a spatula. The test is terminated when the amount of oil used is exactly sufficient to produce a very stiff, putty-like paste. The number of milliliters used is read from the burette and multiplied by the specific gravity (0.93) to give the weight of linseed oil in relation to that of the pigment.

ASTM D 1483-60 describes another method for determining oil absorption. This is the Gardner-Coleman method, in which the oil is mixed with the pigment simply by stirring, without rubbing.

B. Tests on Pigmented Materials

The appearance of the pigment in presscake or powder form does not give any precise information as to the shade which it will impart to materials it is intended to color. The most essential tests to be carried out on these materials concern the evaluation of the color of the pigment and its coloring power.

1. *Colorimetric Characteristics*

The pigment can be made up into, say, an ink and a print made with that ink; then it would be possible to determine, by means of a recording spectrophotometer, the colorimetric characteristics: diffuse reflection spectrum, dominant wavelength, trichromatic coordinates of the system of the International Commission on Illumination, hue, value (lightness) and chroma (saturation) of the Munsell system, etc. These facts are given in the catalogs of pigment makers. They enable an ink manufacturer to produce a hue defined by reference to the standardized systems.

However, these precise determinations are not done in the ordinary course of evaluating pigments. In practice, simpler tests are regarded as adequate.

2. *Masstone, Tint, and Tinting Strength*

a. Masstone. The general method consists of dispersing the pigment in a vehicle, which may be linseed oil, a lithographic varnish, or a nitrocellulose lacquer. This produces a full-tone ink (or paint). A reduced ink is also prepared by mixing with the full-tone ink a white ink, which is a dispersion of a white pigment (which may be titanium dioxide, zinc oxide, or lithopone), in the same vehicle.

Preparation of these inks, with an oil, is described in ASTM D 387-60 (Standard method of test for mass color and tinting strength). The pigment and the vehicle are mixed in suitable proportions to give a consistency such that the paste "can just be thrown from the spatula by a gentle whipping motion of the hand." The ink is prepared by rubbing the mixture by hand on a glass plate, with a standard-type glass muller. Rubbing should be carried out under very exact conditions (several cycles of a fixed number of rubs, the paste being heaped together again with a spatula after each cycle). The same operation can be done, with advantage, using an automatic muller (Hoover Muller, Braive Muller), which consists of two glass disks, one of which is fixed, while the other rotates. The pressure on the plates is adjusted, and the number of rotations is recorded by a counting device.

The full-tone ink is applied with a spatula onto a metal or glass panel, or onto a sheet of bond paper. The mass color can then be observed. It is usual to compare this with an ink prepared in an identical manner, with a standard pigment, and applied on the panel alongside that of the pigment under test. This comparison provides information as to brilliance, possible bronzing, and degree of dispersion. The *mass color* is defined by ASTM (D 16-64) as follows: "The color, when viewed by reflected light, of a pigment-vehicle mixture of such thickness as to obscure completely the background. Sometimes called overtone or masstone."

However, Pratt[465] draws a distinction between *masstone*, "the heavy upper portion of the ink on the full-tone paper test," and *overtone*, "the lighter lower portion of the ink on the full-tone paper test examined directly."

b. Undertone. It is of interest also to evaluate the *undertone*, defined by Pratt as follows: "the overtone portion examined by transmitted light," and by ASTM: "the color of a thin layer of pigment-vehicle mixture applied on a white background." Comparison of the undertone of a pigment and of a standard pigment shows up slight differences in hue. On the other hand, if there is a big difference in color between the masstone and the undertone of the pigment, a considerable variation in print color will result from varying the film thickness.

c. Tint. Another evaluation, of still greater importance, is that of the *tint* of the pigment, which is defined by ASTM as "a color produced by the mixture of white pigment or paint in predominating amount with a colored pigment or paint, not white. The tint is, therefore, much lighter and much less saturated than the color itself." Tint is evaluated by examining the reduced ink, applied on a panel. In practice, the degree of reduction used varies between wide limits, from 5 to 200 of white pigment to 1 of the colored pigment. The amount of white pigment necessary is lower in the case of titanium dioxide than in that of zinc oxide. The tint of the pigment to be evaluated is compared with that of the standard applied alongside it, and at the same degree of reduction. This comparison may reveal slight differences of hue, cleanness, and strength.

d. Tinting Strength. The tinting strength of a pigment may be defined as its ability to color a dispersion of a white pigment. If the comparison

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[465] L. S. Pratt, "Chemistry and Physics of Organic Pigments," p. 269. Wiley, New York, 1947.

of the tint with that of the standard of the same reduction ratio reveals a difference of strength, it is necessary to repeat the comparison between the tints at different reduction ratios, until the two tints being compared appear to be equivalent in color strength. From this, it is possible to calculate the tinting strength, which is the ratio, expressed as a percentage, of the weight of the pigment to the weight of the standard, in equivalent reduced pastes.

Estimation of the tinting strength can only be exact if there is no difference in hue between the pigment under examination and the standard. The estimation is less reliable, the greater the difference in hue. It is, however, easier if the tints are compared at high reduction ratios.

Evaluations of masstone and tint in materials such as rubber and plastics obviously require different techniques. The pigment in powder form (or masterbatch) is incorporated in these materials in powerful mixers with heated cylinders. The tints are produced by adding a white pigment in suitable quantity. The principle of comparison remains the same.

3. *Ease of Grinding and Dispersibility*

It is important to evaluate the aptitude of pigments to disperse in the medium which they are intended to color. This property depends not only on the fineness of the particles and the friability of aggregates (texture softness); it also depends on the surface state of the particles (hydrophilic or organophilic) and on the nature of the medium to be colored.

To prepare paints and inks, dispersion of the pigment in varnish is obtained by grinding, similar to the method described in Section III,B,2. It can be done in a roll mill, a burr-stone mill, a ball mill, etc. It is desirable that the pigment should rapidly attain its maximum state of dispersion, so that the mechanical work of grinding may be as short as possible. The ease of grinding a pigment can be evaluated in two different ways.

The first method is based on the practice in the paint industry. It consists in following the progress of the fineness of dispersion in relation to the time of grinding. At varying intervals of time, the fineness is evaluated by means of a gauge (Hegman gauge or North gauge). The working principle of a fineness gauge is described in ASTM D 1210-64. The gauge is a block of steel containing a calibrated tapered groove. The paint is spread in this groove, then drawn down the length of it by means of a scraper. At some point along the groove, particles or agglomerates will become visible. A direct reading from the calibrated scale is made at this point.

A second method consists in following the development of color yield in the course of grinding. The tinting strengths attained after varying times of grinding are evaluated by comparison with that of a complete grinding, to which the value of 100 is given. The graph of tinting strength as a function of time of grinding can then be drawn; its form is very representative of the ease of grinding. This method, which is used notably in France, is more suitable than the first one for evaluating the dispersibility of organic pigments in vehicles.

It is also useful to assess dispersibility in plastics, especially in PVC. The pigment and PVC are mixed in a heated cylinder mixer at a fixed temperature, say 160°. The working time necessary to reach total dispersion can be gauged by direct visual observation; normally it will vary between 5 and 30 minutes.

Another more significant and more severe evaluation of dispersibility in PVC can be made by the following method: The pigment and the PVC are mixed in an extruder under the action of constant mechanical work. The extruded rod is then submitted to maximum mechanical work on a cylinder mixer. The dispersibility of the pigment is excellent if the extruded rod and the PVC sheet obtained after mixing are uniformly colored to the same depth. On the contrary, dispersibility is adjudged to be the poorer, the paler is the rod in comparison with the mixed sheet; it is particularly bad if there are deep spots on the rod.

4. *Stability of Dispersion*

It sometimes happens that pigments flocculate in paints which contain them. Moreover, certain pigments "crystallize," i.e., pass into another polymorphic modification, with the growth of crystals. Both flocculation and crystallization result in a loss of coloring power. The best known example is that of Copper Phthalocyanine Blue, α form, which crystallizes when it is dispersed in a vehicle containing aromatic hydrocarbons.[466]

ASTM D 963-65 describes two tests for evaluating (a) dispersion stability and (b) storage stability of a Copper Phthalocyanine Blue. The first is considered as being essentially a test for resistance to flocculation, while the second is said to be rather a test of resistance to crystallization. In effect, it is not possible to distinguish the part played by each phenomenon in the alteration observed. The principle of these tests, which are also valid for other pigments, is as follows. The Phthalocyanine Blue is dispersed in a vehicle based on alkyd resin and toluene, and a similar dispersion is prepared with titanium dioxide.

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[466] See Section II,H,1.

For test (a), suitable proportions of the two dispersions are mixed, and a portion of the tint obtained is immediately sprayed on to a panel. When the film has dried sufficiently to become tacky, a streak is rubbed gently on the panel with the finger. Thirty minutes later, another portion of the tint is poured onto a part of the previously sprayed panel. After drying for 2 hours at room temperature and baking for 1 hour at 105° the differences in strength between the sprayed portion and the rubbed and poured areas are noted. If the latter are deeper, then flocculation has occurred (the examination is done in comparison with a standard).

For test (b), a tint is also prepared, which is immediately sprayed onto a panel. The rest of the dispersion of Blue is held for 6 weeks at 50–60° in a tightly closed container. After cooling to room temperature, a fresh tint is prepared from this, and it is again sprayed. This gives an evaluation of the loss of tinting strength resulting from crystallization or flocculation.

5. *Hiding Power and Transparency*

The hiding power of a pigment is its aptitude for opacifying the medium in which it is dispersed. The pigment is said to be opaque if this aptitude is high, and transparent if it is low. In paints, opacity is desirable, but in other applications (inks, textiles colored in the mass) it is transparency which, on the contrary, is more often required.

According to ASTM (D 16-64), *hiding power* is "the ability of a paint, or paint material as used, to hide or obscure a surface to which it has been uniformly applied. When expressed numerically, it is generally in terms of the number of square feet over which a gallon of paint, or a pound of pigment, as used, can be uniformly spread to produce a specified contrast ratio." The term *covering power* is also used, but it "actually has no precise meaning." The terms equivalent to "hiding power" are, in French "pouvoir opacifiant," and in German "Deckvermögen."

The *contrast ratio*, which arises in evaluation of hiding power and transparency, is defined by ASTM as the "ratio of the reflectance of a dry paint film over a black substrate of 5% or less reflectance, to the reflectance of the same paint, equivalently applied and dried, over a substrate of 80% reflectance."

The hiding power of a pigment only has significance in a given binder at a given concentration. According to AFNOR T 30-001, it can be defined as the maximum area of a black and white surface which it is possible to cover uniformly with a unit weight of a pigment dispersed in that binder and at that concentration, so as to hide the contrast.

Evaluation of the hiding power of a pigment, therefore, implies that it is measured in the medium which it is used to color, at a known concentration. The relative dry hiding power of paints can be evaluated by comparison with a standard, according to the method described in ASTM D 344-39. Relative dry hiding power is quantitatively expressed in terms of the proportional spreading rate of paint required to produce the same contrast reduction as obtained with the paint chosen as standard. The method consists in applying fixed weights of the sample paint and of the standard paint to identical smooth-surfaced paper charts, having adjacent black and white areas. After drying the test surfaces, a visual examination is made to see whether the sample reveals a degree of contrast which is equal to, inferior to, or greater than that produced by the standard. If there is any divergence, the examination is repeated with different weights of standard paint. If the pigment concentration is the same in both paints, this test will show the relative hiding power of the sample pigment as against that of the standard. Measurement of the contrast ratio gives a good idea of the transparency of a paint or an ink. It is determined on a film of given thickness, with a reflectometer. Reflectances are measured on black and white backgrounds, and the ratio is established from this.

A very simple apparatus, the Pfund's Cryptometer, consisting of two glass plates enclosing a layer of paint in the form of an angle, gives a rapid measurement of the hiding power of a fresh paint.

6. *Fastness to Light*

The lightfastness of a pigment depends on the medium in which it is dispersed. Certain media have a protective effect, while others accelerate any change in shade. Determinations are carried out on paints, prints, pigmented plastic or rubber sheets, etc.

Evaluation of lightfastness is done by the well-known methods used for dyed textiles, by comparison with a standard scale—generally the 1–8 scale (BS 1006, AFNOR, G 07-011). There is also a 1–10 scale. Exposure is made to daylight under glass; it may take from several months to 1 year. If rapid information is required, an exposure of 100 to 500 hours is sufficient in an apparatus such as the Xenotest or the Fadeometer. The fastness values obtained in this way are, however, not always entirely reliable and may differ from those obtained by exposure to daylight.

Granted that lightfastness depends on depth of shade, it is necessary to carry out the test in masstone and especially in tints (at least two tints at different degrees of reduction). In general, with tints, fading is more rapid the higher the degree of reduction. Darkening is rarely observed on tints, but frequently on masstones. However, in the latter case, change of shade generally takes place only after long exposure.

For pigments used in exterior paints, notably in stoving enamels intended for automobile coachwork, exposure to light must be supplemented by an exposure to weathering in a suitably selected region.

7. *Fastness to Heat*

The resistance of pigments to heat assumes special importance when they are to be used for stoving enamels, inks for tin printing, plastics, and elastomers.

In paints and inks, tests are carried out at several depths of shade (generally three). The paints or inks are applied to metal panels, which are submitted to fixed temperatures in a hot air stove, for more or less prolonged periods of time. The most usual tests are done at three temperatures: 120, 150, and 180°. The times of stoving depend on the nature of the binder; they may be of the order of 15 minutes to 1 hour.

The fastness to heat can be defined by the highest temperature which the pigment will withstand without any change of shade or strength. In certain cases, it is evaluated on a 1–5 scale (5 = no change), compared with a control which is an unstoved panel.

For tin prints, steam sterilization tests are carried out in an autoclave at 120° and at 133°, for 1 hour.

For pigments used in rubber, tests are made for resistance to vulcanization in live steam, in an autoclave at 143° for 45 minutes. In this test, the sheet of pigmented rubber is covered with a calico cloth. Both the change in shade and the staining of the calico are observed and rated from 1 to 5.

For use in plastics, a test of 30 minutes at 170° is generally sufficient in the case of PVC. Resistance to higher temperatures, up to 280 or 300° for 15 minutes, is necessary in the case of polystyrene and of polyolefins. Any possible efflorescence is ascertained by wiping with a white cotton cloth.

8. *Fastness to Overspray*

Tests for overspray refer essentially to pigments intended for paints. They are, however, of general interest for the information which they provide regarding the resistance of a pigment to bleeding. They are, in fact, bleeding tests which are often more significant than those made on the pigment in powder form.

Under the heading "Bleeding of pigments" ASTM D 279-31 describes four tests for overspray, the first of which concerns pigments to be used in cellulose ester lacquers. A suitable amount of the pigment is rubbed up with dibutyl phthalate, using a spatula, to give a thick paste. This is stirred with the lacquer, and the paint obtained is applied to a panel, leaving a 2.5-cm margin of unpainted metal around the painted portion. After drying for 30 minutes, a coat of white paint is applied over the whole surface of the panel, just sufficient to hide the colored paint completely. It is allowed to dry for 24 hours, then the two sections of the panel are examined. If the color of the section containing the pigment under test does not match that of the adjoining area containing only the white lacquer, the pigment is reported as bleeding.

The tendency of a pigment to diffuse, or not, into the white paint depends both on the medium in which it is dispersed and on the nature of the binder of the white paint. Tests are always done on full tone or strong shade patterns.

Fastness to overspray is particularly important for baking enamels. In this case, three identical patterns are generally stoved before overspraying, at 110 or 120° for 30 to 45 minutes. They are then oversprayed with a white finish of similar composition, and finally stoved at 120, 150, and 180°, respectively. The fastness to overspray at the different temperatures is rated on a 1–5 scale (5 = no bleeding into the white enamel).

9. *Resistance to Migration*

Evaluation of migration can also be considered as a bleeding test. It is important to know the tendency to migrate of pigments intended (a) for elastomers; (b) for most plastics—polyvinyl chloride (especially if plasticized), polyolefins, cellulose acetate and acetobutyrate, and polyurethane.

a. Test for Rubber. Before vulcanization a sheet of rubber colored with the pigment under test and a sheet pigmented with white are placed in contact. This assembly is then placed in a stove at 80° for 24 hours. Migration of the pigment into the white rubber is rated on a 1–5 scale.

b. Test for PVC. According to AFNOR 51-028, a mixture composed of 100 parts PVC, 65 parts of dioctyl phthalate, and 1 part calcium stearate is colored with 1 part of pigment. The sheet obtained from this is placed in contact for 72 hours at 70°, in a ventilated stove, with an identical unpigmented sheet, or better, one pigmented with 1 part of titanium dioxide. Migration into the latter is rated from 1 to 5 (5 = no migration).

Another test is used by PVC printers. It consists of making a print on a sheet of PVC pigmented with white. The ink used consists of the pigment under test, polyvinyl acetochloride, and a ketonic solvent. After stoving for 15 minutes at 170–175°, the transmigration of the color on the back of the sheet is evaluated.

10. *Various Tests for Resistance*

These are further tests for bleeding or for resistance to chemical agents. Among these very varied tests, it is interesting to mention those which are made on rubber and on prints for wrappers. In the case of ratings for staining, on the 1–5 scale, the depth of the staining can be evaluated by comparison with a gray scale (AFNOR G 07-012).

a. Tests for Rubber. Fastness to water and alcohol are evaluated by immersing 1 g of pigmented rubber in 10 ml of the liquid for 24 hours at room temperature. A similar test is done with benzene, but after 5 minutes immersion only.

Fastness to alkalis is assessed after treating for 30 minutes in a boiling 2% solution of caustic soda. Fastness to soap is determined by rubbing the sample of pigmented rubber with a wad of white cotton impregnated with soapy water (evaluate the coloration on the wad).

b. Tests for Inks Intended for Wrappers. The following tests are standardized in Europe (CEI). Several of these tests consist in pressing the print between two sheets of absorbent paper impregnated with water or with an aqueous solution for 24 hours. In this way, tests are carried out for fastness to water (CEI 03-59); to alkalis, with a 2.5% solution of caustic soda (CEI-05-59); to soap, with a 1% solution of a standard soap (CEI 06-59); to detergents, with a 1% solution of a detergent (CEI 07-59). After drying, the coloration of the absorbent paper which was in contact with the printed face is evaluated.

Tests for fastness to solvents (CEI 04-59) are done by immersion of the print for 5 minutes. The solvents used are, notably, ethanol, and a mixture of *n*-butyl acetate, toluene, and *n*-butanol. Fastness to waxes and paraffins are assessed after immersing for 5 minutes in the molten substance at 80° (CEI 10-60).

Finally, tests are also made for contact with foodstuffs: for cheeses, contact of the print with the rind and with a freshly cut slice (CEI 08-60); for fats and oils used in food, contact of the printed face with a sheet of absorbent paper impregnated with the oil or melted fat (CEI 09-60).

CHAPTER VII

HAIR DYES

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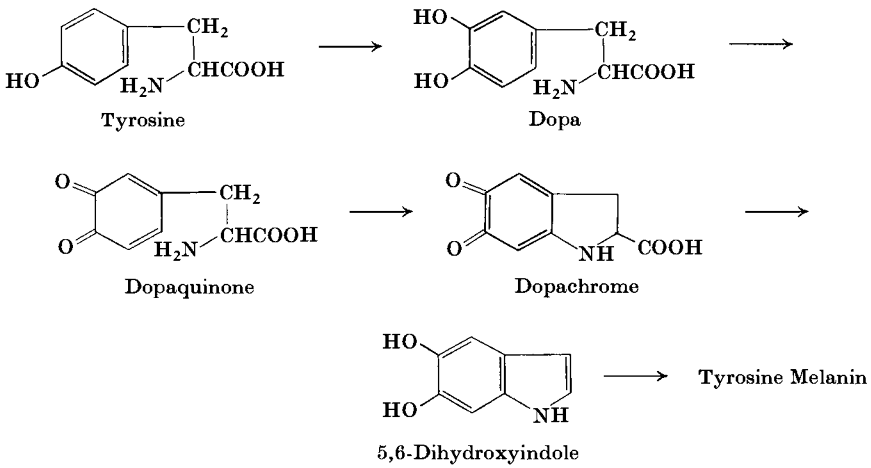
I. Introduction

The natural color of human hair ranges from the lightest blonde (albino) to jet black, embracing a wide variety of brown shades, and through various shades of red. All brown-black–pigmented hair derives its color from a single pigment–melanin. Variations in shade arise from variations in concentration of the pigment and, more important, from the size and physical distribution of the melanin granules within the hair shaft.[1] A method for the instrumental measurement and classification of natural hair color has been described by Den Beste and Moyer.[2] Despite considerable interest in the chemical structure of melanin,[3] the final stages of its formation and the ultimate structure of the polymeric pigment have still to be elucidated. The initial stages of melanogenesis, starting from tyrosine, are shown in Chart 1. This scheme was originally proposed by Raper[4] and is still generally accepted.[5] Natural red hair is reported[6] to owe its color to a red, iron-containing pigment, which has been named trichosiderin.[7] While tryptophan has been suggested as a precursor of this pigment, recent work suggests that it is a metalloprotein.[8]

CHART 1
Early Stages of Melanogenesis



Dissatisfaction with the natural color of hair appears to have existed from early times and artificial coloring has been practiced for over 2500

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[1] J. M. Schopping and J. K. H. van Sluis, *Perfumery and Essent. Oil Record* **51**, 181 (1960).

[2] M. Den Beste and A. Moyer, *J. Soc. Cosmetic Chemists* **19**, 595 (1968).

[3] R. A. Nicolaus and M. Piattelli, *J. Polymer Sci.* **58**, 1133 (1962), and refs. therein.

[4] H. S. Raper, *Biochem. J.* **21**, 89 (1927); W. L. Dulière and H. S. Raper, *ibid* **24**, 239 (1930); R. D. H. Head and H. S. Raper, *ibid* **27**, 36 (1933).

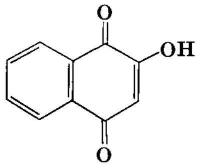
[5] R. H. Thomson, "Chemistry of Natural and Synthetic Colouring Matters, and Related Fields" (T. S. Gore, B. S. Joski, S. V. Sunthankar, and B. D. Tilak, eds.), p. 99. Academic Press, New York, 1962.

[6] H. C. Sorby, *J. Anthrapol. Inst. G.B.* **8**, 1 (1878).

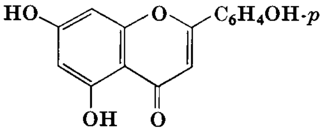
[7] S. Rothman and P. Flesch, *Proc. Soc. Exptl. Biol. Med.* **53**, 134 (1943).

[8] P. Flesch, E. J. Esoda, and S. A. Katz, *J. Soc. Cosmetic Chemists* **11**, 777 (1967).

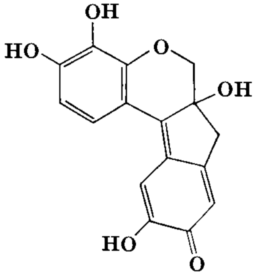
years.[9, 10] Prior to the introduction of synthetic dyes, plant extracts such as henna, camomile, logwood, and nutgalls were used. The active constituents of these materials are, respectively, 2-hydroxy-1,4-naphthoquinone (I); 4′,5,7-trihydroxyflavone (II); hematin (III); and pyrogallol.



(I)
CI 75480



(II)
CI 75580



(III)
CI 75290

Despite the emotive appeal of "natural," as opposed to "synthetic" dyes for use on the human head, the latter have become increasingly important over the last fifty years and now completely dominate the market. The increasing social acceptance of hair dyeing during the present century is reflected in the sales of hair color products in the United States, which reached 100 million dollars in 1966.[11] The response of the industry to the increasing market can be seen from the numbers of hair color patents issued during various periods (Table I).

TABLE I

World Issue of Hair Color Patents 1883–1966

Period	*1883–1930*	*1930–49*	*1950–59*	*1960–65*	*1966*
No. of patents[a]	85	48	50	47	31
Average per year	2	2.5	5	8	31

[a] Convention filings are not included.

Examination of these patents reveals that during the period 1883–1950 the emphasis was mainly on the oxidative dye systems. During the period 1950–60, autoxidative dyes became evident and, in addition, a number of patents dealt with processes for the application of textile dyes

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[9] F. E. Wall, "Cosmetics—Science and Technology" (E. Sagarin, ed.), p. 479. Wiley (Interscience), New York, 1957.

[10] G. R. Hughes, *J. Soc. Cosmetic Chemists* **10**, 159 (1959).

[11] A. Rostenberg and G. S. Kass, *Soap, Perfumery Cosmetics* **39**, 45 (1966).

to human hair. From 1960, an increasing number of patents have appeared which claim direct dyes—particularly nitro dyes and anthraquinone dyes—specifically for use on human hair. These various aspects of synthetic hair dyes will be discussed in the following sections of this chapter.

Before progressing to a detailed discussion of the synthetic dyes, mention should be made of the specifications for a good hair dye.[12] The coloration of the fiber should be achievable in a short time (10–30 minutes), at ambient temperature and without injury to the hair shaft or to the skin. In addition the dyes should impart a natural appearance to the hair and should produce a minimum of scalp staining. The necessity for dyeing at low temperatures, from a short dyebath (about 2:1), is in marked contrast with normal wool-dyeing practice. Furthermore, diffusion of material into human hair is considerably slower than diffusion into wool under identical conditions.[13] In view of these contrasts, it is not surprising that attempts to use textile (particularly wool) dyes in hair color products have met with little success. It is generally found that low molecular weight dyes give the most satisfactory results and it is for this reason that oxidative, autoxidative and nitro dyes have received considerable attention. Wilmsmann[14] has shown that rapid diffusion into hair keratin only occurs with molecules having an effective diameter of less than 6 Å. Similarly, Holmes[15] found that, while dyes with an effective diameter of less than 6 Å diffused rapidly in water-swollen hair, dyes of effective diameter greater than 10 Å diffused very slowly. *p*-Phenylenediamine (4.7 Å) and other benzoid derivatives are thus able to diffuse rapidly, as are naphthalene derivatives and substituted diphenylamines. Simple anthraquinone derivatives are probably the largest molecules for which the diffusion rate is sufficiently high for dyeing in a short time at ambient temperatures. Holmes also showed that diffusion into bleached or waved hair is faster than diffusion into virgin hair.

II. Oxidative Hair Dyes

A. GENERAL

Dyeing of hair with oxidative dyes involves essentially an in fiber synthesis of the colored species and is analogous to fur-dyeing practice.

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[12] R. G. Harry, "Modern Cosmetology," Vol. I, p. 482. Leonard Hill, London, 1955; D. L. Underwood, *J. Soc. Cosmetic Chemists* **12**, 155 (1961).

[13] J. Menkart, L. J. Wolfram, and I. Mao, *J. Soc. Cosmetic Chemists* **17**, 769 (1966).

[14] H. Wilmsmann, *ibid* **12**, 490 (1961).

[15] A. W. Holmes, *ibid* **15**, 595 (1964); *Proc. 3rd Intern. Wool. Textile Res. Conf. Paris, 1965, Vol. III*, p. 79.

Most compositions contain three types of reactive species: (i) the dye intermediates[16a] or primary intermediates[16b]; (ii) the color coupler or modifier[16]; (iii) the oxidizer.

The primary intermediates are normally *o*- or *p*-diamines and *o*- or *p*-aminophenols, which produce colors when oxidized by the oxidizer. The couplers may be *m*-diamines, *m*-aminophenols, phenols, pyrazolones, or β-diketones; these do not produce any color when oxidized alone, but form dyes when oxidized in the presence of a primary intermediate. The oxidizer is normally hydrogen peroxide, although other oxidizers such as persulfate,[17] perborate,[18] urea peroxide,[19] dichromate,[20] chlorate,[19] oxygen/vanadate,[20] ozone,[21] chloramines,[22] and aminotriazineperhydrates[23] have been suggested. In addition, the commercial dye products contain other components such as stabilizers, detergents, and pH adjusters (the process is usually performed at pH 9–10), discussion of which is outside the scope of the present review; interested readers are referred to a number of review articles[24] and to recent hair dye patents for further information on these aspects. Many compositions also include direct dyes—particularly nitro dyes—which do not participate in the chemical color-forming reactions but are included for their tonal effect.

The coloring power of *p*-phenylenediamine, on oxidation, was first noted by Hofmann,[25] in 1863, and the first patent for its exploitation as a hair dye was taken out by Monnet,[20] in 1883. According to this patent, hair is dyed to brown shades by immersion in a solution of the diamine or of 2,5-toluenediamine, and hydrogen peroxide or other oxidizing agent. This can be regarded as the foundation stone of the modern

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[16] This terminology was introduced by (a) F. E. Wall, ref. 9, pp. 503–505, and (b) G. S. Kass and L. Hoehn (*J. Soc. Cosmetic Chemists* **12**, 146, 1961). The terms (i) "developer" and (ii) "coupler" could also be used, in view of the close chemical similarity between oxidative hair dyeing and the color photography process, in which these terms are standard (see Chapter VI, Volume IV).

[17] *FP* 460,566.

[18] Rule, *BP* 200,375.

[19] F. E. Wall, "Cosmetics—Science and Technology" (E. Sagarin, ed.), p. 507. Wiley (Interscience), New York, 1957.

[20] P. Monnet, *FP* 158,558.

[21] P. Monnet, *FP* 482,012.

[22] Schwarzkopf, *SAfr.P* 61/937.

[23] Therachemie, *BP* 896,197.

[24] F. Winter, *Am. Perfumer Essent. Oil Rev.* **63**, 418 (1948); idem, *ibid* **64**, 138 and 213 (1949); R. L. Goldemberg, *J. Soc. Cosmetic Chemists* **2**, 291 (1948); G. S. Kass, *Am. Perfumer Aromat.* **71**, 25 and 47 (1956); R. Heilingotter, *ibid* **75**, 19 (1960); R. L. Goldenberg and H. H. Tucker, *J. Soc. Cosmetic Chemists* **19**, 423 (1968).

[25] A. W. Hofmann, *Jahr. Chem.* 42 (1863).

oxidative dye system and was further elaborated in a series of patents[26] granted to H. and E. Erdmann in the period 1888–1897. The Erdmann patents added *p*-aminophenol, 2,4-diaminophenol, 2,3,6-triaminophenol, some *N*-substituted derivatives of *p*-phenylenediamine and *p*-aminophenol, and 1,5-dihydroxy and 1,5-diaminonaphthalene to the list of oxidation bases. During the next 30 years, more than 150 further compounds were claimed in over 75 patents. A full list of the bases patented during this period is given in a review by Charle and Sag.[27] It must be pointed out that many of these early patents were held by textile dye companies and were concerned, primarily, with the dyeing of furs and pelts rather than with on-head application to human hair. The oxidation bases included, in addition to those mentioned above, derivatives of *o*-aminophenol, *m*-phenylenediamine, dihydroxybenzenes, 4,4′-diaminodiphenylamine, and a variety of polyhydroxy and polyamino naphthalenes and aminonaphthols.

In the period since 1930, almost 100 patents have been granted in the area of oxidative dyes. The majority of these patents have been concerned with compositions, using previously claimed dye precursors, and many of the remainder claim only minor variants of the earlier compounds. Among these, a number of patents[28] claim the use of *C*-alkylated and *C*-alkoxylated derivatives of phenylenediamines and aminophenols.

A recent patent[29] deals with a method for dyeing hair which is essentially an application of the color photography process to hair. Thus, an *N*,*N*-dialkyl-*p*-phenylenediamine is used in conjunction with phenols, 1,3-diketones, and/or pyrazolones, and the color is developed by the use of hydrogen peroxide.

Recently, Lange[30a] has introduced a new class of oxidation dyes based on amino and hydroxy derivatives of pyridine and quinoline. Few heterocyclic compounds had been claimed in the earlier art. Other heterocyclic compounds have now been found useful both as primary intermediates and as couplers. Thus, 4-amino-3-pyrazolone produces colored species on peroxide oxidation in the presence of conventional couplers.[30b] On the other hand, 5-amino- and 5-hydroxy-3-pyrazolones

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[26] H. Erdmann and E. Erdmann, *DRP* 47,349; 51,073; 80,814; 92,006; 98,431.

[27] R. Charle and G. Sag, *Manufacturing Chemist Aerosol News* 33 (1967).

[28] Schwarzkopf, *DRP* 1,145,746, *BP* 1,015,022; Wella, *USP* 3,216,899; Interpal, *BP* 983,207; L'Oreal *BP* 1,079,553; Therachemie, *Can. P* 812,216.

[29] L'Oreal, *BP* 1,025,916.

[30a] F. W. Lange, *Fette, Seifen Anstrichmittel* **67**, 222 (1965); *Arch. Biochim. Cosmet.* **9**, 185 (1966); *Am. Perfumer and Cosmetics* **80**, 33 (1965); R. Heald, Schimmel Briefs No. 377 (1966); K. Bergwein, *Ruchstoffe, Aromen, Korperpflegemittel* **136** (1967).

[30b] Therachemie, *BP* 1,146,061.

can be used as couplers in conjunction with *p*-diamines, *p*-aminophenols, or 4-amino-3-pyrazolone.[30c]

B. COLORS PRODUCED IN OXIDATIVE DYEING

1. *Benzene Derivatives*

The popularity of oxidative dyes owes much to their ability to produce natural shades. The brownish colors are produced by oxidation of the primary intermediates alone and these can be modified by the presence of a coupler.[31–33] The colors produced by the more commercially important primary intermediates, when oxidized on hair with 3% hydrogen peroxide at pH 9.7, are given, together with references to the original patents, in Table II. While numerous other dyes of this type have been examined, it appears that all those derivatives which do not contain other amino or hydroxy substituents give colors similar to those of the simple precursor, although the depth of shade is usually weaker.[34]

In practice, most dye compositions contain an excess of the primary intermediate together with a lesser amount of various couplers. The couplers serve to add the desired nuance to the shade. In order to give an appreciation of the coloristic function of the various couplers, the colors given in Table III are for dyeings produced in the presence of an equimolar amount or even excess of coupler.

Inspection of Table III shows that the couplers can be grouped into classes which are based both on coupler structure and coloristic effect. Thus *m*-diamines produce blue or purple shades, monohydric phenols produce purple shades, dihydric phenols and *m*-aminophenols having no substituent para to the amino group result in a light brown dyeing, pyrazolones and *m*-aminophenols with a methyl group para to the amino group produce magenta dyes, and β-diketones give yellow dyes. Although many other couplers are reported in the patent literature, there are no notable exceptions to these generalizations. Recent patents indicate that *N*,*N*-disubstituted[29] and *C*-alkylated *p*-phenylenediamines[35] give colors with the various types of couplers similar to those given by the parent compound.

Colors given by *p*-aminophenol with various couplers are given in

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[30c] Therachemie, *SAfr.P* 68/2753.

[31] G. S. Kass, *Am. Perfumer Aromat.* **71**, 35 (1956).

[32] G. S. Kass and L. Hoehn, *J. Soc. Cosmetic Chemists* **12**, 146 (1961).

[33] H. H. Tucker, *ibid* **18**, 609 (1967).

[34] R. Heilingotter, *Am. Perfumer Essent. Oil Rev.* **69**, 345 (1954).

[35] L'Oreal, *BP* 1,079,553.

TABLE II

COLORS PRODUCED BY PRIMARY INTERMEDIATES

Compound	*Color on hair*	*References*[a]
p-Phenylenediamine	Dark brown	1
p-Tolylenediamine	Light reddish brown	1
p-Aminodiphenylamine	Dark gray-black	2
4,4′-Diaminodiphenylamine	Gray-red	3
p-Aminophenol	Light auburn	4
2-Amino-5-hydroxytoluene	Golden blond	5
5-Amino-2-hydroxytoluene	Reddish blond	5
N-Methyl-*p*-aminophenol	Pale blond	5
Hydroquinone	Golden brown	6
2,4-Diaminodiphenylamine	Violet-brown	7
o-Phenylenediamine	Orange-gold	8
3,4-Diaminotoluene	Blond	8
o-Aminophenol	Deep gold	9
Catechol	Dark gray	10
Pyrogallol	Deep gold	11

[a] Key to references:

1. P. Monnet, *FP* 158,558.
2. H. and E. Erdmann, *DRP* 92,006.
3. *Idem. DRP* 98,431.
4. *Idem. DRP* 47,349.
5. *Idem. DRP* 80,814.
6. *Idem. DRP* 51,073.
7. Silver Springs Bleaching and Dyeing Co. *BP* 270,075.
8. Farbwerke Hoechst, *DRP* 293,581.
9. A.-G. Anilin-Fabrik, *DRP* 103,505.
10. *Idem. DRP* 276,761.
11. Bertram, *DRP* 255,858.

Table IV. The resulting dyes, particularly those with *m*-diamines, suffer from the disadvantage of being pH-sensitive over the whole of the pH range 6–12.[36]

Table V gives the colors produced using *p*-aminodiphenylamine as the primary intermediate. It will be seen that this *p*-diamine produces rather darker shades than does *p*-phenylenediamine.

While numerous naphthalene derivatives have been claimed in patents,[27, 37] both as primary intermediates and as couplers, they do not appear to have achieved commercial importance. In the case of amino derivatives of naphthalene, the well-known carcinogenicity of some

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[36] E. Konrad, *Parfuem. Kosmetik* 48, 32 (1967); J. F. Corbett, *J. Chem. Soc. B* 823 (1969).

[37] Therachemie, *BP* 1,023,327.

TABLE III

COLORS PRODUCED BY *p*-PHENYLENEDIAMINE IN THE PRESENCE OF VARIOUS COUPLERS

Coupler	*Color on hair*	*References*[a]
None	Dark brown	—
m-Phenylenediamine	Bluish purple	1
2,4-Diaminotoluene	Bluish purple	1
2,4-Diaminoanisole	Purple-blue	2
m-Aminophenol	Light brown	3
4-Methyl-3-aminophenol	Light brown	4
α-Naphthol	Bluish purple	4
m-Methoxyphenol	Magenta	4
6-Methyl-3-aminophenol	Magenta	5
2,5-Xylenol	Bluish purple	6
2,6-Xylenol	Bluish purple	6
1-Phenyl-3-methylpyrazolone	Magenta	6
Acetoacetic ester	Yellow	6
Resorcinol	Greenish brown	7
Hydroquinone	Light gray-brown	8
Catechol	Gray-brown	9

[a] References in this table are to the original patent for the use of the coupler and not necessarily to statements of the color produced under these conditions.

1. A.-G. Anilin-Fabrik, *DRP* 255,858.
2. Farbwerke Hoechst, *DRP* 228,245.
3. Schmid, *DRP* 210,643.
4. J. F. Corbett, unpublished work.
5. Schwarzkopf, *BP* 973,599.
6. L'Oreal, *BP* 1,025,916.
7. Farbwerke Meister, Lucius, and Brunig, *DRP* 162,625.
8. IG, *DRP* 51,073.
9. A.-G. Anilin-Fabrik, *DRP* 276,761.

compounds indicates the need for extensive long-term testing of such derivatives. Benzidine derivatives, which also produce good dyeings,[38] may well suffer from the same disadvantage.

2. HETEROCYCLIC COMPOUNDS

Oxidative dyes based on pyridine derivatives have been reported to produce less sensitization and more stable colors than those based on benzene derivatives.[30a] The colors given by some typical dyes mentioned in the patent literature are given in Table VI.

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[38] Schwarzkopf, *DRP* 1,176,318.

TABLE IV

COLORS PRODUCED BY *p*-AMINOPHENOL WITH VARIOUS COUPLERS

Coupler	*Color on hair*	*References*[a]
None	Light auburn	1
m-Phenylenediamine	Blue (at pH 8–11)	2
m-Aminophenol	Red-brown	3
3,5-Diaminophenol	Gray-brown	3
6-Methyl-3-aminophenol	Bright orange	3

[a] Key to references:
1. G. S. Kass and L. Hoehn, *J. Soc. Cosmetic Chemists* **12**, 146 (1961).
2. L'Oreal, *BP* 1,025,916.
3. H. H. Tucker, *J. Soc. Cosmetic Chemists* **18**, 609 (1967).

TABLE V

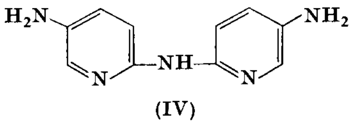
COLORS PRODUCED BY *p*-AMINODIPHENYLAMINE WITH AN EQUIMOLAR AMOUNT OF VARIOUS COUPLERS[a]

Coupler	*Color on hair*
None	Brown-black
m-Aminophenol	Blue-black
3,5-Diaminophenol	Reddish brown-black
6-Methyl-3-aminophenol	Dark gray-purple

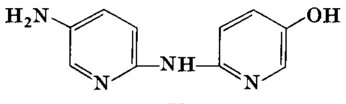
[a] H. H. Tucker, *J. Soc. Cosmetic Chemists* **18**, 609 (1967).

Another patent[39] claims the use of 2,2′-bis(pyridyl)amines such as (IV) and (V) and *N*-phenyl-2-aminopyridines such as (VI). Disubstituted quinolines (VII) and isoquinolines have also been examined.[40]

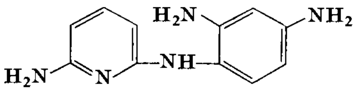
Compound (VII) gives violet-brown dyeings when used in conjunction



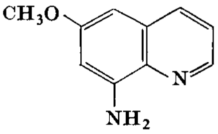
(IV)



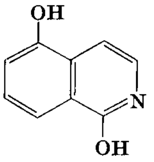
(V)



(VI)



(VII)



(VIII)

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[39] Schwarzkopf, *BP* 1,024,414.

[40] Schwarzkopf, *FP* 1,398,193.

TABLE VI

COLORS FROM PYRIDINE OXIDATIVE DYES

Pyridine derivative	*Color on hair*	*References*[a]
2,5-Diamino	Yellow-red	1
2,5-Diamino-6-methyl	Orange	2
3,4-Diamino	Light orange	2
2-Dimethylamino-5-amino	Blue-violet	2
2,3-Diamino	Light blond	3
2,6-Diamino	Light greenish blond[b]	3
2,6-Dihydroxy	Light gray/blue-violet	4
2,5-Dihydroxy	Green	5
2-(β-Hydroxyethylamino)-5-amino	Claret	6
2,3,6-Triamino	Green	6, 7
2,6-Dihydroxy-3-amino	Blue-violet	6

[a] Key to references:
1. Schwarzkopf, *BP* 1,026,978.
2. F. W. Lange, *Proc. Intern. Color Meeting*, Lucerne (1965), Musterschmidt-Verlag, Gottingen, 1966, II p. 606; Schwarzkopf *BP* 1,153,196.
3. Schwarzkopf, *USP* 3,200,040.
4. Schwarzkopf, *FP* 1,398,193.
5. R. Heald, Schimmel Briefs No. 337 (1966).
6. Schwarzkopf, *BP* 1,153,247.
7. Warner-Lambert, *USP* 3,359,168.

[b] Gives blue dyeings when used in conjunction with 2,5-diaminotoluene (ref. 6 above).

with *p*-phenylenediamine, as does its isomer 4-methoxy-8-aminoquinoline, and compound (VIII) gives dark brown under similar conditions. The colors produced from some quinoline derivatives are given in Table VII.

TABLE VII

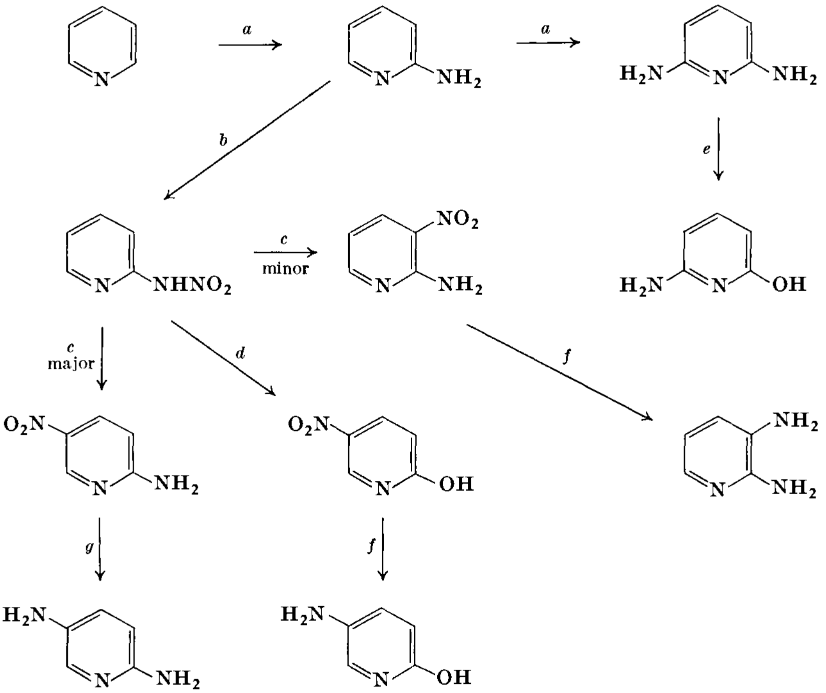
COLORS FROM QUINOLINE OXIDATIVE DYES

Quinoline derivative	*Color on hair*	*References*[a]
2,4-Dihydroxy	Blue-violet	1
1,5-Dihydroxy (iso)	None	1
5-Amino-8-hydroxy	Red-brown	2
5,8-Diamino	Orange	2
4-Methoxy-8-amino	None	2
N-(2′-Hydroxy-4′-aminophenyl)	Gray-blue	2
5-Hydroxy-8-amino (iso)	Gold-blond	2

[a] Key to references:
1. Schwarzkopf, *FP* 1,398,193.
2. K. Bergwein, *Riechstoffe Aromen, Korperpflegemittel*, 136 (1967).

CHART 2

Synthesis of Pyridine Oxidation Dyes



a, $NaNH_2$ in $Me_2NC_6H_5$, at 250–300°; *b*, HNO_3/H_2SO_4, cold; *c*, H_2SO_4, at 50°; *d*, 10% NaOH, at 90°; *e*, 70% H_2SO_4, at 100°; *f*, H_2/Pt; *g*, H_2/Pd

Synthetic routes to the heterocyclic oxidative dyes have been outlined by Lange,[41] who gives references to methods for the preparation of 22 of the more common derivatives. The routes to important intermediates in the pyridine series are outlined in Charts 2 and 3.

C. Chemistry of Oxidative Dyeing

1. *The Oxidation of* p-*Phenylenediamine*

Vigorous chemical oxidation of *p*-phenylenediamine is well known to give *p*-benzoquinone presumably via *p*-benzoquinonediimine (IX) and the corresponding monoimine (X). The intermediacy of (X) in the

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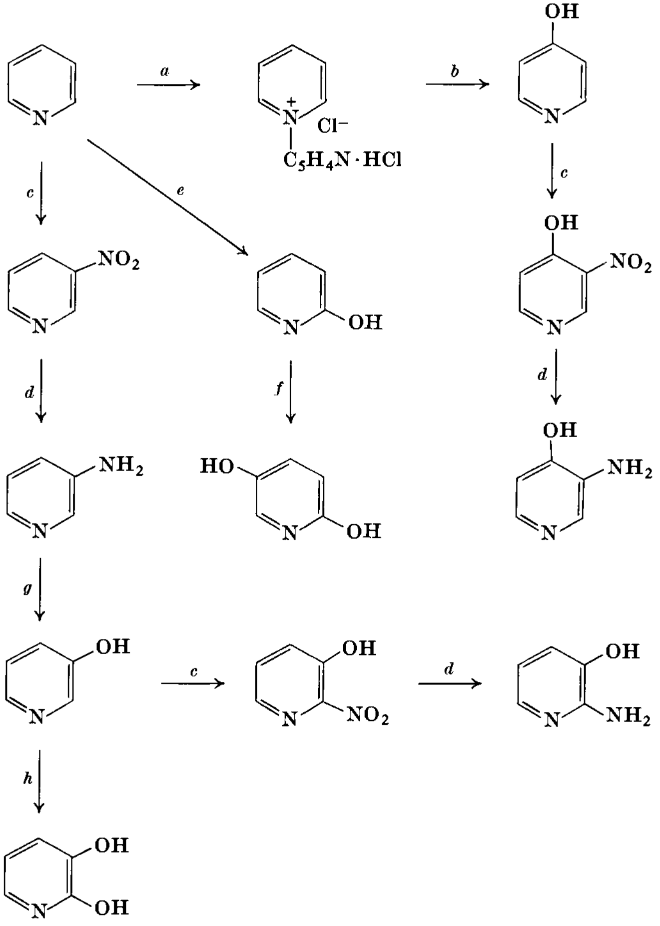
[41] F. W. Lange, *Fette, Seifen Anstrichmittel* **69**, 349 (1967); *Perfumery Essent. Oil Rev.* 447 (1967).

CHART 3

Synthesis of Pyridine Oxidation Dyes



a, $SOCl_2$, at 100°; *b*, H_2O, at 100°; *c*, HNO_3/H_2SO_4; *d*, H_2/Pt; *e*, NaOH, at 250°; *f*, $Na_2S_2O_8/OH^-$, followed by acid hydrolysis; *g*, HNO_2; *h*, KOH, at 300°

hydrolysis of (IX) has been demonstrated by Tong[42] and kinetic studies of the hydrolysis of both imines have shown that both neutral and protonated species suffer hydrolysis by water and the cations are hydrolyzed more rapidly than the free bases.[42, 43]

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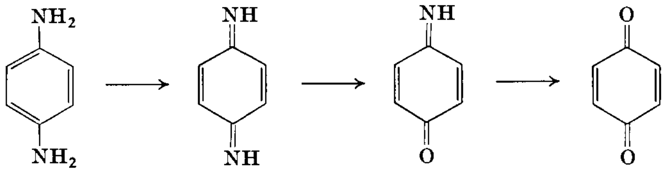
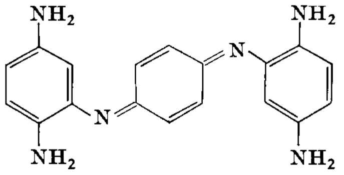
[42] L. K. J. Tong, *J. Phys. Chem.* **58**, 1090 (1954).

[43] J. F. Corbett, *J. Chem. Soc. B* 213 (1969).

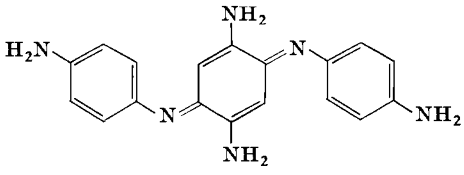


(IX) (X)

In 1894, Bandrowski[44] observed that mild oxidation of the diamine gave a base of formula $C_{18}H_{18}N_3$, to which he assigned a structure which, in modern terms, would be written as (XI). This structure was first written as such by Erdmann,[45] who obtained the base in 89% yield by oxidation of the diamine with hydrogen peroxide in alkali and suggested that it was formed by trimerization of the diimine (IX). However, the polymer formed by dissolving pure diimine in alkaline buffer has been shown to differ in properties from Bandrowski's base.[46] In 1913, Green[47] suggested an alternative formulation (XII) for the base, but did not support it experimentally. Since that time, evidence has been presented in support of both the structures (XI)[48] and (XII)[49] and reviews of hair dye chemistry[50] have continued to use the original structure. The most convincing evidence in favor of (XII) and against (XI) was that of Lauer and Sunde,[51] who synthesized the reduced base of (XI) by an unequivocable route and showed that on oxidation it gave a compound, presumably (XI), which was different from Bandrowski's base.



(XI)



(XII)

[44] E. Bandrowski, *Ber.* **27**, 480 (1894).

[45] E. Erdmann, *Ber.* **37**, 2906 (1904).

[46] R. Willstatter and E. Mayer, *Ber.* **37**, 1494 (1904).

[47] A. G. Green, *J. Chem. Soc.* **103**, 933 (1913).

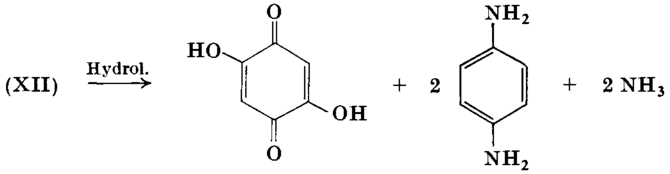
[48] A. Heidushka and E. Goldstein, *Arch. Pharm.* **254**, 584 (1916); J. J. Ritter and G. H. Schmidt, *J. Amer. Chem. Soc.* **51**, 1588 (1929).

[49] L. F. Fieser, *J. Am. Chem. Soc.* **52**, 4915 (1930); W. M. Lauer and C. J. Sunde, *J. Org. Chem.* **3**, 261 (1938).

[50] A. Ginzel, *Melliand Textiber.* **29**, 384 (1948); W. Wittenberger, *Seifen-Ole-Fette-Wasche* **77**, 314 (1951); F. W. Lange, *Am. Perfumer Cosmetics* **80**, 33 (1965).

[51] C. J. Sunde and W. M. Lauer, *J. Org. Chem.* **17**, 609 (1952).

More recently, the author[52] has studied the hydrolysis of Bandrowski's base in acid solution and, in addition to the previously reported[53] formation of *p*-phenylenediamine, found 2,5-dihydroxybenzoquinone (XIII). In addition, the dark-colored hydrolyzate and residue were found to be chromatographically identical with that formed on boiling a 2:1 mixture of the diamine and (XIII) in acid solution. These results, together with NMR data,[54,55] point unequivocably to structure (XII) for the base.



(XIII)

Kinetic studies[56a] of the reaction between *p*-benzoquinonediimine and *p*-phenylenediamine have indicated that the reaction is essentially a trimerization of the diimine, but that the diamine is a vital catalyst. The rate-controlling step involves electrophilic attack of the protonated diimine on a molecule of the neutral diamine. The intermediate triaminodiphenylamine then suffers further attack by diimine and the resulting reduced base is oxidized by a third molecule of diimine, thus regenerating a molecule of diamine. This scheme is shown in Chart 4. In normal dyeing practice, the formation of the diimine by peroxide oxidation of the diamine is probably an additional slow step.

Recent in vitro studies of the peroxide oxidation of *p*-phenylenediamine[55] have shown that, in addition to Bandrowski's base, *p*-nitroaniline, 4,4′-diaminoazobenzene, 2-(4′-aminoanilino)-5-hydroxy-1,4-benzoquinonediimine (XIV), and an unidentified dark product are formed in small quantities.

The question as to whether or not Bandrowski's base is formed during the in fiber oxidation of *p*-phenylenediamine has not yet been satisfactorily resolved.[54,56b] Austin[57] suggested that Bandrowski's base

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[52] J. F. Corbett, *J. Soc. Dyers Colourists* **85**, 71 (1969).

[53] H. E. Cox, *Analyst* **59**, 3 (1934); H. E. Cox and J. U. Lewin, *ibid* **60**, 350 (1935).

[54] M. Altman and M. Rieger, *J. Soc. Cosmetic Chemists* **19**, 141 (1968).

[55] M. Dolinsky, C. H. Wilson, H. H. Wisneski and F. X. Demers, *ibid* **19**, 41 (1968).

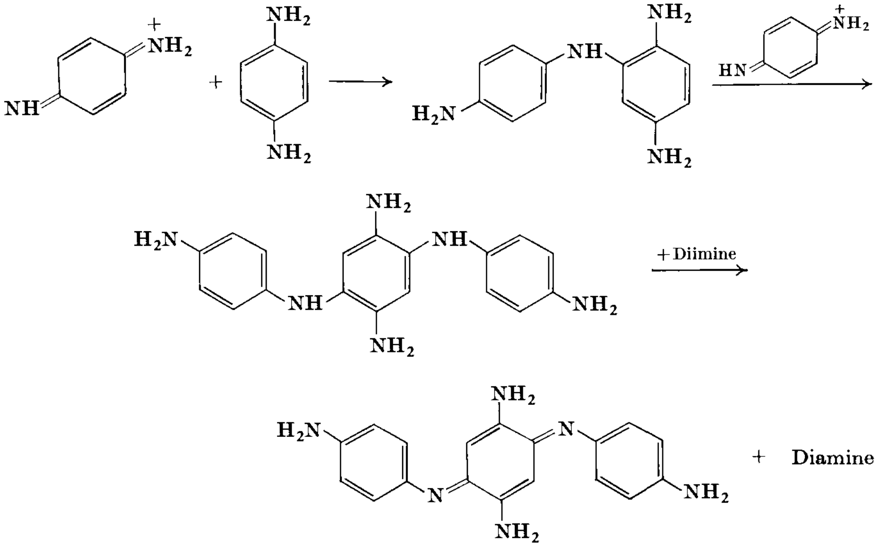
[56a] J. F. Corbett, *J. Chem. Soc. B* 818 (1969).

[56b] M. Altman and M. Rieger, *J. Soc. Cosmetic Chemists* **20**, 395 (1969); cf. R. Heilingotter, *ibid* **19**, 823 (1968); *Am. Perfumer Cosmetics* **83**, 12, 35 (1968).

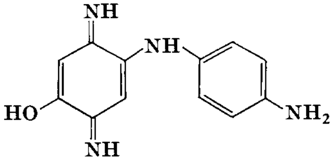
[57] W. E. Austin, "Principles and Practice of Fur Dressing and Fur Dyeing," p. 164. Van Nostrand, New York, 1922.

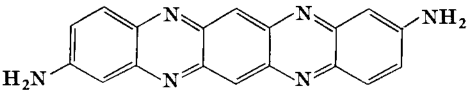
CHART 4

Formation of Bandrowski's Base



suffered further oxidation to an azine (XV). This proposition has been discussed by Sandberg[58] but no experimental evidence has been presented. Altman and Rieger[54] reported that they were able to extract little or no Bandrowski's base from dyed hair, while Cox[59a] reported the extraction of some of the base from dyed wool. It is evident that further studies of the in fiber reaction are necessary in order to resolve the situation.


(XIV)


(XV)

2. Color Coupling Reactions

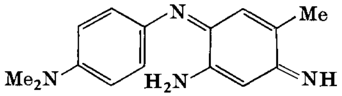
Until recently, little was known about the structure and mechanism of formation of the colored species formed during dyeing with *p*-phenylenediamine and various couplers. The author has shown that in vitro

[58] G. Sandberg, *J. Soc. Dyers Colourists* **72**, 277 (1956); W. E. Austin, *ibid* **72**, 574 (1956).

[59a] H. E. Cox, *Analyst* **65**, 393 (1940).

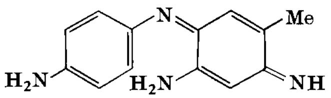
studies of the reaction of p-benzoquinonediimine with the couplers is a good model for the color-forming processes in oxidative dyeing,[59b] and evidence has been presented which indicates that the diimine is the vital intermediate in the dyeing process.[59c]

a. m-Phenylenediamines. The formation of a blue dye when p-phenylenediamine is oxidized in the presence of 2,4-diaminotoluene was first observed by Bernthsen and Schweitzer.[60] By analogy with toluene blue (XVI),[61a] the structure (XVII) was assigned to the blue dye, which was found to undergo oxidative cyclization to the red diaminophenazine (XVIII).[60] The structural assignment has been confirmed, and it has been demonstrated that the formation of such blue dyes from the oxidation of mixtures of p- and m-diamines is a general reaction.[59b] Thus, with p-phenylenediamine and 2,4-diaminoanisole, the methoxy indamine (XIX) is formed.



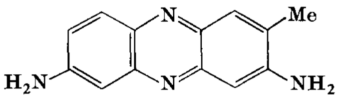
Blue

(XVI)



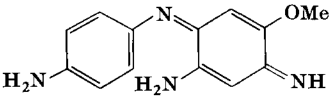
Blue-violet

(XVII)



Red

(XVIII)



Violet-blue

(XIX)

Kinetic studies of the formation of indamine dyes[61b] have shown that, in vitro, the rate-controlling coupling step involves electrophilic attack by protonated diimine on neutral m-diamine to give the leuco-indamine which is converted to the dye by oxidation by a further molecule of p-benzoquinonediimine or by some other oxidizing agent. When oxygen or hydrogen peroxide is used as the oxidant, the initial oxidation of the p-diamine constitutes a further slow step in the overall reaction.

A characteristic property of the blue indamine dyes is their conversion into red phenazines under relatively mild conditions. In solution, the

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[59b] J. F. Corbett, *Proceedings of the Joint Conference on Cosmetic Science, The Toilet Goods Assoc.* Washington, D.C. 159 (1968).

[59c] J. F. Corbett, *J. Soc. Cosmetic Chemists* **20**, 253 (1969).

[60] A. Bernthsen and H. Schweitzer, *Ann*, **236**, 332 (1886).

[61a] R. Nietzki, *Ber.* **16**, 464 (1883); O. N. Witt, *Ber.* **12**, 931 (1879).

[61b] J. F. Corbett, *J. Chem. Soc. B* 827 (1969).

reaction is complete within 48 hours but on fibers at normal humidities the blue color is still detectable after a few weeks.[62]

b. Monohydric Phenols. The constitution of indoaniline dyes, e.g., (XXI), formed by oxidation of mixtures of *p*-diamines and monohydric phenols was proved by Heller in 1912.[63] In the literature reports of their formation, the oxidants employed have been lead and manganese oxides,[64] or hypochlorite.[65] In addition, the dyes are obtained by the reaction of *N*-chloro-*p*-benzoquinonemonoimine with anilines.[66a] The same dyes are found to be formed when oxygen, hydrogen peroxide, or ferricyanide are used as oxidants.[66b] Again, the reaction is general and occurs with *N*,*N*-dialkyl-*p*-phenylenediamines[67] (as used in color photography) or *C*-substituted diamines,[29] and a wide variety of phenols. In all cases investigated, coupling occurs para to the hydroxy group.[66b]

The probable mechanism of the reaction has been deduced from studies of the reaction of *p*-benzoquinonediimine with phenols.[66b] The rate versus pH relationship shows that coupling involves reaction between the protonated diimine and both the phenoxide ion and the undissociated phenol. Although the latter is usually about 10^3 times less reactive than the former, reaction with the phenol becomes the significant reaction at $\text{pH} < 7$. Coupling with a phenol having hydrogen para to the hydroxy group gives the leuco-indoaniline, e.g., (XX), which is then oxidized to the dye (XXI) by a further molecule of the diimine or by some other oxidant. Coupling of a diimine with phenols bearing a methoxy group or chloro para to the hydroxy gives the dye directly, methanol or hydrogen chloride being eliminated.[62] The mechanism of the reaction with phenols is shown in Chart 5.

c. Polyhydric Phenols. Resorcinol and pyrogallol are used extensively in oxidative hair dyes and are known to produce light, drab brown colors when used in conjunction with *p*-phenylenediamine. The reactions involved have not been elucidated, although it has been reported[68] that, *in vitro*, a polymeric product is formed with *p*-phenylenediamine and resorcinol. When diimine reacts with resorcinol in dilute solution, a magenta color develops which can be ascribed to the formation of the indoaniline (XXII). The initial color rapidly gives way to a greenish brown color.[59b]

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[62] J. F. Corbett, unpublished results.

[63] G. Heller, *Ann.* **392**, 25, 43 (1912).

[64] AGFA, *DRP* 179,294–5.

[65] AGFA, *DRP* 204,596.

[66a] H. D. Gibbs, W. L. Hall, and W. M. Clark, *U.S. Publ. Health Rep. Suppl.* No. 69 (1920).

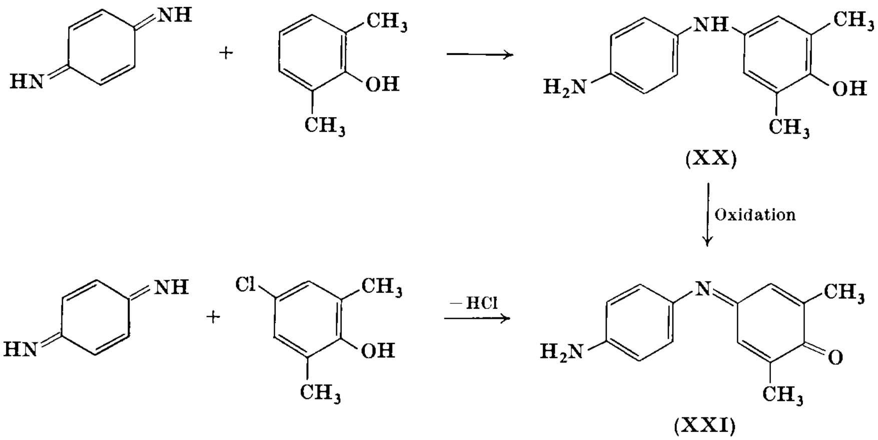
[66b] J. F. Corbett, *J. Chem. Soc. B* 1418 (1970).

[67] L'Oreal, *BP* 1,025,916.

[68] F. Brody and M. S. Burns, *J. Soc. Cosmetic Chemists* **19**, 361 (1968).

CHART 5

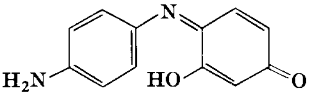
Formation of Indoaniline Dyes



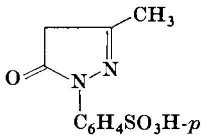
(XX)

(XXI)

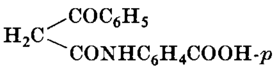
d. Pyrazolones and β-Diketones. The use of pyrazolones and β-diketones, e.g., (XXIII) and (XXIV), in hair dyes has been suggested recently.[29] The magenta and yellow colors produced on hair, with these couplers, suggest that the oxidative coupling reaction gives azomethine dyes of the types (XXV) and (XXVI) which are analogous to those formed in color photography processes (see Chapter VI, Volume IV).[69]



(XXII)

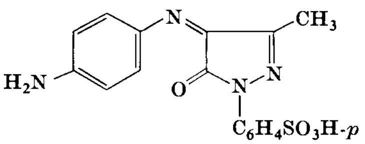


(XXIII)



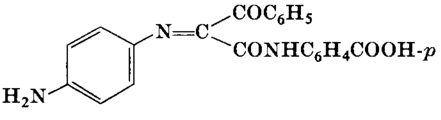
$H_2C{<}^{COC_6H_5}_{CONHC_6H_4COOH\text{-}p}$

(XXIV)



Magenta

(XXV)



Yellow

(XXVI)

3. *Summary*

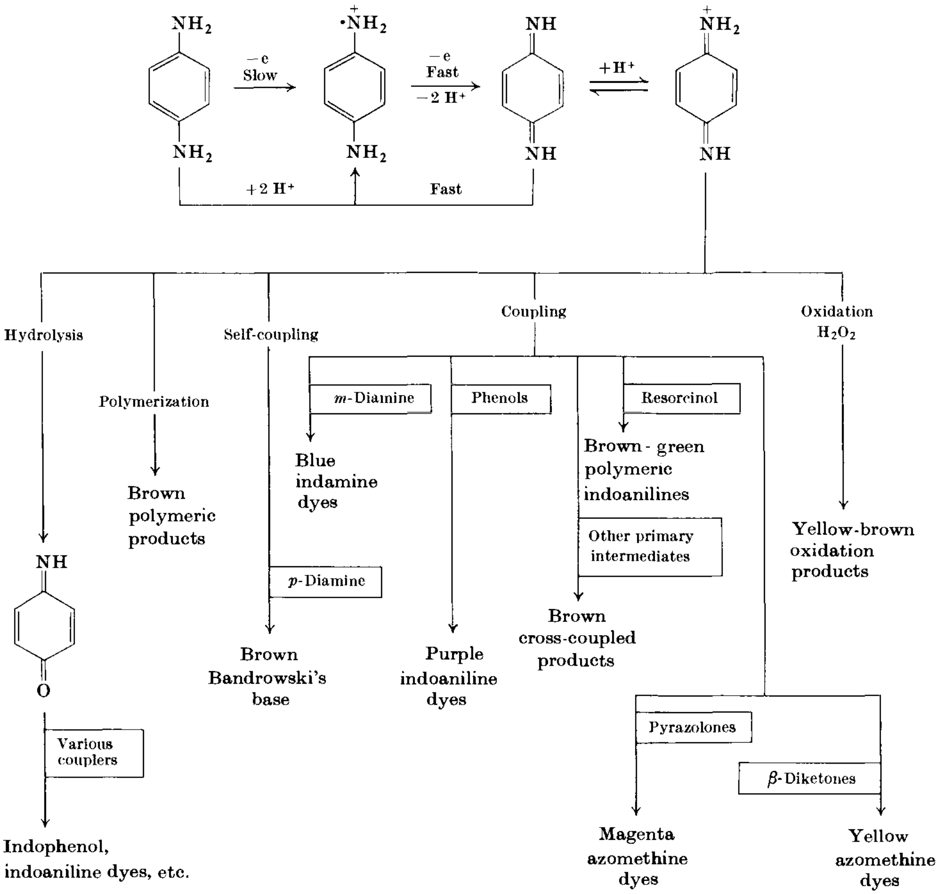
To date, studies on the mechanism of oxidative dyeing have been concerned with the color-forming reactions, in which *p*-benzoquinonediimine is evidently an important intermediate.[59c] On the basis of this

[69] J. F. Corbett, *Chimia* (supplement) *3rd Intern. Symp. Color Chem.* 140 (1968).

work, it is possible to propose a tentative mechanism for oxidative dyeing. This mechanism is outlined in Chart 6[59b] and can be seen to involve a complex system of consecutive, competing, and autocatalytic reactions

CHART 6

Outline Mechanism of Oxidative Dyeing



in which the final color result will be dependent upon the efficiency with which the various couplers compete with one another, and with the self-coupling of the primary intermediates, for the available diimine. The process may be further complicated by reactions involving hydrolysis, oxidation, and homopolymerization of the diimine.

In this scheme, *p*-benzoquinonediimine is formed by oxidation of *p*-phenylenediamine. It is suggested that this may be an autocatalytic process in which the semiquinone radical could play an important role —in spite of its very low equilibrium concentration at the pH used in practical dyeing.[70] The subsequent fate of the diimine is dependent upon reaction conditions and on the nature and concentrations of the couplers in the dye composition. Thus it has been shown that the diimine, in its protonated form, reacts with *p*-diamine to give the brown Bandrowski's base (Chart 4), with *m*-diamines to give blue indamine dyes, with monohydric phenols to give purple indoaniline dyes (Chart 5), and with pyrazolones and β-diketones to give, respectively, magenta and yellow azomethine dyes. Coupling with polyhydric phenols is more complex and evidently leads to brown polymeric indoanilines. These coupling reactions compete with polymerization of the diimine, which would be favored by locally high concentrations of the diimine. In addition, it is possible that some of the diimine might be oxidized further to nitroso and nitro compounds and that the former might react with amines to give azo dyes. Hydrolysis of the diimine to give *p*-benzoquinonemonoimine, and subsequent coupling of the latter to give additional dye species, would normally constitute a minor side reaction. Further work on the reactions in more concentrated solutions and on the identification of colored species in dyed hair will be necessary if a more detailed picture of the process is to be established.

III. Autoxidative Hair Dyes

A. GENERAL

The autoxidation of *p*-phenylenediamine is slow and the use of hydrogen peroxide is necessary to accomplish dyeing in a reasonable time. Two disadvantages which thus arise are the necessity of a two-package product (one for the dye precursors and one for the peroxide) and the potential hair damage resulting from the use of hydrogen peroxide. These can be avoided if readily autoxidizable precursors are employed. The use of air as the oxidant was first recorded in the early Erdmann patents,[26] one of which included the readily autoxidizable 2,4-diaminophenol as an oxidation base. In spite of this early report and of the inclusion of a number of readily autoxidizable bases in the early patents, intensive studies of autoxidative dyeing did not start until about 1950, when dyeing of hair with 1,2,4-benzenetriol and its *C*-alkyl

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[70] L. K. J. Tong and M. Glesmann, *Phot. Sci. Eng.* **6**, 319 (1964); J. F. Corbett, *J. Chem. Soc. B* 207 (1969).

and *C*-alkoxy derivatives, which had been patented earlier,[71] was discussed in a series of articles.[72] Subsequently it was found that 1,2,4-trisubstituted benzenes in which the substituents are amino and/or hydroxy form the best class of autoxidative dyes and, since 1950, 30–40 patents have been published dealing with trihydroxybenzenes, diaminophenols, dihydroxyanilines, and triaminobenzenes and their *N*-, *O*- and *C*-substituted derivatives.

The variety of colors obtained using single autoxidative dyes can be seen from Tables VIII–X. Data in Table VIII relate to dyeings carried out in the author's laboratory.[69] Examination of other patent examples indicates that *N*-hydroxyalkyl and *N*-aminoalkyl derivatives give colors similar to those obtained from the analogous *N*-methyl derivative.

Color data for some tetrasubstituted benzene derivatives is given in Table IX. Examination of the data in Tables VIII and IX shows that it is almost impossible to predict from the structure of the dye precursor the color produced in autoxidative dyeing. Noteworthy regularities are that most of the blue and violet shades are produced from derivatives of 2-hydroxy-*p*-phenylenediamine, and that a number of derivatives of 1,2,4-triaminobenzene give purple shades. The bright turquoise dyeing given by 4-dimethylaminocatechol is unique.

Table X gives the colors produced from autoxidative dyes of the naphthalene series and the quinoline series. The orange-red color from 1,2,4-trihydroxynaphthalene is undoubtedly due to its oxidation to the 1,4-quinone, lawsone. It is interesting to note that 2-hydroxy-1,4-diaminonaphthalene, like its benzene analogs, gives blue dyeings, presumably due to the formation of a phenoxazinium salt.

From the data in these tables it can be seen that a wide range of colors is available from autoxidative precursors. This range can be extended by the use of mixtures of precursors and by their use in the presence of oxidative dye couplers. Among the attendant problems of the commercial exploitation of this class of dyes are the extreme susceptibility of the solid precursors, even as their salts, to air oxidation and their ability to react slowly with one another during storage in aqueous solution. Nevertheless, some products based on these dyes are available for home use.

B. SYNTHESIS

The synthetic routes to the autoxidative dyes embody most of the classical reactions of benzene chemistry, in particular, nitration followed

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[71] Winthrop Chem. Co. *USP* 2,162,458.

[72] H. Burton and J. L. Stoves, *Nature* 165,569 (1950); *J. Soc. Dyers Colourists* **66**, 474 (1950); H. Burton, *J. Soc. Cosmetic Chemists* **2**, 240 (1951).

TABLE VIII
Colors from Trisubstituted Benzene Autoxidative Dyes

Substituents				
1	2	4	*Color on hair*[a]	*References*[b]
OH	OH	OH	Mid-brown	1
OH	OMe	OH	Pink-red	2
NH_2	NH_2	OH	Orange	3
NHMe	NH_2	OH	Red-brown	4
NMe_2	NH_2	OH	Gray	4
NH_2	NHMe	OH	Pink	2
NH_2	NMe_2	OH	Khaki	2
NH_2	NH_2	OMe	Yellow-orange	2, 3
NH_2	OH	NH_2	Purple	3, 4
NH_2	OH	NHMe	Violet	2
NH_2	OH	NMe_2	Blue	5, 6
NHMe	OH	NH_2	Purple-brown	3
NMe_2	OH	NH_2	Beige	4
NH_2	OMe	NH_2	Purple-gray	4
OH	NH_2	NH_2	Red-brown	7
OH	NH_2	NHMe	Dark gray	4
OH	NH_2	NMe_2	Brown-gray	4
OH	NHMe	NH_2	Flat brown	8
OH	NMe_2	NH_2	Deep brown	2
OMe	NH_2	NH_2	Yellow-brown	6
NH_2	OH	OMe	Orange-brown	2
OH	OH	OMe	Auburn	8
OH	OH	NH_2	Mid-brown	9
OH	OH	NHMe	Light brown	4
OH	OH	NMe_2	Turquoise	5
OH	OMe	NH_2	Very light brown	2
OMe	OH	NH_2	Chestnut	4
OH	NH_2	OH	Khaki	10
OH	NHMe	OH	Brown	10
OH	NMe_2	OH	Pale pink	4
OH	NH_2	OMe	Brown	11
OMe	NH_2	OH	Pink-brown	4
NH_2	NH_2	NH_2	Brown-red	12
NHMe	NH_2	NH_2	Purple	4
NMe_2	NH_2	NH_2	Yellow	4
NH_2	NHMe	NH_2	Mauve	2
NH_2	NMe_2	NH_2	Light gray	3
NH_2	NH_2	NHMe	Pink-gray	2
NH_2	NH_2	NMe_2	Light mauve	2
NH_2	OH	OH	Pale pink	9
NHMe	OH	OH	Dark brown	13
NMe_2	OH	OH	Brown-gray	4
NH_2	OMe	OH	Gray-brown	2

[a] From aqueous bath, at pH 6.8–8.0.

[b] Key to references: 1. Winthrop Chem. Co. *USP* 2,162,458; 2. Gillette, *BP* 1,063,979; 3. Gillette, *BP* 1,012,793; 4. J. F. Corbett, unpublished results; 5. Gillette, *BP* 1,056,250; 6. Farbwerke Hoechst, *DRP* 263,105; 7. H. Erdmann and Erdmann, *DRP* 80,814; 8. L'Oreal, *BP* 802,554; 9. L'Oreal, *BP* 831,851; 10. L'Oreal, *BP* 857,070; 11. L'Oreal, *BP* 951,509; 12. L'Oreal, *BP* 987,342; 13. L'Oreal, *BP* 805,746.

TABLE IX

COLORS FROM TETRASUBSTITUTED BENZENE AUTOXIDATIVE DYES

Substituents						
1	2	3	4	5	*Color on hair*	*References*[a]
OH	OH	H	OH	OH	Orange	1
OH	NH_2	OH	H	OH	Golden brown	2
OH	OH	H	NH_2	Br	Brown	2
OH	OH	OH	H	NH_2	Brown	2
NH_2	OH	NH_2	H	NMe_2	Green	3
OH	NH_2	H	OH	OMe	Orange	3
NH_2	OH	NH_2	H	OH	Ash blond	3
NH_2	OH	NH_2	H	OMe	Khaki	3
NH_2	OH	NH_2	H	NH_2	Greenish	4
OMe	OH	NH_2	H	NH_2	Auburn	4
Br	NH_2	OH	H	NH_2	Purple	5
NH_2	NH_2	H	NH_2	OH	Light brown	5
NH_2	OH	H	NH_2	OH	Gray	5
NH_2	OH	H	NH_2	Me	Royal blue	1
NH_2	OH	H	NH_2	OMe	Violet	3
NH_2	NH_2	NH_2	H	NH_2	Brown	6
NH_2	NH_2	H	NH_2	NH_2	Yellow-brown	6
NH_2	OMe	Me	NH_2	Me	Violet	7

[a] Key to references:

1. J. F. Corbett, unpublished work.
2. Gillette, *BP* 992,150.
3. L'Oreal, *BP* 987,342.
4. L'Oreal, *BP* 831,851.
5. Gillette, *BP* 1,012,793.
6. Gillette, *BP* 995,870.
7. L'Oreal, *FP* 1,461,395.

by reduction, nucleophilic displacement of halogen or hydroxy groups, and *N*-alkylation. These are exemplified by the routes to the six isomeric aminohydroxy-*N*-methylanilines of the 1,2,4-series.

The amination reaction by which a 1-hydroxy group of a 1,2,4-tri-donor-substituted benzene is replaced by an amino or substituted amino group was first reported by Lantz and Michel for the conversion of 1,2,4-benzenetriol into 2,4-dihydroxyanilines.[73] The reaction appears to be general and was embodied in patents for autoxidative hair dyes.[74,75]

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[73] R. Lantz and E. Michel, *Bull. Soc. Chim. France* 2402 (1961).

[74] L'Oreal, *USP* 3,236,734.

[75] L'Oreal, *BP* 754,948; 889,812.

TABLE X

COLORS FROM NAPHTHALENE AND QUINOLINE AND PYRIDINE AUTOXIDATIVE DYES

Naphthalenes				
1	2	4	*Color on hair*	*References*[a]
OH	OH	OH	Orange-red	1
NH_2	OH	OH	Brown	2
OH	NH_2	OH	Yellow	2
OH	OH	NH_2	Orange	2
OH	NH_2	NH_2	Brown	2
NH_2	OH	NH_2	Blue	2
OH	NH_2	NH_2	Orange-brown	2
NH_2	NH_2	NH_2	Brown	2
Naphthalenes				
OH	NH_2	OH		
1	2	5	Brown-black	3
1	4	6	Blond	3
1	2	6	Black	3
1	2	7	Blond	3
Quinolines				
5	6	8		
OH	OH	OH	Orange-brown	2
OH	OMe	OH	Light brown	2
OH	NH_2	NH_2	Brown	2
NH_2	OMe	NH_2	Gray	2
5	7	8		
NH_2	NH_2	OH	Red-brown	2
2	4	6		
OH	OH	NH_2	Violet	4
Pyridines				
2,3,6-Triamino			Green	4
2,3,4-Trihydroxy			Indigo blue	4

[a] Key to references:
1. Winthrop Chem. Co. *USP* 2,162,458.
2. J. F. Corbett, unpublished work.
3. Therachemie Chem. Therap. Ges. *BP* 1,023,327.
4. F. W. Lange, *Perfumery Ess. Oil Record* 447 (1967).

The application to amination of 2,4-dihydroxyanisole and to amine exchange in 2,4-dihydroxyanilines was reported in a second paper,[76] and

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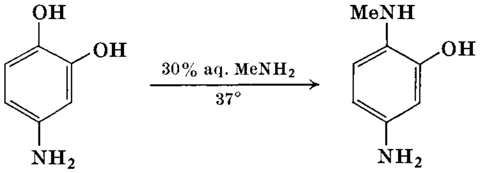
[76] R. Lantz and E. Michel, *Bull. Soc. Chim. France* 353 (1962).

the reaction was later extended to the 1-amination of 4-aminocatechol, where it can be used in the synthesis of 4-amino-2-hydroxy-*N*-methylaniline (Chart 7).[77]

CHART 7

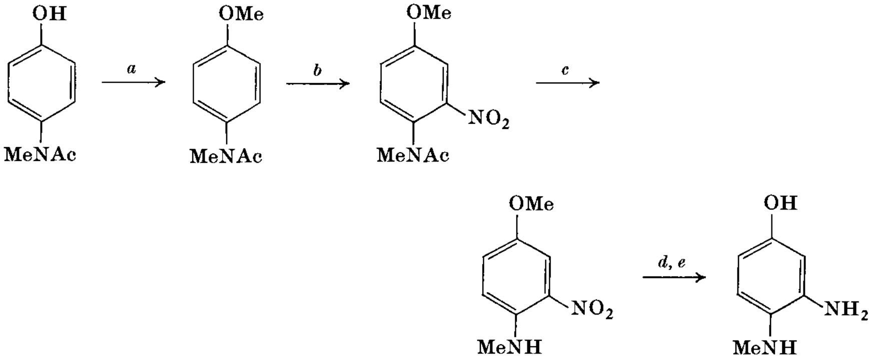
Synthesis of 4-Amino-2-hydroxy-*N*-methylaniline



In the synthesis of 3-amino-4-methylaminophenol (Chart 8),[69] the nitration step[78] is unusual in that nitration does not normally occur ortho to an *N*-methylacetamido group.[79] It is likely that under the conditions employed the nitronium ion is not the attacking species, and it is noteworthy that with 80% nitric acid only the 2-nitro isomer is formed.[78] The use of aluminum chloride for demethylation of the anisole has been found useful in dealkylating a number of nitroaminophenyl ethers.[80]

CHART 8

Synthesis of 2-Amino-4-hydroxy-*N*-methylaniline



a, Me_2SO_4/aq. NaOH; *b*, 50% aq. HNO_3, at 50–55° (some 2-nitro isomer also formed); *c*, 15% aq. KOH; *d*, $AlCl_3/C_6H_6$; *e*, H_2/Pd-C

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[77] idem, *ibid* 534 (1964).

[78] J. Uyeyanagi, *Ann. Report Takeda Res. Lab.* 8, 22 (1949); *CA* 47,4854 (1953).

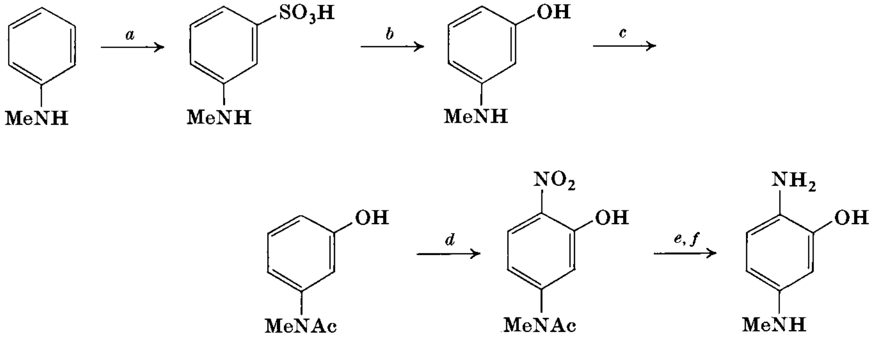
[79] G. W. Amery and J. F. Corbett, *J. Chem. Soc.* (*C*) 1053 (1967).

[80] P. E. Verkade, C. P. van Dijk, and W. Meerburg, *Rec. Trav. Chim.* **65**, 346 (1946).

The nitration step[79] in the synthesis of 2-hydroxy-4-methylamino aniline (Chart 9)[81] exemplifies the failure of the nitronium ion to attack ortho to a methylacetamido group—none of the isomeric 2-nitro-5-hydroxy-*N*-methylacetamidobenzene is obtained.

CHART 9

Synthesis of 2-Hydroxy-4-methylaminoaniline

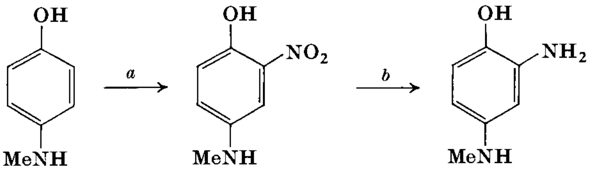


a, oleum; *b*, fusion with KOH; *c*, Ac_2O; *d*, HNO_3/H_2SO_4, at −25°; *e*, 5*M* HCl; *f*, Sn/HCl

p-Aminophenol is reported to undergo nitration and sulfonation on treatment with mixed acids,[82] however, if the temperature is maintained below 0° during dissolution of the amine in sulfuric acid and during subsequent nitration, 2-nitro-4-aminophenol can be obtained in 60% yield.[83] Similarly 4-*N*-methylaminophenol gives a 92% yield of the 2-nitro derivative,[79] which on reduction gives 2-amino-4-methylaminophenol (Chart 10).[83]

CHART 10

Synthesis of 2-Amino-4-methylaminophenol



a, HNO_3/H_2SO_4, at <0°; *b*, Sn/HCl

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[81] Gillette, *BP* 1,063,979.

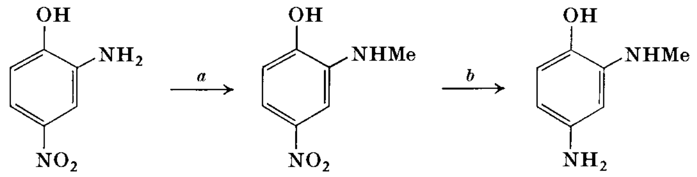
[82] E. R. Riegel, H. W. Post, and E. E. Reid, *J. Amer. Chem. Soc.* **51**, 505 (1929).

[83] J. F. Corbett, unpublished work.

4-Amino-2-methylaminophenol is obtained by the route shown in Chart 11.[84] The intermediate nitro compound can also be obtained by nitration of 2-methylacetamidophenol.[79]

CHART 11

Synthesis of 4-Amino-2-methylaminophenol

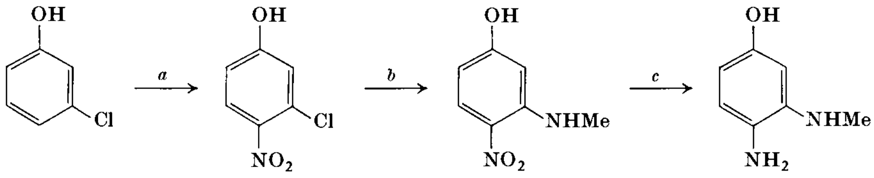


a, Me_2SO_4/KOH; b, Sn/HCl

The final isomer, 4-hydroxy-2-methylaminoaniline, is obtained as shown in Chart 12.[81] The nucleophilic displacement of chlorine from the chloronitriphenol also occurs with dimethylamine.[79]

CHART 12

Synthesis of 4-Hydroxy-2-methylaminoaniline



a, 50% HNO_3; b, aq. MeNH, at 20°; c, $H_2/Pd\text{-}C$

Synthetic routes to other autoxidation dyes can be found in the references given in Table VIII.

C. Chemistry of Autoxidative Dyeing

The nature of the dyes formed in autoxidative dyeing has been elucidated in only a few cases. It has been shown that the first step in the autoxidation of benzenetriols involves oxidation to hydroxyquinones and the formation of hydrogen peroxide.[85] It has also been shown that alkaline peroxide can convert hydroxyquinones into colorless cyclopentane derivatives.[86] This may explain the observation that many autoxidative dyes, particularly di- and trihydroxy compounds, give weaker dyeings when used in conjunction with hydrogen peroxide than when used under autoxidative conditions. During the autoxidation of

[84] L'Oreal, *BP* 802,554.

[85] J. F. Corbett, *J. Chem. Soc.* (*C*) 611 (1967).

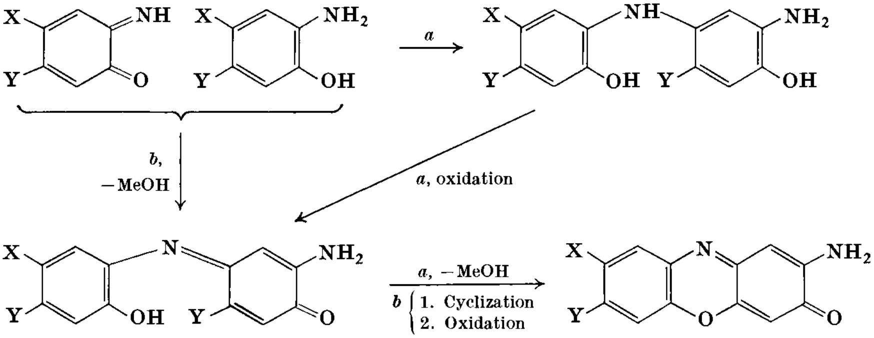
[86] idem, *ibid* 2308 (1966).

benzenetriols considerable free radical formation is observed[87] and it is likely that this gives rise to polymeric products by carbon–carbon coupling.

Autoxidation of 4- and 5-methoxy-2-aminophenols has been found to yield the corresponding methoxy-2-aminophenoxazinones,[88] which are responsible for the orange-brown colors produced on dyeing with these compounds. It is interesting to note that the methoxy group, unlike methyl,[89, 90] can be eliminated at either the nitrogen–carbon coupling step or at the oxygen–carbon cyclization step, according to the mechanism shown in Chart 13.

CHART 13

Autoxidation of Methoxy-2-aminophenols



a, X = H, Y = MeO
b, X = MeO, Y = H

The blue dye formed from the autoxidation of N^4,N^4-dimethyl-2-hydroxy-*p*-phenylenediamine (XXVII) is the oxygen analog (XXVIII) of methylene blue.[91] At high pH, the autoxidation of (XXVII) is reported[92] to yield the red dye (XXIX), but no evidence for its in fiber formation can be seen from dyeings performed in baths having pH 6–10. In solution the optimum pH for the formation of the red dye is 10 and, for the formation of the blue dye, 6.5.[88] It seems likely that the purple and

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[87] J. F. Corbett, *J. Chem. Soc.* (*C*) 2101 (1970).

[88] J. M. Bird and J. F. Corbett, *J. Chem. Soc.* (*C*), in press.

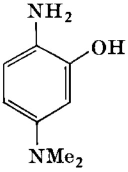
[89] K. von Auwers and E. Borsch, *Ber.* **48**, 1710 (1915); *ibid* **54B**, 1291 (1921).

[90] F. Kehrmann and M. Mattisson, *Ber.* **39**, 135 (1906); K. von Auwers, E. Murbe, K. Saurwein, G. Deines and J. Schornstein, *Fortch. Chem. Phys.* **18** (2), 42 (1924–6).

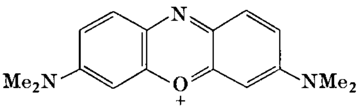
[91] F. Kehrmann and W. Poplawski, *Ber.* **42**, 1275 (1909).

[92] R. Möhlaü, *Bet.* **25**, 1055 (1892).

blue dyes formed from simple 2-hydroxy-*p*-phenylenediamines have structures such as (XXX) and (XXXI). A small quantity of (XXX) has in fact been obtained by autoxidation of the parent compound.[91]

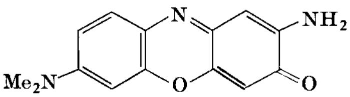


(XXVII)



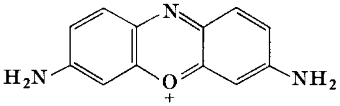
Blue

(XXVIII)



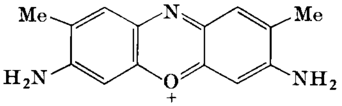
Red

(XXIX)



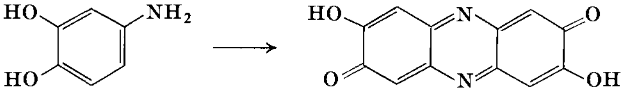
Purple

(XXX)



Royal blue

(XXXI)



Brown

(XXXII) (XXXIII)

Horner and Sturm[93] reported that the autoxidation of 4-aminocatechol (XXXII) gave an oxidized derivative, (XXXIII), of tetrahydroxyphenazine. By analogy with the chemistry of oxidative dyeing, it seems likely that this is formed by nitrogen–carbon coupling of hydroxybenzoquinonemonoimine, formed by oxidation of (XXXII) with a molecule of unoxidized (XXXII). The resulting intermediate would give (XXXIII) by nitrogen–carbon oxidative cyclization and further oxidation.

The polyaminophenazines (XXXIV) and (XXV) have been reported to be formed during the autoxidation of 1,2,4-triaminobenzene[94] and of 1,2,4,5-tetraminobenzene,[95] respectively. It is likely that *N*-alkylated polyaminobenzenes give rise to similar products.

Further complications can occur if the autoxidation is carried out in the presence of ammonia. Thus with 1,2,4-benzenetriol, the exchange reaction[73] can result in the formation of 2,4-dihydroxyaniline, which can

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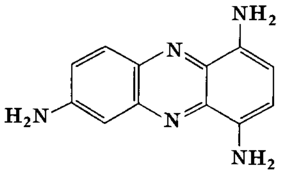
[93] L. Horner and K. Sturm, *Ann.* **608**, 128 (1956).

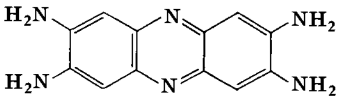
[94] E. Muller, *Ber.* **22**, 857 (1889).

[95] E. Rodd, "Chemistry of Carbon Compounds," Vol. IIIA, p. 229. Elsevier, New York, 1954.



Red-brown

(XXXIV)



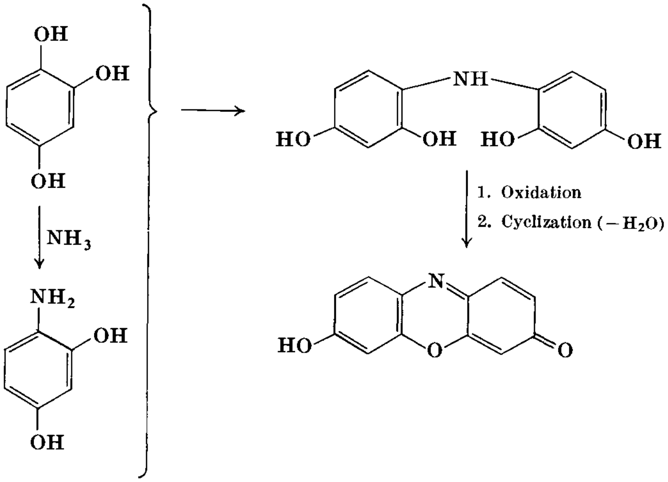
Yellow-brown

(XXXV)

then give rise to the dye resorufin as shown in Chart 14.[96] Heinrich and Gotz obtained 2,9-dimethylresorufin on air oxidation of 5-methyl-2,4-dihydroxyaniline.[97]

CHART 14

Autoxidation of 1,2,4-Benzenetriol in Ammoniacal Solution



In addition to the phenoxazines, phenazines, and phenoxazinium salts mentioned above, it is likely that some autoxidative dyes may give polymeric species as a result of carbon–carbon or carbon–nitrogen oxidative coupling.

IV. Metal Chelate Dyes

While the use of salts of lead[98] and bismuth[99] in hair color "restorers" has been practiced for many years,[100] the dyeing of hair using metal salts and organic chelating agents is of comparatively recent origin. In the

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[96] H. Musso, *Angew. Chem.* **73**, 665 (1961).

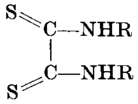
[97] F. Henrich and F. Götz, *Ber.* **58**, 1055 (1925).

[98] H. S. Redgrove, *Perfumery and Essent. Oil Record* **31**, 199 (1940).

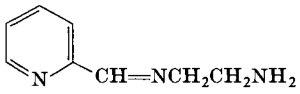
[99] Welwert, *Seifensieder-Ztg.* **62**, 267 (1935).

[100] F. E. Wall, p. 515.

older process, color is developed by the slow formation of metal sulfides in the hair as a result of exposure to sulfurous materials both in the hair and in the atmosphere. In the second process, dyes are formed in the fiber by treatment with a solution of a metal salt followed by a solution of a chelating agent. For this purpose, dithiooxamides (XXXVI), polyaminoethylenes, dithiocarbamates, thioureas, and thioglycolates have been claimed.[101] An alternative approach has been to treat the hair with an aqueous solution of a complex metal cation and then adjust the pH to 10–11 to fix the colored complex in the hair.[102] For this



(XXXVI)



(XXXVII)

TABLE XI

Colors Produced by Metal Chelate Dyes

Chelating agent	*Metal ion*	*Color on hair*	*References*[a]
Dithiooxamide	Ni^{2+}	Blue	1
	Cu^{2+}	Gray-green	1
	Co^{2+}	Orange-brown	1
N,*N*′-Dimethyldithiooxamide	Ni^{2+}	Red	1
Diethyldithiocarbamate	Cu^{2+}	Golden brown	2
Dithiooxamide + ethylenediamine	Cu^{2+}	Black	2
Amm. thioglycollate	Ni^{2+}	Reddish brown	3
1,8-Phenanthroline	Fe^{2+}	Orange	4
2,2′-Bipyridyl	Fe^{2+}	Red	4
2,5-Tris-2′-pyridyltriazine	Fe^{2+}	Blue	4
2-Acetylpyridine methylhydrazone	Cu^{2+}	Yellow	5
2-Acetylpyridine 2′-pyridylhydrazone	Co^{2+}	Red	6
2-Quinolinealdehyde-2′-quinolinylhydrazone	Co^{2+}	Lilac	6

[a] Key to references:
1. Shulton *BP* 932,489.
2. Ashe Laboratories *BP* 942,499.
3. Revlon *BP* 1,010,973.
4. Unilever *BP* 1,107,463.
5. Unilever *BP* 1,134,347.
6. Unilever *BP* 1,134,348.

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[101] Shulton, *BP* 932,489; Ashe Chemical Ltd. *BP* 942,499; Revlon, *BP* 1,010,973; C. Westerberg, *USP* 2,719,104; Yamahatsu Sangyo Kaisha *DFP* 1,439,307.

[102] Unilever, *BP* 1,107,463; 1,134,347; 1,134,348.

purpose complexes of iron, cobalt, and copper with compounds containing the group –N═C—C═N– are particularly suitable. Examples of such chelating agents are 1,10-phenanthroline, 2,2′-bipyridyl, and 1-(α-pyridylmethyleneimine)-2-aminoethane (XXXVII).

Examples of the colors available from dyeing with metal chelates are given in Table XI. The process has the advantage that the uptake of the metal ions and small chelating agents is relatively fast, but suffers some limitation with respect to the safety of certain metal salts for application to the human head.

V. Direct Dyes for Human Hair

A. INTRODUCTION

The first synthetic direct dyes to be used in the dyeing of human hair were nitro derivatives of oxidation bases introduced in 1898[103] for use in conjunction with oxidation dyes. In addition to these nitro dyes, extensive use was made of acid dyes, a limited number of basic dyes, and particularly of the F. D. and C. colors,[104] in temporary hair color products.

The early literature contains few reports of the synthesis of direct dyes specifically for use as hair colorants. However, since 1950 numerous patents have been published in this area.[25, 105, 106] These patents have dealt, in particular, with nitro dyes, anthraquinone dyes, and derivatives of naphthaquinone.

Few of the dyes reported in these patents give natural hair colors when used alone. Attempts to prepare drab browns and blacks have, for the most part, been unsuccessful, owing to the large molecular size of such dyes, which prevents their ready diffusion into hair at ambient temperatures. The aim has thus been to obtain series of dyes which are compatible with one another with regard to dyeing and fastness properties, and which can be used in admixture to produce natural shades. The nitro dyes provide an excellent range of yellow, orange, red-brown, and violet shades but are deficient in pure blues. For this reason, much effort has also been devoted to aminoanthraquinone dyes, which include many pure blue shades. Azo dyes do not appear to have received much attention, except in Germany (see Section E).

[103] AGFA, *DRP* 103,505.

[104] F. E. Wall, p. 486; R. L. Goldenberg, see ref. 24; M. H. Daniels, *Drug Cosmetic Ind.* **82**, 158,243 (1958).

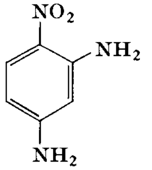
[105] J. C. Brown, *J. Soc. Cosmetic Chemists* **18**, 225 (1967); P. Alexander, *Am. Perfumer and Cosmetics* **82**, 31 (1967).

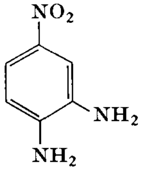
[106] R. C. Heald, *ibid* **78**, 40 (1963).

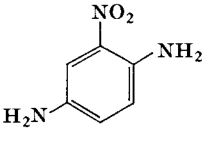
B. Nitro Dyes

1. *Types and Colors*

Among the nitro dyes introduced in 1898[103] were 4-nitro-*m*-phenylenediamine (XXXVIII) and 4-nitro-*o*-phenylenediamine (XXXIX). The isomeric 2-nitro-*p*-phenylenediamine (XL) has also been used for a considerable time. These dyes can be considered the parent group to a series of 1,2,4-trisubstituted benzenes having one nitro group and two electron-donor substituents, such as hydroxy, methoxy, amino, or substituted amino. It has been found[107] that in each isomeric group of didonor nitrobenzenes, the 2,5-isomer [e.g., (XL)] gives the bluest shade and the 2,4-isomer [e.g., (XXXVIII)] gives the yellowest shade. This can be seen from the data in Table XII, and it has been shown that the relationship is a consequence of additivity of the spectral shifts caused by each of the auxochromic groups.[108] From Table XII it can be seen that the methylamino and dimethylamino groups are the most effective auxochromes, and dyes such as (XLI) give red-violet to blue-violet dyeings on hair.


Yellow
(XXXVIII)


Orange-yellow
(XXXIX)


Red
(XL)

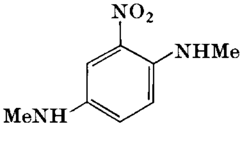

Violet
(XLI)

TABLE XII

Colors of Didonor Nitrobenzenes on Hair

Donor groups				
D	D′	2,4-D,D′	3,4-D,D′	2,5-D,D′
NH_2	NH_2	Yellow	Yellow-orange	Red
NHMe	NHMe	—	—	Violet
NH_2	NMe_2	Orange-yellow	—	Violet
OH	NH_2	Yellow	Orange-yellow	Orange
NH_2	OH	Yellow	Orange	Orange-red
OH	OH	Yellow	Yellow	Orange

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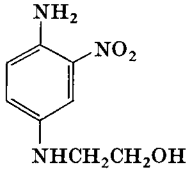
[107] J. F. Corbett, *J. Soc. Dyers Colourists* **83**, 273 (1967).

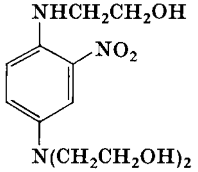
[108] J. F. Corbett, *Spectrochim. Acta* **23A**, 2315 (1967).

One of the deficiencies of the simple *N*-alkylated nitro dyes is their low solubility in water,[69] and much effort has been devoted to increasing the solubility by the introduction of hydrophilic groups.[106] The first patent in this area was granted in 1951[109] and claimed the use of mono-*N*-hydroxyalkylated derivatives of a wide variety of nitro dyes, including all isomers of nitrophenylenediamines and nitroaminophenols. Di- and tri-*N*-hydroxyalkylated derivatives were claimed in a second patent.[110] Dyes claimed in these patents included (XLII)–(XLIV). Since 1952, other patents have appeared claiming various permutations of N-alkyl,[111–113] *N*-hydroxyalkyl,[113–114] *N*-alkyl-*N*-hydroxyalkyl,[113, 115, 116] and *N*-aryl[113] derivatives of 2-nitro-*p*-phenylenediamine and 4-nitro-*o*-phenylenediamine, *N*-alkyl derivatives of 4-nitro-*m*-phenylenediamine,[115] and *N*-alkylated and *N*-hydroxyalkylated nitroanilines.[117a, b]



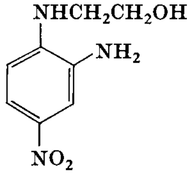
Red-violet

(XLII)



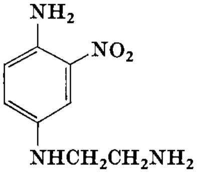
Ultramarine

(XLIII)



Golden

(XLIV)



Violet

(XLV)

An alternative modification to improve the dyeing properties (e.g., rate of strike and equilibrium uptake) and water solubility of the nitrophenylenediamines is the introduction of *N*-aminoalkyl substituents.

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[109] Unilever, *BP* 707,618.

[110] Unilever, *BP* 741,334.

[111] L'Oreal, *BP* 768,220; *BeP* 621,355.

[112] Bristol Meyers, *BP* 955,743; Clairol *BP* 990,334.

[113] Clairol, *USP* 3,168,442.

[114] Unilever, *BP* 1,080,154.

[115] L'Oreal, *BP* 1,061,515; 1,104,970; *BeP* 680,002; 715,165; 715,166; *FP* 1,411,124.

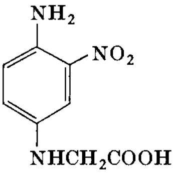
[116] Sandoz, *Swiss P* 479,302.

[117a] Clairol, *BP* 1,136,659.

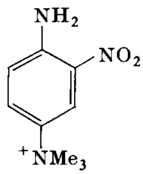
[117b] Clairol, *BP* 1,140,445, Revlon *FP* 2,000,450.

The first of these dyes, (XLV), was introduced in 1955.[118] Further patents have appeared relating to other aminoalkyl and dialkylaminoalkyl derivatives,[119a,b] and to their quaternary ammonium salts.[119b, 120] Dyes containing hydroxyaminoalkyl substituents have also been described.[121] The aminoalkyl nitro dyes probably owe their increased rate of strike and of total uptake to their behaving as basic dyes. *N*-Substituted derivatives of 2-nitro-*p*-phenylenediamine and 4-nitro-*o*-pheneylenediamine, in which the substituent may contain one of the functions OR, NHCOR, $NHSO_2R$, $NHCONH_2$, $NHCO_2R$, $NHCSNH_2$, CN, SO_2NR_2, SO_2R, or COR (where R is alkyl, hydroxyalky, or aryl) linked to the ring nitrogen by an alkylene chain, have been described in recent patents.[117b]

A number of patents have dealt with acidic nitro dyes which owe their acidity to a carboxyl,[118, 122] (XLVI) or sulfonic acid[123] group attached to an *N*-alkyl substituent.

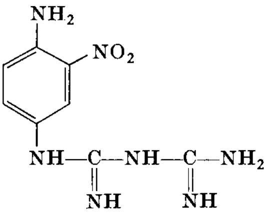


(XLVI)



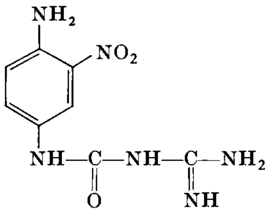
Yellow

(XLVII)



Orange-yellow

(XLVIII)



Orange-yellow

(XLIX)

Dyes quaternized on a nitrogen adjacent to the ring, such as (XLVII),[120] lose the auxochromic effect of the amino group and are thus

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[118] L'Oreal, *BP* 812,211.

[119a] L'Oreal, *BeP* 690,591.

[119b] L'Oreal, *BP* 1,008,844; *BeP* 684,859; 684,763; 701,743; 701,774; 715,165; 715,166.

[120] Therachemie, *BP* 909,700

[121] Revlon, *BP* 1,093,506.

[122] Therachemie, *DRP* 1,087,565; L'Oreal, *BP* 867,220, 1,076,915.

[123] Therachemie, *DRP* 1,114,775.

yellow dyes. Similar effects, and an enhanced rate of dyeing are caused by the introduction of biguanyl and guanylurea groups,[124] which gives dyes (XLVIII) and (XLIX) having a similar color to that of the *N*-acetyl derivatives.

Apart from the types of substitution mentioned in the preceding paragraph, the *N*-substituted 2-nitro-*p*-phenylenediamines give colors which are more dependent on the number and position of the substituents than on their nature. The colors for the various substitution patterns are given in Table XIII. It can be seen that monomethylation of the 1-amino group produces a greater shift towards blue than does monomethylation of the 4-amino group. On the other hand, 4-dimethylation produces a greater shift than does 1-dimethylation. This contrast is ascribable to the steric overcrowding between the nitro group and the *o*-dimethylamino group. In general, the bluest dyeings are obtained with the N^1,N^4-dimethyl and the N^1,N^4,N^4-trimethyl compounds and, of the 100 nitro-*p*-phenylenediamine dyes specifically described in patents, 40 and 20 have these respective substitution patterns.

TABLE XIII

COLORS FROM *N*-METHYLATED 2-NITRO-*p*-PHENYLENEDIAMINES ON HAIR

Benzene substituents			
1	2	4	*Color on hair*
NH_2	NO_2	NH_2	Bright red
NHMe	NO_2	NH_2	Purple
NMe_2	NO_2	NH_2	Red-brown
NH_2	NO_2	NHMe	Red-purple
NH_2	NO_2	NMe_2	Purple-red
NHMe	NO_2	NHMe	Violet
NHMe	NO_2	NMe_2	Blue-violet
NMe_2	NO_2	NHMe	Purple-brown
NMe_2	NO_2	NMe_2	Red-brown

In addition to nitroamines, nitroaminophenols are used extensively in hair color products. Of particular importance are 2-amino-4-nitrophenol, 4-amino-2-nitrophenol, picramic acid (L), and *N*-methylisopicramic acid (LI). *N*-Hydroxyalkyl derivatives of the nitroaminophenols and of

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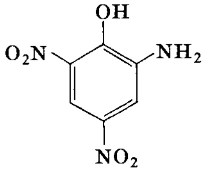
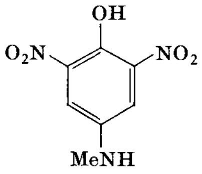
[124] Clairol, *BP* 990,334.

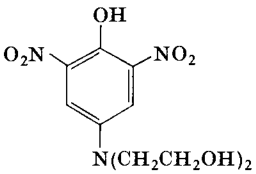
picramic and isopicramic acids have also been described.[121] *N*,*N*-Disubstituted isopicramic acids, (LII), are reported to be useful as blue-violet dyes.[125]


Red-orange

(L)


Blue-violet

(LI)


Violet

(LII)

The only reports of *C*-substituted nitroamines or nitroaminophenols are concerned with C^5- alkyl, alkoxy, or halo derivatives of *N*-substituted 4-nitro-*m*-phenylenediamine,[119a] *C*-alkylated *N*-substituted 2-nitro-*p*-phenylenediamines,[114] and 5-methoxy-2-nitro-*p*-phenylenediamine, which is reported to give reddish brown dyeings.[126]

2. *Synthesis*

a. Nitration. The high susceptibility of phenylenediamines and of aminophenols to oxidation generally renders direct nitration impracticable. 2-Nitro-N^1,N^1,N^4-trimethyl-*p*-phenylenediamine can be obtained by treatment of the diamine with nitrous acid and subsequent removal of the *N*-nitroso group from the resulting 2-nitro-N^4-nitroso derivative with hydrochloric acid.[127] It has also been found possible to prepare *N*-alkylisopicramic acid (LI) by the direct nitration of the 4-alkylaminophenol at low temperatures.[128]

In most cases nitration of *N*-acetyl derivatives of the diamine or aminophenol has to be employed. Thus, nitration of the bis(acetamido)-benzene is used in the synthesis of 2-nitro-*p*- and 4-nitro-*m*-phenylenediamine. The nitration of N^1,N^4-bis(acetyl)-N^1-methyl-*p*-phenylenediamine gives exclusively the 3-nitro isomer,[129] no nitration occurring ortho to the methylacetamido group; this is also noted in the failure of N^1,N^4-bis(methylacetamido)benzene to nitrate, even under drastic conditions.[127]

4-Dimethylaminoacetanilide can be nitrated in either the 2- or 3-positions by suitable choice of reagents (Chart 15).[130] The reactions

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[125] Unilever, *BP* 1,050,489, 1,053,369.

[126] Revlon, *FP* 1,496,528.

[127] J. F. Corbett and A. G. Fooks, *J. Chem. Soc.* (*C*) 1136 (1967).

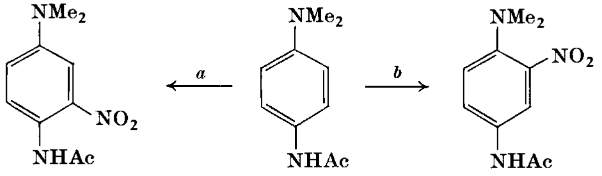
[128] Gillette, *BP* Appl. No. 32963/68.

[129] L'Oreal, *BP* 867,220.

[130] H. H. Hodgson and J. H. Crook, *J. Chem. Soc.* 2976 (1932).

CHART 15

Nitration of 4-Dimethylaminoacetanilide



a, HNO_3/H_2SO_4; *b*, $HNO_2/HOAc$

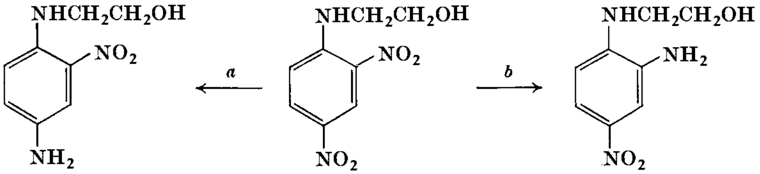
have been shown to be applicable to other *N*,*N*-disubstituted *p*-phenylenediamines.[131]

4-Nitro-2-aminophenol[132] and 2-nitro-4-aminophenol[133] are obtained by nitration of the appropriate acetamidophenol; in the former case some of the 6-nitro isomer is also obtained and, by further nitration, the mixed isomers can be converted to *N*-acetylpicramic acid.

b. Selective Reduction. Reduction of 2,4-dinitroaniline and its *N*-substituted derivatives with ammonium sulfide occurs selectively at the 2-nitro group to give 4-nitro-*o*-phenylenediamines,[134] although some of the 2-nitro para isomer is also formed.[135] Since *N*-substituted 2,4-dinitroanilines are readily obtained by the reaction of 2,4-dinitrochlorobenzene with primary or secondary amines, this method has been used extensively for the preparation of *N*¹-hydroxyalkyl,[109, 114] *N*¹-aminoalkyl,[118] and *N*¹-dialkylaminoalkyl[136] derivatives of 4-nitro-*o*-phenylenediamine (Chart 16).

CHART 16

Selective Reduction of *N*-Hydroxyethyl-2,4-dinitroaniline



Purple Orange-yellow

a, $H_2/Pt/50\%$ aq. H_2SO_4 in ethanol; *b*, Na_2S_x

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[131] D. P. Ainsworth and H. Suschitzky, *J. Chem. Soc.* (*C*) 111 (1966).
[132] H. King, *J. Chem. Soc.* 1059 (1927).
[133] F. Reverdin and A. Dresel, *Ber.* **38**, 1593 (1905).
[134] O. L. Brady, J. N. Day, and C. V. Reynolds, *J. Chem. Soc.* 2264 (1929).
[135] F. Kehrmann, *Ber.* **28**, 1708 (1895).
[136] L'Oreal, *BP* 1,008,844.

A recent patent[113] claims that reduction of 2,4-dinitroanilines with hydrogen and platinum under acidic conditions occurs selectively at the 4-nitro group—thus giving a route to *N*¹-substituted 2-nitro-*p*-phenylenediamines (Chart 16). It has been found that while the *p*-isomer is the major product, some of the *o*-isomer is also produced in this process. The two isomers are readily separable for identification purposes by electrophoresis under mildly acidic conditions.[137a] Selective reduction of 2,4-dinitro-1-naphthylamine by stannous chloride to give 2-nitro-1,4-diaminonaphthalene has been reported.[137b]

c. N-*Alkylation.* Alkylation of 2-nitro-*p*-phenylenediamine normally occurs at the 4-amino group and has been used extensively in the synthesis of nitro dyes. Thus bis-hydroxyethylation has been accomplished using 2-bromoethanol[138] or 2-chloroethanol[113] in aqueous sodium carbonate or sodium hydroxide, and with ethylene oxide in aqueous ethanol.[113] Monohydroxyethylation can also be achieved by treatment of the free amine[109] or the N^4-tosyl derivative[113] with 2-chlorethanol. It is noteworthy that although *N*-monomethylation of a 4-amino group has been described,[113] the reaction is not readily controlled and some dimethylation occurs.[127] The N^4-alkylation or hydroxyalkylation is equally applicable to compounds already having one N^4-alkyl group.[138, 139a] Under drastic conditions, hydroxyalkylation of 2-nitro-*p*-phenylenediamine can yield the N^1,N^4,N^4-tris(hydroxyalkyl) derivative,[110] while that of the N^4-methyl compound can give the N^1,N^4-bis hydroxyalkyl derivative.[139a] It has been reported[139b] that N^1,N^4-dimethylation of 2-nitro-*p*-phenylenediamines can be achieved by the use of formaldehyde/sulfuric acid at 40°–120°.

According to another patent,[121] reaction of 2-nitro-*p*-phenylenediamine with 1-chloro-2,3-epoxypropane gives the N^1,N^4-bis(3-chloro-2-hydroxypropyl) derivatives such as (LIII) which is used in the synthesis of (LIV).

N^1-Alkylation of 2-nitro-*p*-phenylenediamines can be accomplished by the routes shown in Chart 17. While the hydrolytic rearrangement of the chloroethyl ester of the 3-nitrocarbamic acid is interesting,[139a] the alternative route, involving N^1-tosylation of an N^4-acetyl derivative, has been more widely used.[138] More recently, Halasz[139c] has reported the direct N^1-isopropylation of 2-nitro-*p*-phenylenediamine by prolonged

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[137a] J. F. Corbett, *J. Soc. Cosmetic Chemists* **18**, 693 (1967).

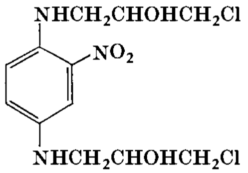
[137b] M. Bil, *Chem. Ind.* 694 (1969).

[138] L'Oreal, *FP* 1,411,124; *BP* 1,061,515.

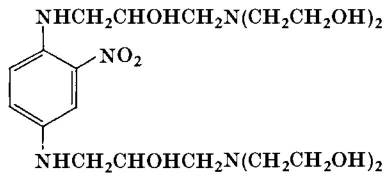
[139a] L'Oreal, *BP* 1,104,974.

[139b] Bristol-Meyers, *FP* 2,008,431.

[139c] A. Halasz, *Chem. and Ind.* 955 (1969).



(LIII)



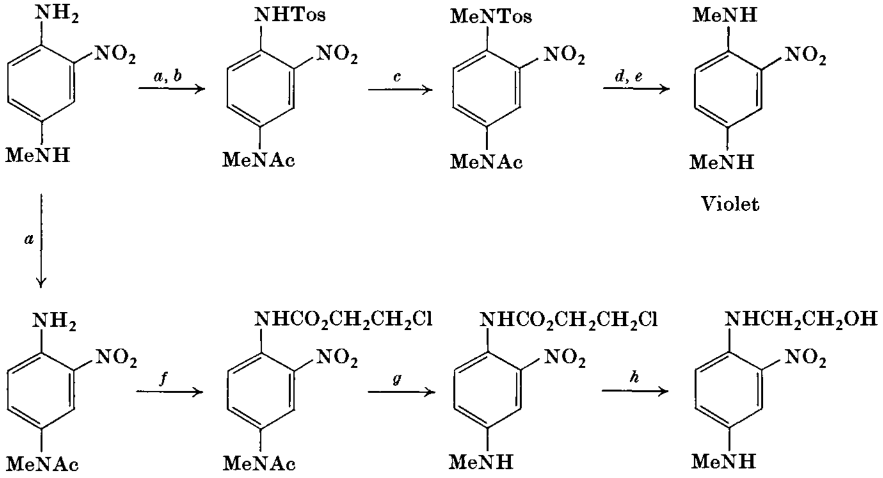
Red-violet

(LIV)

heating with isopropanol in 80% sulfuric acid. N^1,N^4-Bis-alkylation can be achieved via alkylation of the bis-tosyl derivative of 2-nitro-*p*-phenylenediamine.[139d]

CHART 17

N^1-Alkylation of 2-Nitro-*p*-phenylenediamines



a, Ac_2O; *b*, TosCl/pyridine; *c*, Me_2SO_4/NaOH;

d, conc. H_2SO_4 at 0–5°; *e*, aq. HCl under reflux;

f, $ClCO_2CH_2CH_2Cl/CaCO_3$, in iso-BuCOMe under reflux;

g, $HCl/H_2O/HOAc$, under reflux; *h*, 11% KOH in EtOH, under reflux

Aminoalkylation of an amino group meta to the nitro group can be achieved directly using dialkylaminoalkyl chlorides,[136, 140] or indirectly via the *N*-(chloroalkyl) or *N*-(bromoalkyl) derivative, using 1-chloro-2,3-epoxypropane[121] or 1,2-dibromoethane[140, 141] followed by an amine

[139d] Gillette, *BP Appl.* 52306/68.

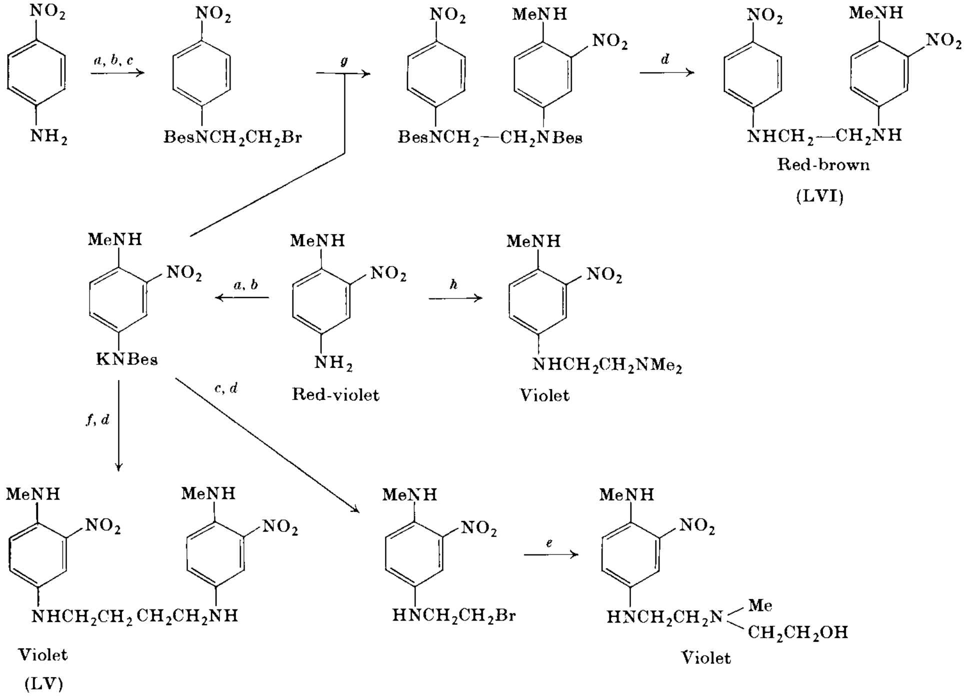
[140] L'Oreal, *BeP* 684,859.

[141] L'Oreal, *BeP* 684,863.

(Chart 18). The N^4-bromoalkyl derivatives are also intermediates in the synthesis of unsymmetrical binuclear nitro dyes, e.g., (LV),[142] as shown in Chart 18. Symmetrical binuclear nitro dyes, e.g., (LVI), can be obtained by a similar route but in a single step (Chart 18).[143] A similar technique, using the scheme in Chart 17, but employing 1,2-dibromoethane as the alkylating agent, gives a route to N^1-aminoalkylated dyes, e.g. (LVIII),[140, 141] as indicated in Chart 19.

CHART 18

Synthesis of Other *N*-Alkylated Nitro Dyes



Bes = Benzenesulfonyl

a, BesCl/pyridine, at 45°; *b*, KOEt in EtOH; *c*, $BrCH_2CH_2Br$ in dimethylformamide (DMF), at 80°; *d*, conc. H_2SO_4 at RT;

e, $MeNHCH_2CH_2OH$ at 120°; *f*, $Br(CH_2)_4Br$ in DMF at 95°;

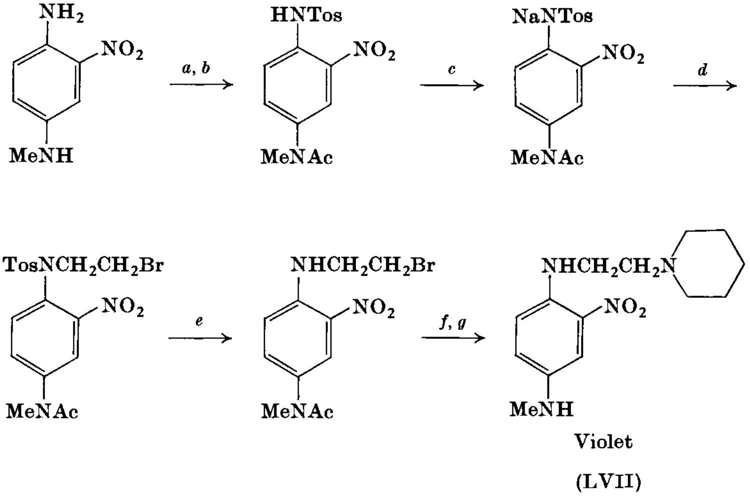
g, in DMF at 120°; *h*, $Me_2NCH_2CH_2Br/CaCO_3$, in H_2O under reflux

N-(Chloroalkyl) derivatives of nitro dyes can also be obtained by treatment of the appropriate *N*-hydroxyalkyl compound with thionyl chloride.[141]

[142] L'Oreal *BeP* 701,743.

CHART 19

N^1-Aminoalkylation of 2-Nitro-*p*-phenylenediamines



(LVII)

a, Ac_2O; *b*, TosCl in pyridine, at 35°; *c*, NaOEt in EtOH; *d*, $BrCH_2CH_2Br$ in DMF, at 100°; *e*, conc. H_2SO_4 at 0–5°; *f*, piperidine, at reflux; *g*, conc. HCl at 100°

N-Alkylation of 4-nitro-*o*-phenylenediamine normally occurs at the 2-amino group and can thus be used in the preparation of N^2-substituted derivatives which are not available by the selective reduction route (see above).[109]

N^4-Aminoalkyl derivatives of 4-nitro-*m*-phenylenediamine can be obtained by treatment of the N^4-tosyl or benzenesulfonyl derivative with haloalkylamines.[116]

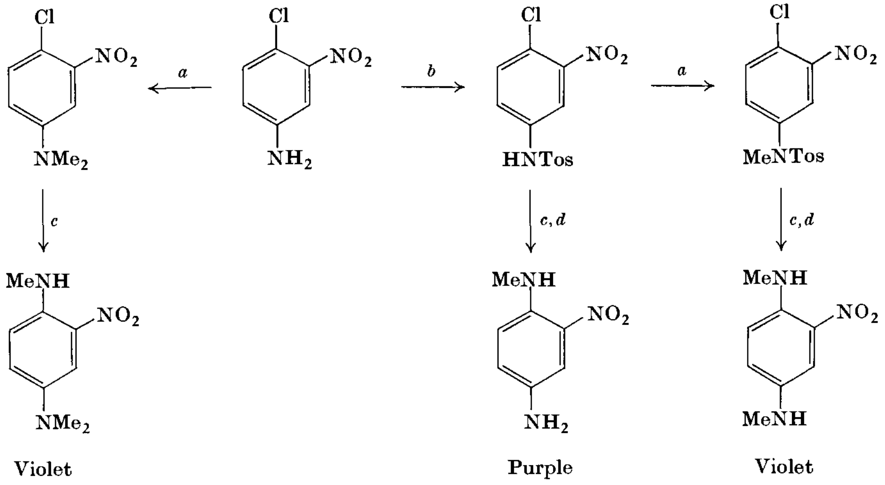
Many of the procedures described above have also been applied to the *N*-alkylation and/or hydroxyalkylation of picramic acid,[109, 121] isopicramic acid,[125] and other nitroaminophenols.[84]

d. Nucleophilic Substitution. *N*-Substituted 2-nitro-*p*-phenylenediamines can be obtained from 4-amino-2-nitrochlorobenzene by the routes shown in Chart 20.[127] It should be noted that the N^4-tosyl group must be retained during the reaction with the amine when the 4-amino group is other than tertiary.

Nucleophilic displacement methods have also been employed in the aminoalkylamination of binuclear nitro dyes.[142, 143a]

[143a] L'Oreal, *BeP* 701,744.

CHART 20
Synthesis of Nitro Dyes from 4-Chloro-3-nitroaniline



a, $Me_2SO_4/NaOH$; *b*, TosCl in pyridine; *c*, $MeNH_2$ in EtOH, at 120–150°; *d*, conc. H_2SO_4, at RT

N^3-Aminoalkyl derivatives of 4-nitro-*m*-phenylenediamines are obtained by nucleophilic displacement of either chlorine, in (LVIII), or nitro, in (LX), with aliphatic diamines, to give the dyes (LIX) and (LXI), respectively (Chart 21). N^1-Substituted 4-nitro-*o*-phenylenediamines can be obtained by amination of 2-fluoro-5-nitroaniline.[143b]

4-Fluoro-2-nitroaniline and 4-fluoro-3-nitroaniline may both be used in the synthesis of *N*-substituted 2-nitro-*p*-phenylene diamines.[143c]

Nucleophilic displacement of active chlorine can also be used in the synthesis of certain *N*-substituted nitroaminophenols; see, for example, Chart 12.[84]

C. ANTHRAQUINONE DYES

1. *Types and Colors*

Prior to 1960 no patents had been published relating to anthraquinone dyes for hair, although the use of anthraquinone disperse dyes in hair color products was not unknown. In the period 1960–67, 14 patents issued describing the synthesis of substituted, water-soluble anthraquinones for dyeing hair. The first dyes to be described, (LXII) and its trimethylammonium analog, were included in a patent claiming the use of

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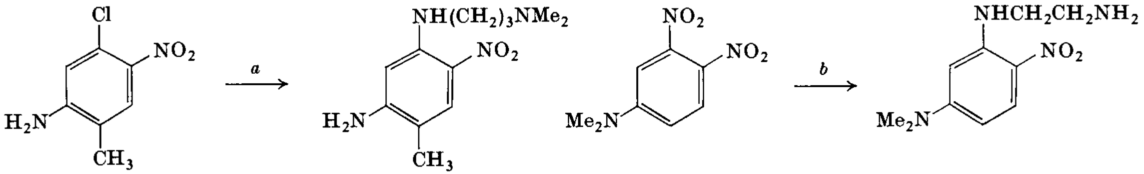
[143b] M. Bil, *Chem. Ind.* 198 (1969).

[143c] Clairol, *BP* 1,206,491; 1,206,492.

CHART 21

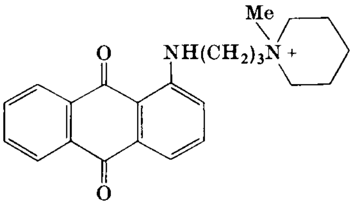
Synthesis of Aminoalkylated 4-Nitro-*m*-phenylene diamines



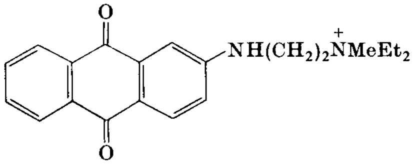
Yellow Bronze

(LVIII) (LIX) (LX) (LXI)

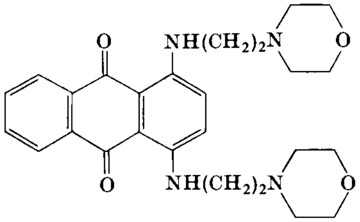
a, $Me_2N(CH_2)_3NH_2$ in pyridine, under reflux; *b*, $H_2N3H_2CH_2NH_2$, under reflux wide variety of organic dyes bearing quaternary ammonium groups.[120] The dialkylaminoalkylamino (DAAA) group and its quaternized variant have since been included in a variety of anthraquinone dyes, thus 1-DAAA-anthraquinones[144] and their 4-hydroxy derivatives,[145]



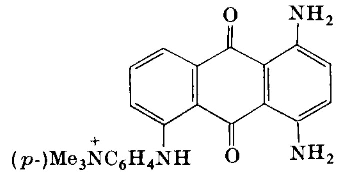
Bordeaux
(LXII)



Golden
(LXIII)



Blue-green
(LXIV)



Blue
(LXV)

2-DAAA-anthraquinones, e.g., (LXIII),[146] 1,4-, 1,5-, and 1,8-bis-(DAAA)anthraquinones, e.g., (LXIV),[147] and 1,4-diamino-5-DAAA-anthraquinones, e.g., (LXV),[148a] have been described in patents. The 5-(ω-aminoalkyl)amino-1,4-diaminoanthraquinones and their N^5-alkyl

[144] L'Oreal. *FP* 1,379,649.

[145] L'Oreal, *BP* 1,053,535.

[146] L'Oreal, *BP* 1,053,536.

[147] L'Oreal, *BP* 1,053,300.

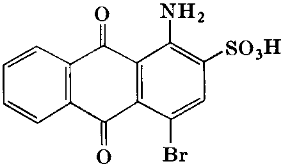
[148a] L'Oreal, *BP* 1,080,164.

and N^1,N^4-alkyl derivatives have also been reported,[148b] as have the N^1,N^4 - bis(ω - dialkylamino - β - hydroxyalkylamino)anthraquinones obtained by reacting the diamine, successively, with epichlorhydrin and a secondary amine.[148c] A further patent claims the quaternary ammonium salts of 2,4-bis(dimethylaminophenylamino)-1-hydroxyanthraquinone as useful blue-gray hair dyes.[149] Some simple 1-aminoalkylaminoanthraquinones and their 4-methylamino derivatives have also been described.[150] Another patent describes dyes containing two NH_2 groups and an aminoalkyl side chain linked to the anthraquinone nucleus via an oxygen or a nitrogen atom.[151] All these dyes are basic by virtue of the amino group remote from the nucleus and, as such, are characterized by a rapid strike and intense coloring power.

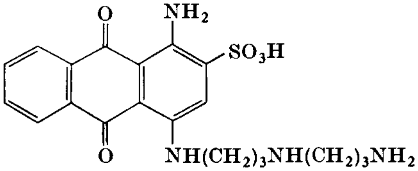
Anthraquinones can also be solubilized by incorporation of polyoxyethylene side chains which can be linked to the nucleus via an oxygen or a nitrogen bridge and may contain a thioether link in the chain, or by an amidomethylene group linked to the nucleus by a sulfur atom.[152] All these solubilizing groups are neutral and the resulting dyes could be considered to be solubilized neutral disperse dyes.

Anthraquinone dyes containing acidic groups have also been reported to dye hair. The dyes described[153] are all 1,4-diaminoanthraquinones containing a 2- or 5-alkylamino or arylamino group having an acidic group on the hydrocarbon residue.

The products of reacting bromamine acid (LXVI) with various amines have been examined and it is claimed that one of these (LXVII) is a particularly good blue hair dye.[154a] Since this dye contains one sulfonic acid group and two aliphatic amino groups it seems likely that it should be considered as a basic dye.



(LXVI)



Blue

(LXVII)

[148b] L'Oreal, *FP* 1,516,943.

[148c] Revlon, *FP* 1,478,780.

[149] L'Oreal, *BP* 1,050,863.

[150] L'Oreal, *BeP* 692,346.

[151] Therachemie, *BP* 1,005,915.

[152] Therachemie, *BP* 957,119.

[153] Therachemie, *BP* 1,005,913.

[154a] Clairol, *BP* 969,377.

A novel class of anthraquinone dye which has recently been patented[154b] is the 1,4-diamino-5-azaanthraquinone and its N^1,N^4-disubstituted derivatives. The substituents may be alkyl, aminoalkyl, dialkylaminoalkyl, hydroxyalkyl, alkoxyalkyl, or aryl. The carbocyclic analogs of these dyes have also been claimed to dye hair.[154c]

The colors available from the variously substituted anthraquinones which have been described are shown in Table XIV. It can be seen that

TABLE XIV

COLORS FROM ANTHRAQUINONE HAIR DYES

Anthraquinone substituents[a]	*Color on hair*	*References*[b]
1-OCH_2R	Yellow	1
1-$HNCH_2R$	Red	2
2-$NHCH_2R$	Golden yellow	3
1,4-bis-$NHCH_2R$	Blue-green to blue	4
1,5-bis-$NHCH_2R$	Violet-pink	4
1,8-bis-$NHCH_2R$	Mauve to violet	4
1-OH-4-$NHCH_2R$	Violet	5
1-SCH_2R-4-NH_2	Violet	1
1,4-di-NH_2-2-OCH_2R	Red	6, 7
1,4-di-NH_2-2-$NHCH_2R$	Red	6, 7
1,4-di-NH_2-2-$N(CH_2R)_2$	Blue-red	6, 7
1,4-di-NH_2-5-OCH_2R	Blue-red	1, 6
1,4-di-NH_2-5-$NHCH_2R$	Blue	7, 8
1,4-di-NH_2-5-$N(CH_2R)_2$	Blue	7
1-OH-2,4-bis-$NHC_6H_5NMe_3$	Violet-gray	9
1-NH_2-2-SO_3H-4-NHR	Blue	10
1,4-di-NH_2-2,3-bis-OCH_2R	Blue-red	1

[a] R may be hydrogen, aminoalkyl, polyoxyethylene, *N*-amido, carboxyalkyl or aryl, or a sulfonated alkyl or aryl group.

[b] Key to references:

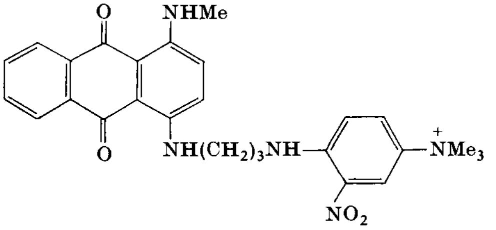
1. Therachemie, *BP* 957,119.
2. L'Oreal, *FP* 1,379,649; *BeP* 692,346.
3. L'Oreal, *BP* 1,053,536.
4. L'Oreal, *BP* 1,053,300.
5. L'Oreal, *BP* 1,053,535.
6. Therachemie, *BP* 1,005,915.
7. Therachemie, *BP* 1,005,913.
8. L'Oreal, *BP* 1,080,264.
9. L'Oreal, *BP* 1,050,863.
10. Clairol, *BP* 969,377.

[154b] Clairol, *BP* 1,134,953.

[154c] Clairol, *SAfr.P* 67/2346.

these range from yellows through to blues and, as noted for nitro dyes, the color is dependent on the substitution pattern on the nucleus, only minor modifications being produced by varying the nature of *N*- or *O*-substituents.

Some unusual anthraquinone dyes, e.g., (LXVIII), have been obtained by reacting 1-methylamino-4-(3′-aminopropylamino)anthraquinone with 3,4-dinitro-*N*,*N*-dialkylanilines and quaternizing the resulting condensate.[142] The green color of (LXVIII) is presumably due to independent absorption of the blue anthraquinone and the yellow nitroaniline moieties, acting additively.



Green

(LXVIII)

The application of basic anthraquinone dyes to hair has been discussed in technical papers.[155]

2. *Synthesis*

The processes employed to introduce the dialkylaminoalkylamino (DAAA) group into the anthraquinone nucleus are the well-known nucleophilic displacement reactions of the anthraquinone system (Charts 22 and 23). Thus, the mono-DAAA-anthraquinones, e.g., the precursors of (LXII) and (LXIII), are obtained by heating 1- or 2-chloroanthraquinone with the appropriate dialkylaminoalkylamine in the presence of a base.[144, 146] 1-Hydroxy-4-DAAA derivatives are obtained by heating quinizarin with a dialkylaminoalkylamine.[145] If the reaction is carried out with an excess of amine and in the presence of zinc powder, both hydroxy groups are replaced and 1,4-bis(DAAA)anthraquinones are obtained (Chart 22).[147] The 1,5- and 1,8-bis(DAAA) compounds are obtained from the appropriate dichloroanthraquinone (Chart 22).[147] 1,4-Diamino-5-DAAA-anthraquinones are obtained by displacement of the nitro group in 1,4-diamino-5-nitroanthraquinone (Chart 23).[148a] Reaction of purpurin with 4-dimethylaminoaniline in the presence of boric acid is reported to result in the replacement of the 2- and 4-hydroxy groups by *p*-dimethylaminophenylamino groups.[149]

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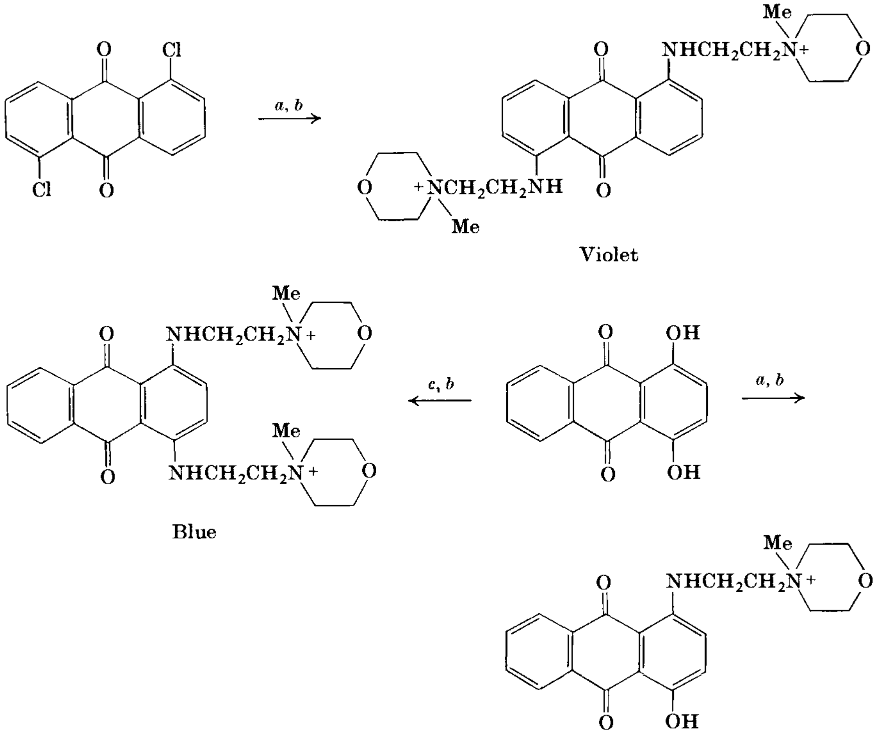
[155] G. Kalopissis, A. Bugaut, and J. Bertrand, *J. Soc. Cosmetic Chemists* **15**, 411 (1964); P. Berth and W. J. Kaiser, *ibid* **18**, 705 (1967).

CHART 22

Synthesis of Dialkylaminoalkylamino Anthraquinones



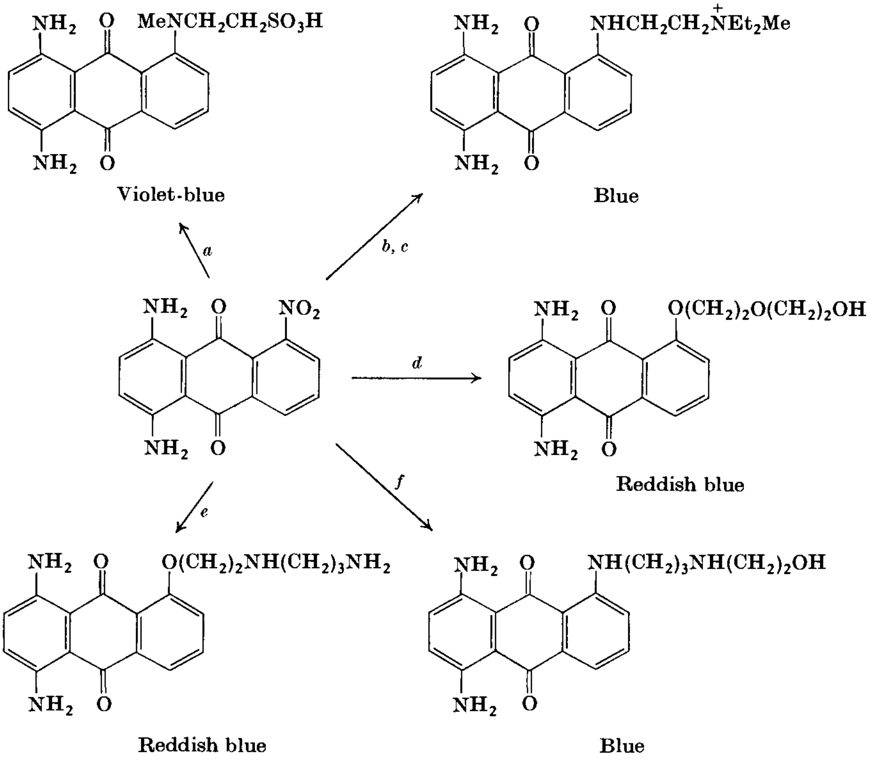
a, *N*-(2-aminoethyl)morpholine (2-AEM) in iso-BuOH, under reflux; *b*, Me_2SO_4 in toluene; *c*, 2-AEM and Zn dust in iso-BuOH, under reflux

Anthraquinones with an acidic side chain are obtained by heating 1,4-diamino-5-nitroanthraquinone or 1,4-diamino-2-chloroanthraquinone with an amino acid, e.g., *N*-methyltaurine (Chart 23).[153] The same starting materials are also used in the synthesis of aminoanthraquinones with neutral side chains (Chart 23).[152] A basic side chain linked to the nucleus by an ether bridge can also be introduced using these two precursors, by reaction with alkanolamines in the presence of sodium hydroxide.[151] By contrast, if the reaction is performed in the absence of sodium hydroxide, the reaction occurs at the aliphatic nitrogen atom (Chart 23).

Aminoalkylamino groups are also introduced by reaction of the appropriate amine with 4-bromo-1-methylaminoanthraquinone[150] or

CHART 23

Synthesis of Anthraquinone Dyes from 5-Nitro-1,4-diaminoanthraquinone



a, *N*-methyltaurine/NaOH in $PhNO_2$ at 50–100°; *b* $Et_2N(CH_2)_3NH_2$ at 105–110°; *c*, Me_2SO_4 in $PhNO_2$, at 80°; *d*, $(HOCH_2CH_2)_2O/Na$; *e*, $HOCH_2CH_2NH(CH_2)_3NH_2$ + NaOH, at 50°; *f*, $HOCH_2CH_2NH(CH_2)_3NH_2$, at 30° (no NaOH).

with bromamine acid (LXVI).[154a] The reaction of leucoquinizarin with diaminoalkanes has recently been the subject of a detailed study. The abnormal spectrum of the reaction product with ethylenediamine, originally attributed to hydrogen bonding,[156] has now been shown to be due to the product being 6-β-aminoethylamino-1,2,3,4-tetrahydronaphtho[2,3*f*]quinoxaline-7,12-dione, formed by oxidative cyclization of the intermediate leuco form of 1,4-bis-β-aminoethylaminoanthraquinone (Chart 24).[157] Greenhalgh and Hughes[158] found that 1,4-bis-(β-aminoethylamino)anthraquinone is the major product when the

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[156] M. S. Symon, *J. Am. Chem. Soc.* **85**, 1974 (1963).

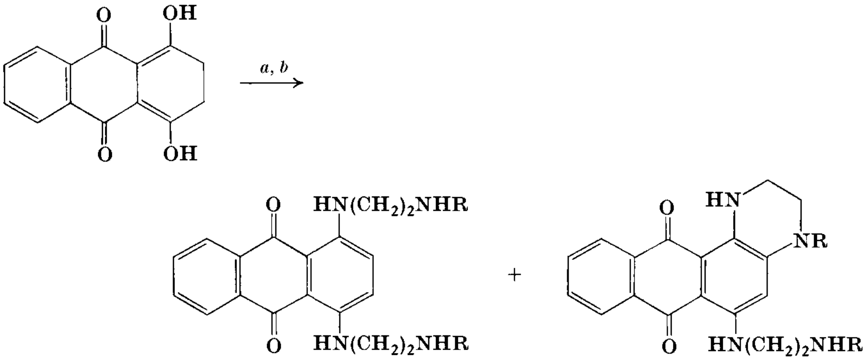
[157] M. S. Symon and D. P. Waller, *Tetrahedron Let.* 1527 (1967).

[158] C. W. Greenhalgh and N. Hughes, *J. Chem. Soc.* (*C*) 1284 (1968).

reaction is performed at 50°, while at 100° the anthraquinone and the quinoxaline are obtained in about equal amounts. 5,8-Dihydroxyleucoquinizarin gives the analogous quinoxaline derivative.[158] The reaction of leucoquinizarin with 2-dialkylaminoethylamines and with 1,3- and 1,4-diaminoalkanes gives the normal 1,4-disubstituted anthraquinones.[158] Similar quinoxaline derivatives are obtained when 1-chloroanthraquinone is reacted with ethylenediamine, *N*-methyl ethylenediamine, and *o*-phenylenediamine.[159] These results indicate that care should be taken in assigning structures to the reaction products of reactive anthraquinones with 1,2-diamines.

CHART 24

Reaction of Leucoquinizarin with 1,2-Diaminoethylenes



a, $RNHCH_2CH_2NH_2$ (R = H, Me, or Et) under N_2; *b*, air bubbled in

D. Naphthoquinone Dyes

2-Hydroxynaphthoquinone (lawsone) was one of the "natural" dyes used in early dyeing practice (see Section I). Other hydroxynaphthoquinones have also been found to be useful in dyeing hair. Thus, 5-hydroxy-1,4-naphthoquinone imparts a golden blond color,[160] the 5,8-dihydroxy compound gives blue-gray shades,[160, 161] and the 5,6,8-trihydroxy compound dyes hair to a titian red.[160, 162]

Substituted 1,4-naphthoquinoneimine dyes, e.g., (LXXI), can be prepared by the condensation of 5-amino-8-hydroxy-1,4-naphthoquinone (LXX) with a primary amine in aqueous solution.[163] The

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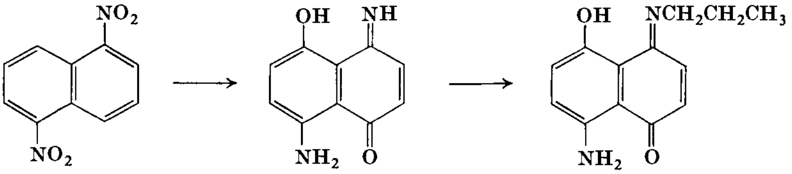
[159] H. P. Kolliker and P. Caveng, *Chimia* **20**, 281 (1966).

[160] Gillette, *BP* 889,813.

[161] Clairol, *BP* 1,003,600.

[162] Clairol, *FP* 1,379,157.

[163] Clairol, *BP* 1,097,271.



Gray-blue

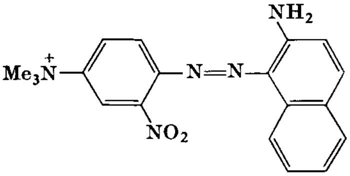
(LXIX) (LXX) (LXXI)

intermediate (LXX) is obtained by the reaction of 1,5-dinitronaphthalene (LXIX) with sulfur in oleum at 95°. In addition to alkylamines, hydroxyamines, alkoxyamines, amino heterocyclic compounds, and aliphatic and aromatic primary amines with a tertiary amino substituent may be used. The dyes so obtained are all gray-blue to deep blue. By using diamines, bis-naphthoquinoneimine derivatives can be prepared. If nitroamines are employed in the condensation, the presence of yellow and blue moieties gives the resulting dye a blue-green color.

5,8-Dihydroxynaphthoquinone undergoes similar condensations with primary amines to give blue dyes.[163]

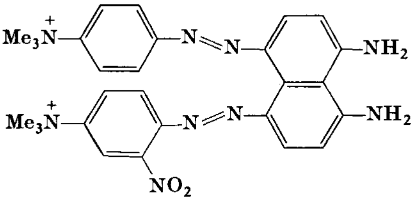
E. Azo Dyes

The patent dealing with quaternary ammonium derivatives of nitro and anthraquinone dyes for hair also included a number of quaternized azo dyes.[120] Yellow to red-violet and black dyes, e.g., (LXXII), are obtained by coupling dimethylaminoanilines with *N*,*N*-dimethylaniline or with naphthylamines and quaternizing the dye, while brown to brown-black disazo dyes, e.g., (LXXIII), are similarly obtained using polyaminonaphthalenes as couplers. Examples of the colors obtainable are given in Table XV. Dyeing data for some of these has been reported.[164] Simple diaminoazo dyes have also been reported to be useful hair dyes,[165] as



Red-brown

(LXXII)



Brown

(LXXIII)

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[164] P. Berth and W. J. Kaiser, *J. Soc. Cosmetic Chemists* **18**, 705 (1967).

[165] Therachemie, *BP* 1,008,858.

have the acid dyes obtained by coupling diazotized anilinesulfonic acids with aromatic amines and with phenols.[166]

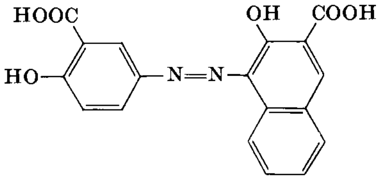
TABLE XV

COLORS FROM BASIC AZO DYES FOR HAIR[a]

Diazonium component	*Coupler*	*Coupling position*	*Methyl quaternary salt*	*Color on hair*
4-Dimethylamino-2-nitroaniline	$PhNMe_2$	4	Mono	Deep red
	$PhNMe_2$	4	Bis	Golden
	1-NH_2-nap	4	Mono	Red-violet
	2-NH_2-nap	1	Mono	Red-brown
	1-Me_2N-nap	4	Mono	Red-violet
	1,5-$(NH_2)_2$-nap	4,8-bis	Bis	Brown
	1,5-$(NH_2)_2$-nap	4	Mono	Brown
	1,3,8-$(NH_2)_3$-nap	4,5-bis	Bis	Black-brown
	1,3,5-$(NH_2)_3$-nap	8	Mono	Black
	2,4,8-$(NH_2)_3$-nap	1	Mono	Black
4-Dimethylamino-aniline	$PhNMe_2$	4	Mono	Orange
	1-Me_2N-nap	4	Mono	Orange

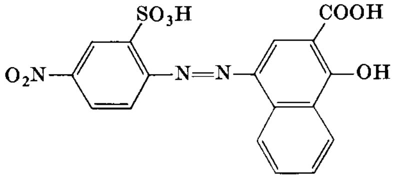
[a] Therachemie, *BP* 909,700.

The acid azo dyes (LXXIV)[167] and (LXXV)[168] have been claimed as particularly good for dyeing hair.



Brown

(LXXIV)



Brown

(LXXV)

Polyhydroxyazobenzenes (e.g., 2,3,4-; 3,4,5-; 2,4,6-; 2,4,2′-; 2,4,4′-; 2,3,4,4′-; 3,4,5,4′-; and 2,4,6,4′-) and dihydroxyaminoazobenzenes (e.g., 2′,4,2-; 2,3′,4-; 4,4′,2-; and 2,4′,4-) are readily prepared by the appropriate coupling reactions and dye hair to yellow, greenish yellow or reddish yellow shades.[169a]

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[166] Therachemie, *BP* 1,014,720.

[167] Breck, *USP* 2,775,972.

[168] DuP *USP* 2,532,588.

[169a] L'Oreal, *BP* 938,045.

Basic azo dyes, based on 4-nitrophenylazoaniline in which the amino group bears an aminoalkyl substituent, are reported to be compatible with basic anthraquinone dyes.[148b] Other basic azo dyes are obtained by coupling 2-aminobenzthiazole with N-(ω-aminoalkyl)-N-alkylanilines and their N^{ω}-substituted derivatives.[169b]

Azopyridine dyes for hair have been obtained by coupling diazotized aminoarenesulfonic acids with diamino, dihydroxy, and aminohydroxy pyridines of the type used in oxidative dyeing (Section III). Heilingotter[170] gives the colors of 66 such dyes, which range from yellow to blue-violet. The colors seem to be dependent mainly on the pyridine component, dyes from 2,3-diaminopyridine being mainly yellow and orange, those from 2,5-diaminopyridine being mostly purple, and those from 2,6-diaminopyridine being predominantly orange to red. A blue-violet dye is obtained from sulfanilic acid → 2-(2′-hydroxyethylamino)-5-aminopyridine and a dull brown dye from 4-aminodiphenylamine-2-sulfonic acid → 2,6-dihydroxypyridine.

F. CARRIER DYEING OF HUMAN HAIR

It has already been mentioned that the different permeability of hair and wool and the mild conditions necessary to "on head" dyeing render many textile dyes of little value in hair dyeing, on account of their molecular dimensions.[14, 15] Factors involved in the comparison between hair and textile dyeing have been discussed by Wilmsmann.[171]

Following the discovery by Peters and Stevens[172] of the carrier action of certain organic solvents in facilitating the dyeing of wool from aqueous baths under relatively mild conditions, considerable efforts were made to apply this process to hair dyeing. Thus, the use of benzyl alcohol, amyl lactate, or amyl alcohol was claimed to promote dyeing by acid dyes, basic dyes, direct dyes, neutral premetallized dyes, and even by pigment dyes.[173] All the dyes used are poorly soluble in an aqueous bath, but in a later patent[174] it was claimed that the process could be applied to soluble anionic dyes provided a cationic surfactant is included in the dye bath. Alternatively, the carrier action can be promoted, using F. D. and C. colors, by the presence of inorganic salts.[175] The carrier-dyeing system is further improved by the addition of a wide variety of

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[169b] L'Oreal, *FP* 1,560,664.

[170] R. Heilingotter, *Fette, Seifen, Anstrichmittel* **69**, 683 (1967).

[171] H. Wilmsmann, *Am. Perfumer and Aromat.* **75**, 41 (1960).

[172] L. Peters and C. B. Stevens, Dyer **115**, 327 (1956); *J. Soc. Dyers and Colourists* **72**, 100 (1956); *ibid* **73**, 23 (1957).

[173] L. Peters and C. B. Stevens, *BP* 826,479; L'Oreal, *BP* 840,904.

[174] Rapidol, *BP* 918,597.

[175] Gillette, *USP* 3,352,755.

solid compounds to the composition.[176] Suitable additives include benzoic acid, phenols, esters, phenylurea, and amides.

In addition to the above-mentioned carriers, Cellosolve, Carbitol, and isoamyl alcohol/ethylene oxide condensates,[177] and isopropanol[178] have been found to be useful. Alkylated ureas particularly tetraethylurea, have been found to act as carriers for disperse dyes.[179]

One of the problems associated with dyeing hair with simple acid dyes is their lack of fastness. This is claimed to be overcome by the addition of cationic surfactants to the dye composition.[180]

Using these various techniques, most textile dyes can be made to impart color to human hair, but products based on them have not obtained a large market, indicating that they do not match up to the popular oxidative and nitro dye types of product. One major disadvantage of the carrier dye systems is the enhanced skin staining which often accompanies the process.

G. REACTIVE DYES

The increased permanence of dyeings achievable with reactive dyes has attracted the attention of the hair dyer. The patented processes involve prior or simultaneous reduction of the hair with one of a variety of reducing agents,[181] prior treatment of the hair with a persulfate or other peroxy compound,[182] or with a polythiolated polymer.[183] The dyes used in these processes include both the substitutive Procion, Drimarene, and Cibacron, and the additive Levafix and Remazol types, although it has been reported that the Procion dyes would not react at the low temperatures and have a tendency to stain the scalp.[184] The necessity to have free thiol groups for reaction with vinyl sulfone dyes is indicated by the ratio 10,000:100:1 for the reactivity of SH:NH:OH groups towards this dye.[185] Shansky[186] has shown that in dyeing with Procion Black HGS it is necessary to reduce the hair and to incorporate a hydrogen bond breaker, such as urea or lithium bromide, in the dyebath. It has been reported that hair can be dyed by precipitation of alginic acid

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[176] Unilever, *BP* 1,096,943.

[177] L'Oreal, *BP* 819,184.

[178] Superma, *BP* 979,292, 979,294.

[179] Clairol, *BP* 979,405.

[180] J. W. Orelup, *USP* 2,208,594, 2,359,783; Avon Products, *CP* 753,613.

[181] Turner Hall, *BP* 951,021; Precision Processes, *BP* 1,016,951.

[182] Unilever, *CP* 771,632.

[183] L'Oreal, *FP* 1,440,691.

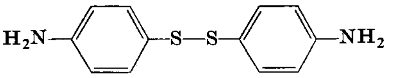
[184] P. Alexander, *Am. Perfumer Cosmetics* **82**, 31 (1967).

[185] J. F. Corbett, *Proc. 3rd Intern. Wool Textile Res. Conf.* Vol. III, p. 321 (Paris), 1965.

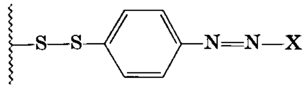
[186] A. Shansky, *Am. Perfumer Cosmetics* **81**, 23 (1966).

within the fiber and treatment with a reactive dye.[187] Alternatively, the alginate may be predyed with a reactive dye and then precipitated within the hair fiber by acid treatment.

Reactive azo dyes containing Bunte salt[188, 189] and vinyl sulfone groups[189] have been prepared and used as hair dyes. A novel type of reactive dye is obtained by coupling the bis-diazonium salt of (LXXVI) with an appropriate coupler and using the resultant dye in the presence of a reducing agent.[190] It is likely that during the dyeing process the disulfide linkage is broken and the resulting thiolated dye could subsequently combine with a cysteine residue, thus becoming covalently bonded to the keratin chain (LXXVII). The shades obtainable by this process range from orange-yellow, using 2-naphthylamine as coupler, to violet-brown, using "phenyl-gamma acid."



(LXXVI)

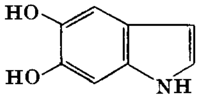


(LXXVII)

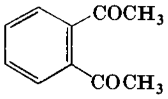
A detailed discussion of the possibilities of dyeing hair with reactive dyes has been published by Broadbent,[191] who concludes that the dyes presently available offer little scope because of the difficulties inherent in the application procedure.

VI. Miscellaneous Dyes

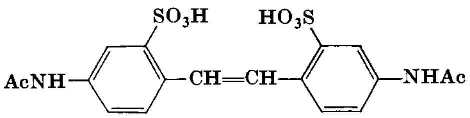
Attempts to simulate the natural hair color process by using melanin precursors have been made. Thus hair can be dyed using 5,6-dihydroxyindole (LXXVIII) in the presence or absence of metal catalysts, and



(LXXVIII)



(LXXIX)



(LXXX)

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[187] Schwarzkopf, *DRP* 1,247,552.

[188] Partipharm, *DRP* 1,194,099.

[189] Partipharm, *BP* 1,009,796.

[190] L'Oreal, *BP* 833,809.

[191] A. D. Broadbent, *Am. Perfumer Cosmetics* 78, 21 (1963).

allowing oxidation to occur within the fiber.[192] Alkyl derivatives of (LXXVIII) may also be used.[193] Another process claims dyeing with "dopa" (see Chart 1) in the presence or absence of tyrosinase.[194] Unfortunately, the melanin formed under these conditions is probably dispersed throughout the fiber, rather than deposited in granules, and the nuances of the natural process cannot be imitated.

The reaction of *o*-diacetylarenes with amino acids, which is similar to that of ninhydrin, has been exploited in a dyeing process employing 1,2-diacetylbenzene (LXXIX) or its 4-nitro derivative.[195] The former gives a russet blonde to red-violet coloration. Similarly, the color-forming reaction of various sugars, e.g., erythrose, in the presence of nitrogeneous compounds, e.g., ammonium salts or glycine, has been claimed for dyeing hair.[196] The products of this type of reaction are brown materials, referred to as Maillard melanoidins.[197]

Finally, it has been claimed that phototropic materials, such as (LXXX), can be used in dyeing hair.[198]

VII. Colored Hair Sprays

The development of hair sprays as fixatives in hair styling was closely followed by the concept of colored hair sprays, for producing a temporary highlighting color effect which is removed by brushing or shampooing. This can be accomplished by incorporating in the spray, colored particles or pigments[199] or dyes.[200] Dyes can have the disadvantage that they might diffuse from the lacquer into the hair fiber, where they would be more difficult to remove. To overcome this, much effort has been devoted to producing colored hair-spray polymers in which the chromophore is covalently bound to the polymer, thus preventing diffusion.

The production of colored polymers can be accomplished by the copolymerization of colorless and colored monomers or by the preparation of polymers containing reactive groups capable of subsequent combination with conventional dye molecules. An example of the first

[192] L'Oreal, *BP* 797,174; 823,503.

[193] L'Oreal, *BP* 887,579.

[194] S. M. Peck, *USP* 2,539,202.

[195] L'Oreal, *BP* 938,045.

[196] S. F. Warren, *BP* 953,170.

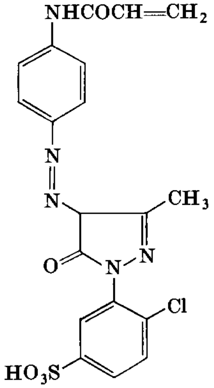
[197] J. E. Hodge, *J. Agr. Food Chem.* **1**, 929 (1953).

[198] V. E. B. Farbenfabriken Wolfen. *DRP* 1,130,114.

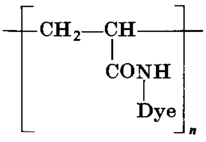
[199] Steiner, *BP* 721,045.

[200] Warner-Lambert, *USP* 3,215,604.

approach is the copolymerization of the dye (LXXXI) with vinylpyrrolidone or with a mixture of vinylpyrrolidone and acrylamide.[201] The dye is obtained by coupling diazotized *N*-acryloyl-*p*-phenylenediamine with the pyrazolone.

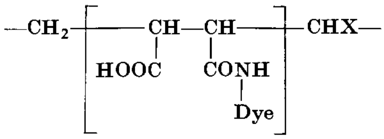


(LXXXI)



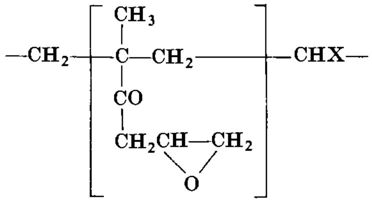
$$\left[-CH_2-\underset{\underset{\underset{\text{Dye}}{|}}{CONH}}{\underset{|}{CH}}-\right]_n$$

(LXXXII)

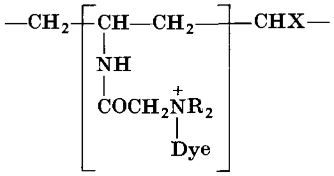


$$-CH_2-\left[\underset{HOOC}{\underset{|}{CH}}-\underset{\underset{\text{Dye}}{CONH}}{\underset{|}{CH}}\right]-CHX-$$

(LXXXIII)



(LXXXIV)



$$-CH_2-\left[\underset{\underset{\underset{\text{Dye}}{COCH_2\overset{+}{N}R_2}}{NH}}{\underset{|}{CH}}-CH_2\right]-CHX-$$

(LXXXV)

Polymers containing the group (LXXXII) can be obtained by reaction of polyacryloly chloride with an aminoanthraquinone or nitrophenylenediamine.[202] Similarly, copolymers of normal vinylic monomers and maleic anhydride can be reacted with a dye containing an amino or hydroxy group to give a colored polymer (LXXXIII).[203] To adjust the number of dye molecules in the polymer, an alcohol may be added during the reaction to combine with a proportion of the anhydride groups. Reactive esters, e.g., monobutyl maleate or vinylic acid chlorides, can similarly be employed in producing reactive polymers for subsequent reaction with a dye.[204] A further alternative is the use of a glycidyl monomer, e.g., glycidyl methacrylate, in the production of reactive

[201] BASF, *BP* 877,402; 965,602.

[202] L'Oreal, *BP* 993,181.

[203] L'Oreal, *BeP* 684,233; 699,974.

[204] L'Oreal, *BeP* 692,343; 702,309.

polymers (LXXXIV).[205] The polymer can then be made to react with a dye of the type Dye—$(CH_2)_n$—NH_2, via the epoxy group.

Polymers containing pendant quaternary ammonium salt dyes, (LXXXV), can be prepared via copolymers of normal monomers and *N*-vinyl- or *N*-allylchloracetamide, which are then reacted with a dye of the type Dye—$(CH_2)_n$—NR_2.[206]

Colored hair sprays have been marketed but, except in Australia, they have had little appeal.[207] The main disadvantages of this type of product are the low tinctorial power and the tendency, when dispensed as an aerosol, to adhere to the skin and to towels and clothing.

[205] L'Oreal, *FP* 1,484,836.

[206] L'Oreal, *BeP* 680,927.

[207] M. J. Root, *Am. Perfumer Aromat.* **75**, 43 (1960).

CHAPTER VIII

FLUORESCENT BRIGHTENING AGENTS

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During the last three decades the idea of "white" has undergone a radical change, since the production of white on paper, textiles, and plastics is no longer dependent on bleaching—mostly with inorganic bleaching compounds—nor on the addition of white pigments. Initiated and developed in Germany, optical brightening agents with which white can be produced by fluorescence on these materials were introduced at the end of the 1930s, first by IG-Farbenindustrie and later also by dyestuff manufacturers in Switzerland, England, and the United States.

In this chapter the performance, production, and application of the most important fluorescent brightening agents on the market will be described.

I. General Considerations

A. DEFINITION OF FLUORESCENT BRIGHTENING AGENTS AS DYES

Fluorescent brightening (or whitening) agents[1] are colorless fluorescent dyes. Although in the literature they are also often called fluorescent or optical bleaching agents,[2] the properties of fluorescent brightening agents cannot be compared with those of bleaching agents; the only characteristic common to both groups of substances is that they increase the whiteness of the material to which they are applied.

In accordance with their definition as "colorless" fluorescent dyes, their coloristic performance is that of fluorescent dyes, without absorbing light in the visible range of the spectrum.

Fluorescent brightening agents are applied as dyes, the fastness properties of the white shades achieved being evaluated on coloristic principles. Special characteristics are required of fluorescent brightening agents when used in combination with detergent products or in the brightening of spinning compounds. In addition to the coloristic properties as colorless fluorescent dyes, further requirements are dispersibility and compatibility with the detergent components, as well as resistance to temperature and sublimation.

Although the trade names reveal the use of the products as fluorescent brightening agents, or indicate the name of the manufacturers, they do not usually show membership in a particular dyestuff range or group of compounds. For example, the fluorescent brightening agents of Farbenfabriken Bayer are marketed as Blankophor and those of Geigy as Tinopal.[3] Only in a few cases does the trade name indicate a particular

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[1] ASTM, *Am. Dyestuff Reptr.* 303 (1968).

[2] In the Chemical Abstracts Register: Code word "bleaching agents" recently also "fluorescent or optical brightening agents."

[3] CI, fluorescent brightening agents (Nos. 1–198).

dyestuff range; for example, Palanil White of Badische Anilin und Soda Fabrik is a fluorescent brightening agent which as a member of the "Palanil dyestuff range" is suitable for the optical brightening of polyester fibers, and "Paper White" is a Du Pont product which is used for the optical brightening of paper. A summary of the most important producers, who also generally hold patent rights, together with the trade names of their products, is given in Table I.

TABLE I

PRODUCERS OF FLUORESCENT BRIGHTENING AGENTS

Manufacturer	*Country*	*Trade name*
Amer. Cyanamid Comp.	U.S.	Branco Calcofluor Calcofluorwhite Fluorwhite
Du Pont	U.S.	Paperwhite Pontaminwhite
General Dyestuff Corp.	U.S.	Antara Brightener Blancophor Brightener Tintofen
Verona Pharma Chemical Co.	U.S.	Phorwhite
Hickson & Welsh	England	Photine (Solium)
Imp. Chem. Ind.	England	Fluolite
Chem. Ind., Basel, Ciba	Switzerland	Uvitex
Geigy	Switzerland	Tinopal
Sandoz	Switzerland	Leukophor, Leucophor Leucopur Sandowhite
Badische Anilin & Soda Fabr.	Germany	Blankit Palanilweiß Ultraphor (Ultraweiß)
Farbenfabriken Bayer	Germany	Blankophor
Farbwerke Höchst	Germany	Hostalux
VEB Wolfen	Germany	Weißtöner Wolfen
Francolor	France	Fluotex
Farbenfabriken Delft	Netherlands	Delftwhite
Sigma	Italy	Optiblanc
Daiton Kagaku	Japan	Daitophor
Mitsui Kayaku	Japan	Mikephor
Nihon Soda K.K.	Japan	Kaycoll
Nippon Kayaku	Japan	Kayaphor
Showa Kayaku	Japan	Hakkol
Sumitomo	Japan	Whitex

The world's annual production of fluorescent brightening agents, including about 200 products of 15 different types, amounts to approximately 27–35 million kilograms, valued at 100–150 million dollars. This represents about 10% of the business in dyestuffs. The total may be broken down as follows:

	%
Detergent mixtures	58
Paper brightening	25
Textile finishing	12
Plastics and spinning compounds	5

In 1966 fluorescent brightening agents to the value of 25 million dollars were used in the United States in soaps and detergents.

B. RELATIONSHIP BETWEEN UV ABSORPTION AND FLUORESCENT BRIGHTENING

The special position of fluorescent brightening agents is due to their specific physical properties; they absorb invisible ultraviolet radiation from daylight and emit visible, predominantly blue, fluorescent light. Because of their ability to absorb ultraviolet radiation, fluorescent brightening agents are UV-absorbers, while they are fluorescent dyestuffs as a result of their ability to emit fluorescent light.

In Figs. 1, 2, and 3 this characteristic spectral behavior of the three

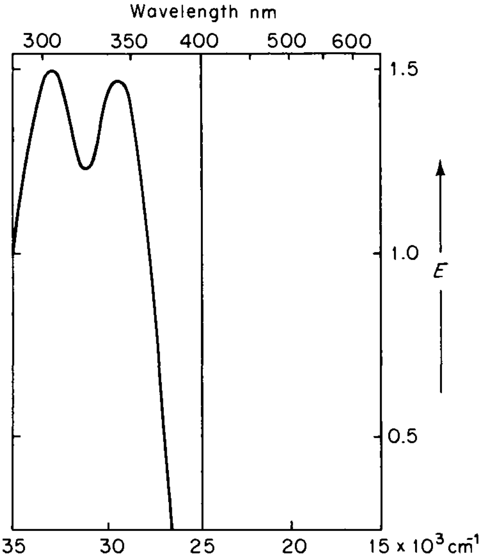

FIG. 1. UV-absorber (Tinuvin P).

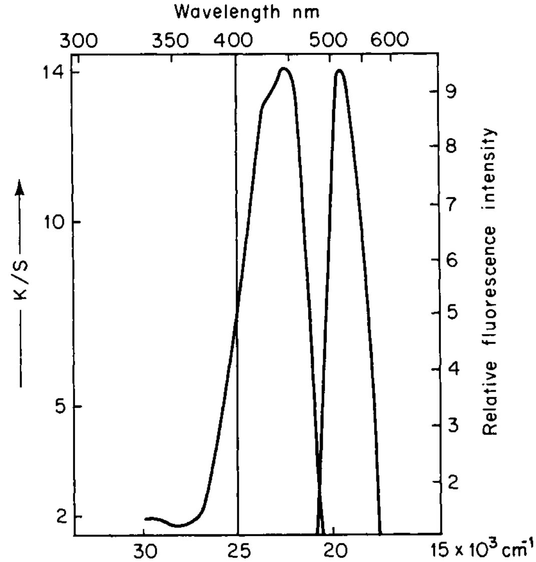

Fig. 2. Fluorescent dyestuff.

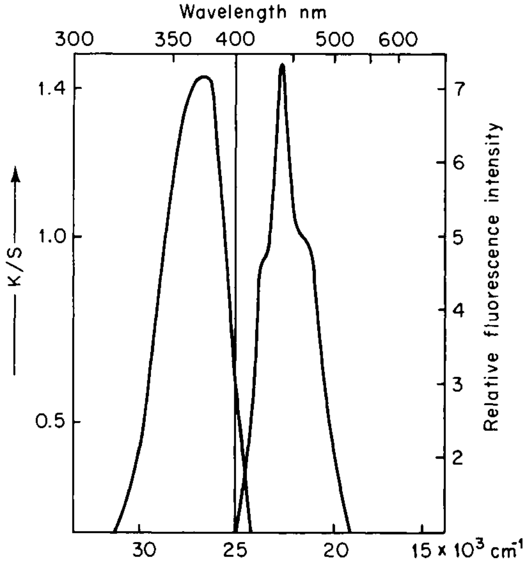

Fig. 3. Fluorescent brightening agent (Blankophor CL).

groups of substances is compared with regard to the UV absorption and the emission of fluorescent light.

The ideal UV-absorber (Fig. 1) absorbs the entire long-wave UV component from daylight. It emits no radiant energy.

The fluorescent dye (Fig. 2) absorbs visible light as a normal dye. Contrary to normal dyes, it transforms the absorbed energy into light of longer wavelength. This combines with the reflected light to produce a total color impression. Fluorescent dyeings are therefore notable for particularly high brilliance.

Similar to a UV-absorber, the fluorescent brightening agent (Fig. 3) absorbs in the longest-wave UV range. In contrast to the UV-absorber, the absorbed energy is transformed into fluorescent light, which is emitted at longer wavelengths in the visible part of the spectrum. Since there is no absorption in the visible spectral range the color impression is produced by pure fluorescent light.

Figures 2 and 3 show that the luminous reflectance curve of the fluorescent light is approximately a mirror image of the absorption curve. Luminous reflectance begins where absorption ends. From the shape and position of the absorption maximum, the shape and position of the luminous reflectance curve, as well as the color of the fluorescent light, can therefore be deduced. In the case of fluorescent brightening agents, the absorption maximum in the UV ranges between 340 and 400 nm, or wave numbers ($\tilde{\nu}$) from 29,400 to 25,000 cm^{-1}. The maximum of the resulting fluorescent light, which determines the color, ranges between 415 and 466 nm (see Table II).

TABLE II

FLUORESCENCE FROM BRIGHTENING AGENTS

Fluorescence maxima	*Color of fluorescent light*
415–429 nm (24,020–23,300 cm^{-1})	Violet
430–440 nm (23,200–22,720 cm^{-1})	Blue
441–466 nm (22,600–21,460 cm^{-1})	Greenish blue

According to investigations carried out by Pestemer,[4] there is a remarkable connection with regard to the position and shape of the characteristic maxima of fluorescent brightening agents and fluorescent dyes between the UV absorption in solution (water, methanol, dimethylformamide) and the fluorescence on a substrate (cotton, polyester, acetate filament, polyamide). Neglecting a wide variety of influences on the absorption and fluorescence band, sufficient proportionality exists between the difference in the absorption and fluorescence maxima, Δ (cm^{-1}), and the low-frequency half-value component nH (cm^{-1}) (see Fig. 4).[4] It can be described by the simple equation $\Delta = 2.5\,(nH)$.

With the aid of the Pestemer rule, the fluorescence maximum, which is important for the color of the fluorescence, can be calculated from a simple measurement of the absorption band in the near-UV. The results of the Pestemer rule give valuable information on the possible use of fluorescent substances as optical brightening agents.

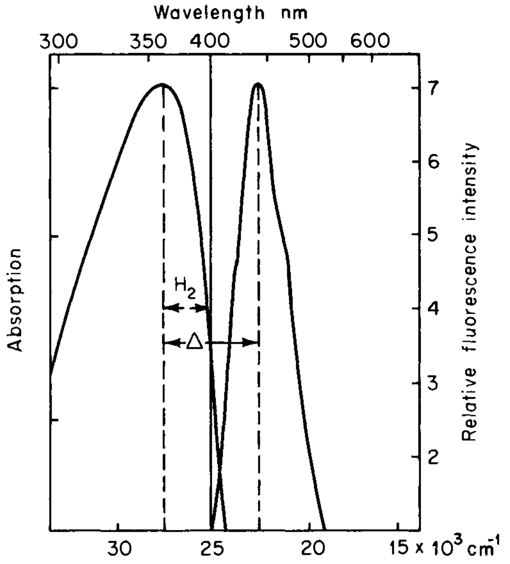

FIG. 4. Pestemer rule.

Deviations from the Pestemer rule are observed, in particular, where the fluorescent brightening agent forms "secondary valency" bonds with the substrate and also, possibly, with the solvent. A marked dependence on the substrate has been described, for example, by Maruyama *et al.*[5] in the case of basic 4-acylamino-*N*-*n*-butylnaphthalimides (see Table III). 4-Diethylaminoacetylamino-*N*-*n*-butylnaphthalimide is a good fluorescent brightening agent for polyacrylonitrile fibers.

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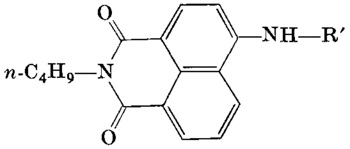
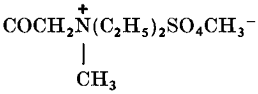
[4] M. Pestemer, A. Berger, and A. Wagner, *SVF* (*Schweiz. Ver. Faerbereifachleuten*) *Fachorgan Textilveredlung* **19**, 420 (1964).

[5] T. Maruyama, D. Kobayashi, N. Kuroki, and K. Konishi, *Kogyo Kagaku Zasshi* **68**, 1707 (1965); *CA* **64**, 11352d (1966).

TABLE III



R′	λ_{max} (nm)	*Fluorescence maxima*[a] (nm)				
		Solution	*Nylon 6*	*Acetate*	*Vinylon*	*PAN*
$\mathrm{COCH_2N(C_2H_5)_2}$	246, 373	453 (dioxane)	450	445	440	435
 $\mathrm{COCH_2\overset{+}{\underset{\underset{CH_3}{\vert}}{N}}(C_2H_5)_2SO_4CH_3^-}$	354	465 (water)	450	—	440	432

[a] In this respect, see color of the fluorescent light in Table II.

For the production of fluorescent light, fluorescent brightening agents depend on the UV component of normal daylight, whose spectral energy quickly falls from 400 nm in the direction of shorter wavelengths to 350 nm (Fig. 5).

To produce a strong violet to blue fluorescent light (about 430 nm) a fluorescent brightening agent must therefore have the following characteristics:

(1) It must possess a high UV absorption capacity above 350 nm, and as near as possible to 400 nm.

(2) The absorption band should fall steeply to the visible (see, for example, Fig. 3) so that a low *nH* value is attained (see Fig. 4).

(3) The absorbed energy should, as far as possible, be transformed quantitatively into fluorescent light (quantum yield close to 1).

C. THE APPLICATION OF FLUORESCENT BRIGHTENING AGENTS

The application of colorless fluorescent dyestuffs as optical brightening agents is based on practical coloristic principles. The possibility of using fluorescent brightening agents depends on the factors summarized in the following paragraphs, account being taken of the above-mentioned theoretical considerations.

(1) A surface is perfectly white when the whole of the daylight of all wavelengths radiated in the visible range is reflected. The spectral energy

distribution of daylight (see Fig. 5) between 400 and 700 nm[6] is without importance for this definition. It is important only that the standard for the perfect white, the magnesium oxide surface, reflects practically 100%. The slight yellowish or yellowish gray discolorations which unbleached substrates naturally possess can be corrected without difficulty by a treatment of the substrate with fluorescent brightening agents in such a manner that the perfect white of the magnesium oxide surface is achieved. Since a selection of fluorescent brightening agents is available for the violet, blue, and green spectral range, any "blue deficiency" can be corrected.

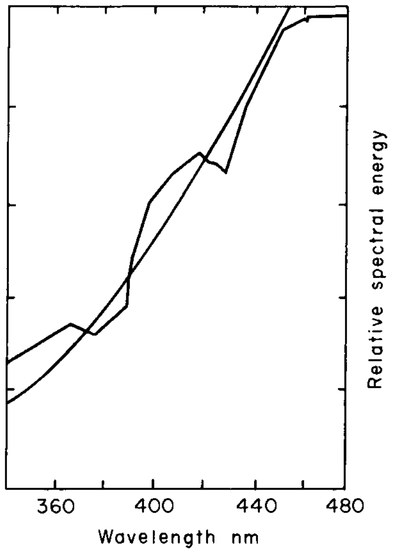


FIG. 5. Relative spectral distribution of daylight.

A perfect white of this type is, however, less appreciated by a normal viewer than a white which reflects more light between 400 and 500 nm than in other parts of the spectrum. The reason is that the human eye associates blueness with white. The physiological conditions which play a part in this phenomenon also give the impression that blued laundered articles are whiter than materials washed in the usual way. The importance of fluorescent brightening agents is therefore associated less with a correction of the blue deficiency than with the production of a white with a predominantly blue luminous effect which can be achieved in no other way.

[6] *CSD I*, p. 307.

Strange to say, the color association with white is evaluated in different ways. Although in Europe preference is given to a blue to violet white, in the United States a white with a greenish blue tint is more appreciated.

Although the absorption and fluorescence of compounds used as optical brightening agents required for this color impression can be described by well-defined physical quantities, the correlation of these quantities with the evaluation data of the physiological impression of white produced on the eye of an average viewer is very complex and can be resolved only by an approximate function.[7] There is no doubt, however, that the preferred whites possess a high brilliance and a hitherto unlimited blue content.

(2) The effect of a fluorescent brightening agent depends to a large extent on its affinity and on the molecular orientation in the substrate to be brightened. In the absence of sufficient affinity, the mere deposition of larger molecular complexes of the fluorescent brightening agent on the surface of the substrate results in yellowish green discolorations. Deposits of this nature can usually be recognized by their poorer fastness to light compared with fast fluorescent brightening effects.

(3) With an increasing concentration of fluorescent brightening agents, the fluorescence increases approximately linearly with the logarithm of the amount of brightening agent taken up by the substrate (Weber–Fechner law) until a saturation limit is attained; the white cannot then be further increased. The position of the saturation limit depends

(a) on the nature of the fluorescent brightening agent (relative to composition, quantum yield, fine division, or solubility),

(b) on the nature of the substrate (relative to the affinity centers), and

(c) in the fluorescent brightening of textiles on the dyeing process (relative to temperature, pH value, concentration of the liquor).[8]

Where the optimum concentration typical of the saturation limit is exceeded, the achieved white may be reduced,[9] which may possibly lead to a total extinction of the fluorescence: self-extinction or concentration extinction.

(4) Owing to the characteristic action of fluorescent brightening agents, the spectral behavior of the substrates is important, particularly in the near-UV range (350–400 nm). The reflectance curves of the main textile substrates between 325 and 475 nm are illustrated in Figs. 6 and 7.[10]

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[7] See the evaluation of fluorescent brightening agents, Section IX.

[8] See the application of fluorescent brightening agents, Section VIII.

[9] J. Rusznak and A. Szekely, *Melliand Textilber.* **42**, 923 (1961).

[10] J. Lanter, *J. Soc. Dyers Colourists* **82**, 127 (1966).

A strong reflectance is shown over the entire spectral range by bleached cotton. In the case of viscose and wool, particularly in the UV region, it decreases rapidly (Fig. 6). All synthetic fibers show in the near-UV a

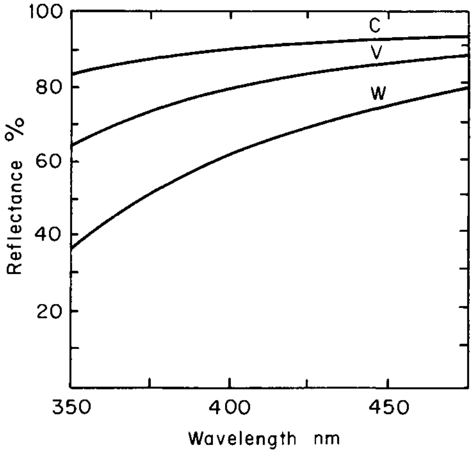

FIG. 6. Reflectance curves of the main textile substrates, I. C represents cotton; V, viscose, and W, wool.

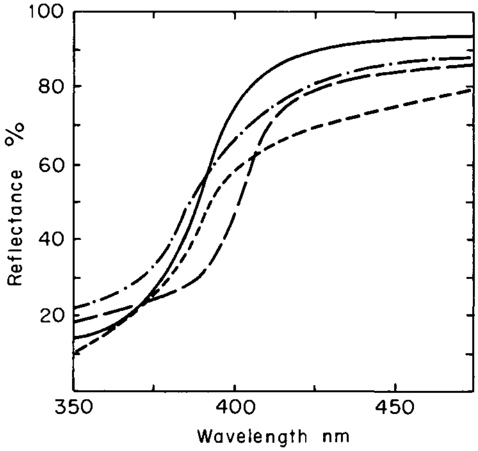

FIG. 7. Reflectance curves of the main textile substrates, II. (———), Polyamide; (— — —), polypropylene; (· · ·), polyacrylic; (·—·—·), polyester.

strong absorption which can be varied according to type and concentration of the delustering agents used (Fig. 7).

The absorption of the substrates in the UV range in which a fluorescent brightening agent receives its excitation is therefore not without influence on the production of white effects. Lanter[11] has pointed out, as a typical example, the reflectance curves of a polyester fiber which was brightened with Uvitex ERN, a fluorescent brightening agent of the type discussed in Section VI,C,1 (see Chart 1 and Fig. 8). With an increasing concentration of fluorescent brightening agent the reflectance of the substrate in the UV range falls, until at a certain concentration the total UV is absorbed. If the brightening agent concentration is further increased, the absorption shifts into the visible range. The substrate becomes yellow and the fluorescence decreases; the fluorescence maximum shifts to longer wavelengths. Since the fluorescence produced by the fluorescent brightening agent is added to the reflectance of a substrate, the strongest fluorescent effect is obtained on those substrates from which the ability to absorb in the UV has been largely removed by chemical bleaching agents. As shown in Fig. 9, because of its UV filter action, with the same quantity of a fluorescent brightening agent only half the brightening effect is obtained on unbleached, untreated cotton as that achieved on a bleached cotton.

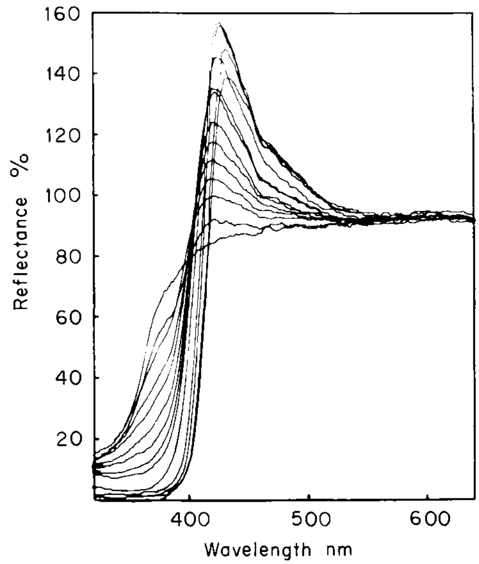

FIG. 8. Reflectance curves of PE fiber brightened with Uvitex ERN.

(5) UV-absorbers, which are often used on substrates, produce the same filter effect. UV-absorbers prevent the build-up of a maximum white.

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[11] J. Lanter, *SVF* (*Schweiz. Ver. Faerbereifachleuten*) *Fachorgan Textilveredlung* **19**, 474 (1964) (cf. 10).

(6) In addition to UV-absorbers, those extraneous materials which do not absorb in the excitation region of the fluorescent brightening agents may reduce, and even destroy, the ability of the latter to fluoresce. Substances which produce this extinction effects to a high degree are, in particular, heavy metal ions and also aromatic compounds: phenols, anilines, iodobenzene, and nitrobenzene. The causes of fluorescence extinction are (a) the formation of nonfluorescent complexes of the optical brightening agents with the extinction substance (static fluorescence extinction), and (b) the bimolecular reaction of the excited optical brightening agent with the extinction substance (dynamic fluorescence extinction).[12]

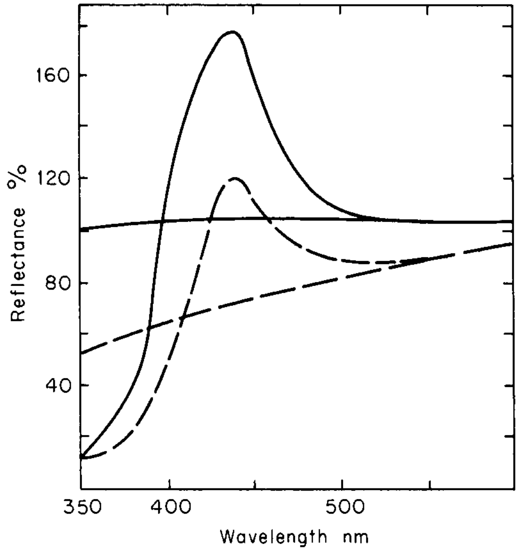

FIG. 9. (———), Bleached and (— — —), untreated cotton brightened with Uvitex CF.

(7) Depending on the dyeing, the use of fluorescent brightening agents on textiles dyed in pastel shades may result in undesirable changes of shade which simulate a lack of color fastness. The emission of fluorescent light by an applied fluorescent brightening agent can be prevented with UV-absorbers (by an optical filter effect) and by extraneous extinction substances (by fluorescence extinction).

(8) To obtain a shaded white, substrates are often stained with blue and blue-violet dyes in concentrations under 1 ppm in combination

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[12] E. Lippert, *Angew. Chem.* **75**, 695 (1961).

with fluorescent brightening agents. In the reflectance curves the dye component appears as a specific absorption located outside the characteristic emission of the fluorescent brightening agent (see Fig. 10).

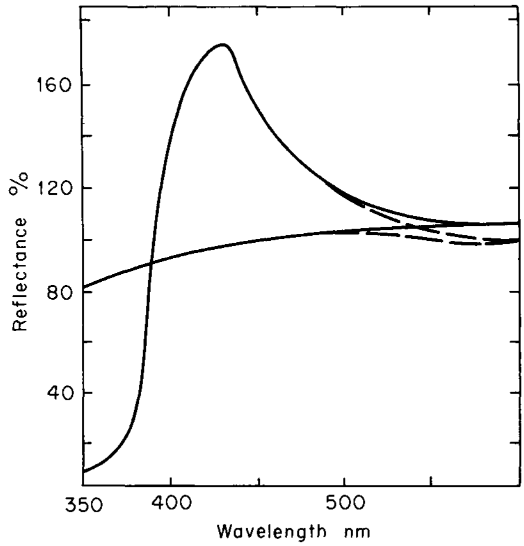

FIG. 10. Cotton brightened with Uvitex CF and Cibacet Brilliant Violet 2R.

D. CLASSIFICATION OF FLUORESCENT SYSTEMS AND FLUORESCENT BRIGHTENING AGENTS

Because of the general laws derived from the relationship between UV absorption and the effect of fluorescent brightening agents, optical brightening agents are members of those groups of compounds and systems which are naturally fluorescent.[13]

Sixty years ago, H. Kauffmann[14] collected and subjected to an empirical classification those organic substances which show as a specific property a "marked and recognizable fluorescence." He named as *luminophores* those basic structures which are common to fluorescent

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[13] For information regarding the fluorescence of organic compounds see T. Förster, "Fluoreszenz organischer Verbindungen Vandenhoeck & Ruprecht." Göttingen, 1951; I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules." Academic Press, New York, 1965; E. L. Wehry and L. B. Rogers, Fluorescence and phosphorescence of Organic Molecules. *In* "Fluorescence and Phosphorescence Analysis" (D. M. Hercules, ed.), pp. 81–143. Wiley (Interscience), New York, 1966.

[14] F. B. Ahrens, *Samml. chem. Vortr.* 8, 1–102 (1907).

compounds. They are promoted by *fluorogens* to *fluorophores*. The term fluorophore had already been introduced by Meyer[15] for fluorescent substances. Typical luminophores are aromatic systems (benzene, naphthalene, phenanthrene, anthracene) and pseudoaromatic heterocyclic systems (coumarin, *s*-triazine, benzoxazole); typical fluorogens are linking groups of atoms and certain substituents, such as –CH═CH–, –CO–, –CH═N–, *p*-phenylene, –CH=CH—COOH, and –CN. In a similar manner to dyestuffs, NH_2, OH, COOH, and SO_3H groups, for example, act as auxochromes or color-deepening groups.[16]

The physical conception of the processes of fluorescence (photoluminescence)[17] is based on the energy present in the above-mentioned molecules or atomic groups in the ground state and in the excited state. Of primary importance in this connection are the atomic vibrations and the electron transitions during the absorption of energy, which can be described with the aid of R. W. Pohl's mechanical model and the Franck–Condon principle.[18] An electron transition occurs in a shorter time than the vibration period of the atom and therefore does not change the atom's kinetic energy. The distance between the atomic nuclei remains unchanged.

This principle applies widely to molecules whose electrons are stabilized in the resonance system. A complete equalization of charge renders the distances between the atomic nuclei insensitive to electron excitation. The energy changes of absorption and emission in fluorescent brightening agents of the methine type (Section VI,D)[4] are typical examples. Where a compensation of the electron excitation is not possible because of the lack of resonance, the change in the linking system of the excited molecule explains an increase in the distances between the atomic nuclei.

All the fluorescent brightening agents known up to the present contain aromatic components or pseudoaromatic (unsaturated) heterocyclic components linked together by direct bonds or small bridges, such as –CO–, –NHCO–, –NHCONH–, –CH═N–, or –CH═CH–. According to the physical conception, their molecules possess more or less extensive resonance or π-electron systems which can be excited sufficiently in the range of 340–400 nm. They can be classified in definite fluorescence systems corresponding to the empirical or physical conceptions. These are, in particular, the systems derived from stilbene, coumarin, 1,3-diphenyl-

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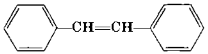
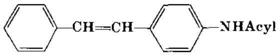
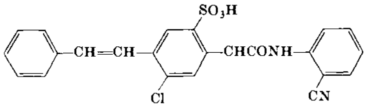
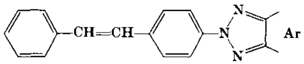
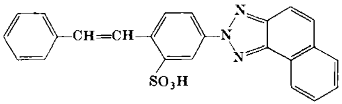
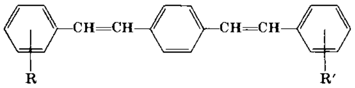
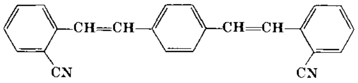
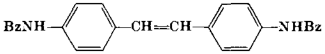
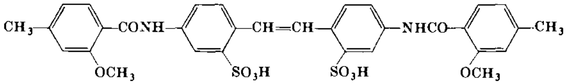
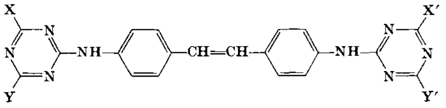
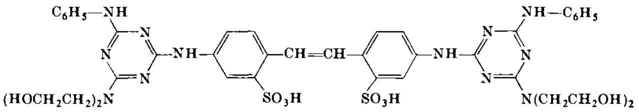
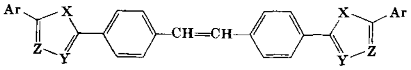
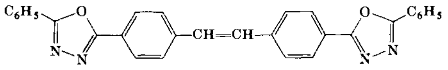
[15] R. Meyer, *Z. Physik. Chem.* **24**, 468 (1897).

[16] T. Förster, "Houben-Weyl," 4th ed., Vol. 3, Part 2, p. 487. Thieme, Stuttgart, 1955.

[17] J. Kurz, *Fette, Seifen, Anstichmittel* **67**, 792 (1966) (summary of the most important literature).

[18] R. W. Pohl, "Optik und Atomphysik." Berlin, 1958; W. Finkelnburg, "Einführung in die Atomphysik." Springer, Berlin, 1962.

CHART 1

Section No. *Class name*	*Characteristic structural unit*	*Example* *fluorescent brightening agent*
II Stilbene compounds		—
II,A,1 4-Acylamino substitution products		
II,A,2 4-Aryl triazolyl-(2) substitution products		
II,A,3 4-Styryl substitution products		
II,B,1,*a* 4,4′-Bis-carboxyamino substitution products		
II,B,1,*b* 4,4′-Bis-triazinylamino substitution products		
II,B,2,*a* 4,4′-*C*-Heterocyclic substitution products		

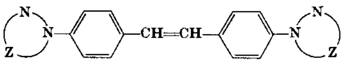
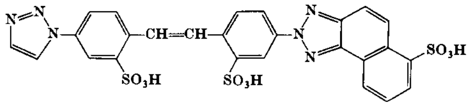
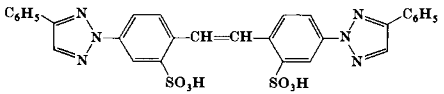
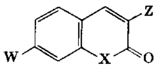
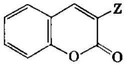
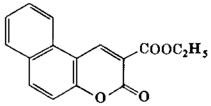
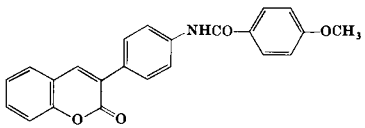
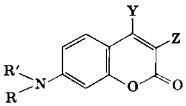
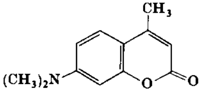
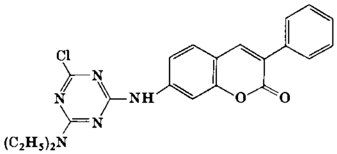
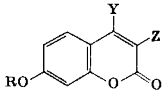
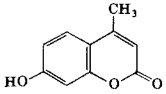
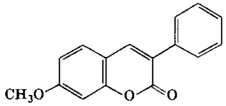
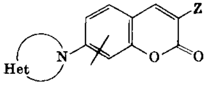
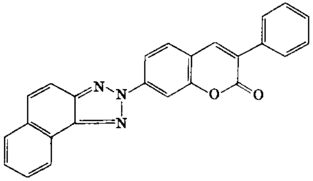
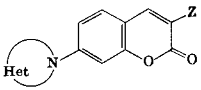
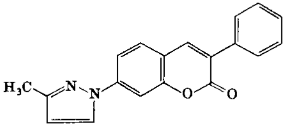
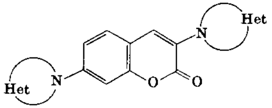
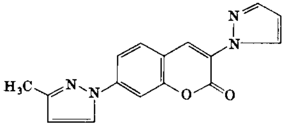
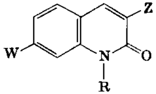
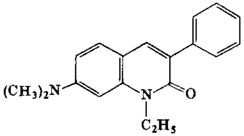
II,B,2,*b* 4,4′-*N*-Heterocyclic substitution products		 
III Coumarins (Carbostyrils)	 X = O, NR	—
III,A,1 3-Substituted coumarins		 
III,A,2 7-Aminocoumarins		 

CHART 1 (*continued*)

Section No. *Class name*	*Characteristic structural unit*	*Example* *fluorescent brightening agent*
III,A,3 7-Hydroxycoumarins		
		
III,A,4 7-*N*-Heterylcoumarins		
		
		
III,B 7-Aminocarbostyrils		

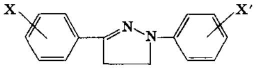
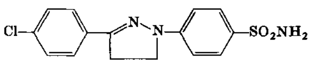
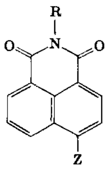
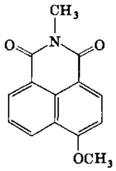
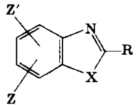
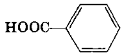
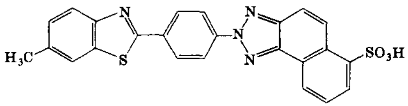
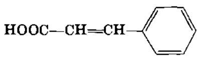
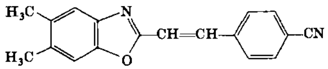
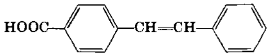
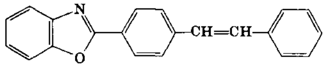
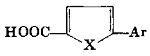
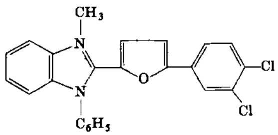
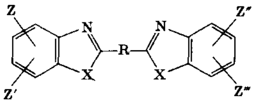
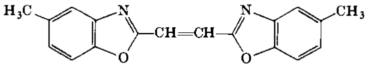
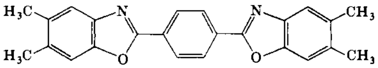
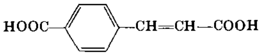
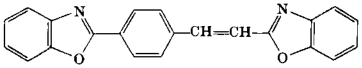
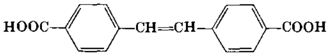
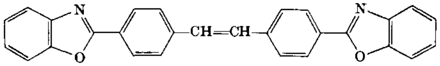
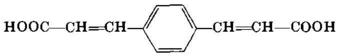
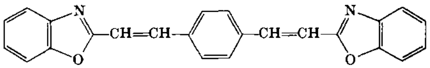
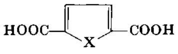
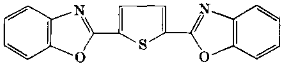
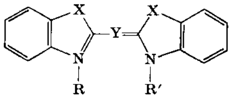
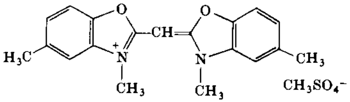
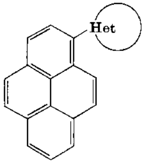
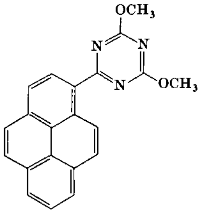
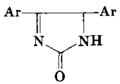
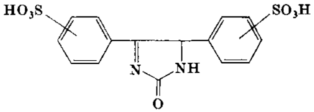
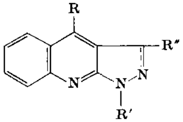
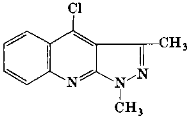
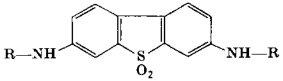
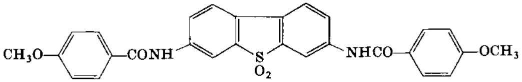
IV 1,3-Diphenylpyrazolines		
V Naphthalimides		
VI,B Aryloazolyl-(2) compounds from monocarboxylic acids		—
VI,B,1 From benzoic acid		
VI,B,2 From cinnamic acid		
VI,B,3 From stilbene-4-carboxylic acid		
VI,B,4 From heterocyclic carboxylic acids		
VI,C Bis-aryloazolyl-(2) compounds from dicarboxylic acids		—

CHART 1 (*continued*)

Section No. *Class name*	*Characteristic structural unit*	*Example* *fluorescent brightening agent*
VI,C,1 From fumaric acid	HOOC—CH=CH—COOH	
VI,C,2 From terephthalic acid		
VI,C,3 From 4-carboxycinnamic acid		
VI,C,4 From stilbene-4,4′-dicarboxylic acid		
VI,C,5 From *p*-phenylenebis (acrylic acid)		
VI,C,6 From heterocyclic dicarboxylic acids	 X = O, S, NH	
VI,D Methine compounds		

VII,A Pyrenes		
VII,B Diphenylimidazolones		
VII,C Pyrazoloquinolines		
VII,D Benzidine sulfone		

pyrazoline, naphthalimide, and from the aryloazoles, all of which allow of numerous variations based on chemical principles.

In Sections II to VII, the fluorescent brightening agents classified according to these systems are described. Chart 1 summarizes the types of fluorescent brightening agents and the sections of this chapter in which they are discussed.

II. Stilbene Compounds

Most fluorescent brightening agents (about 80% of the total production) are derived from the fluorophorous system of stilbene. This hydrocarbon itself possesses a UV absorption band at 324 nm. The UV absorption is shifted to longer wavelengths by the introduction of auxochromic amino groups in the 4 and 4′ position of stilbene: even 4,4′-diaminostilbene has a possibility of excitation at 358 nm (see Table IV).[21–24] It can therefore be understood today that a fluorescent brightening effect was also observed in the light-protective agent Ultrasan of IG-Farbenindustrie AG,[19] which absorbs strongly in the long-wave UV with a maximum at 350 nm. A similar shift of the UV absorption to longer wavelengths is not achieved by the introduction of COOH groups in the 4 and 4′ positions of stilbene. Valuable fluorescent brightening agents have been produced from stilbene carboxylic acids by the introduction of the COOH group into other typical fluorophores.[20] The substitution of stilbene by a styryl radical as a fluorophorous group gives a fluorescent brightening agent which is built up from the simplest luminophore (benzene) and fluorogens (–CH═CH– and *p*-phenylene). 4-Cyanostyryl-4′-cyanostilbene is a valuable fluorescent brightening agent for polyester.

A. MONOSUBSTITUTION PRODUCTS OF STILBENE. STILBENE SYNTHESES

Up to the present, a fluorescent brightening agent has been obtained in the stilbene system by substitution only when the radical of a fluorophore was selected as a substituent. Among these, the arylotriazolyl-(2)-, arylooxazolyl-(2)-, aryloimidazolyl-(2)-, and styryl radicals may be mentioned.

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[19] *DRP* 676,103.

[20] Those fluorescent brightening agents in which stilbene is combined with benzazoles are discussed in Sections VI,B,3 and VI,C,4 on aryloazoles.

[21] P. Pfeiffer and S. Sergiewskaja, *Ber.* **44**, 1110 (1911).

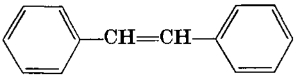
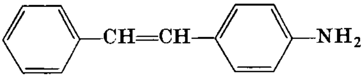
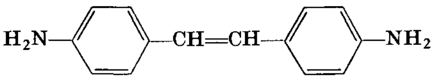
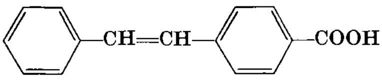
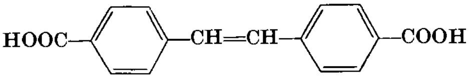
[22] O. Fischer and E. Hepp, *Ber.* **26**, 2232 (1893).

[23] F. Bell and D. W. Waring, *J. Chem. Soc.* p. 1025 (1948).

[24] W. G. Toland, Jr., *J. Am. Chem. Soc.* **75**, 2263 (1953); California Res. Corp., *USP* 2,610,191.

TABLE IV

AMINO- AND CARBOXYL-SUBSTITUTED STILBENES

		Absorption maxima[a]			
	M.p. (°C)	λ (nm)	$\tilde{\nu}$ (cm^{-1})	$\epsilon \times 10^{-4}$	*References*
	125	298	33.550	2.82	—
		310.5	32.200	2.89	—
		324	30.900	1.81	—
	152 253	356.5	28.050	2.20	21
	227	358.4	27.900	3.51	22
	249	321.8	31.150	3.44	23
	460	314	31.900	7.90	24
		331	32.200	7.27	—

[a] In DMF.

1. *Mono-4-acylamino Substitution Products*

An acylamino radical is generally not sufficient to build up from the fluorescent system of stilbene a fluorescent brightening agent with an adequate affinity and color strength. Although suggestions have continually been made in this connection,[25] no commercial products have yet appeared.

2. *Mono-4-arylotriazolyl-(2) Substitution Products*

With the introduction of their Tinopal RBS[26] (I) the firm of Geigy has been eminently successful in combining the fluorophores stilbene and arylotriazole. With a neutral fluorescence and good to very good general

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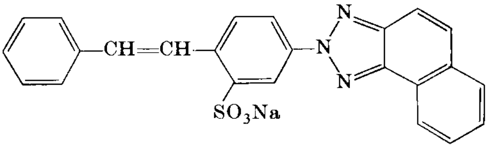
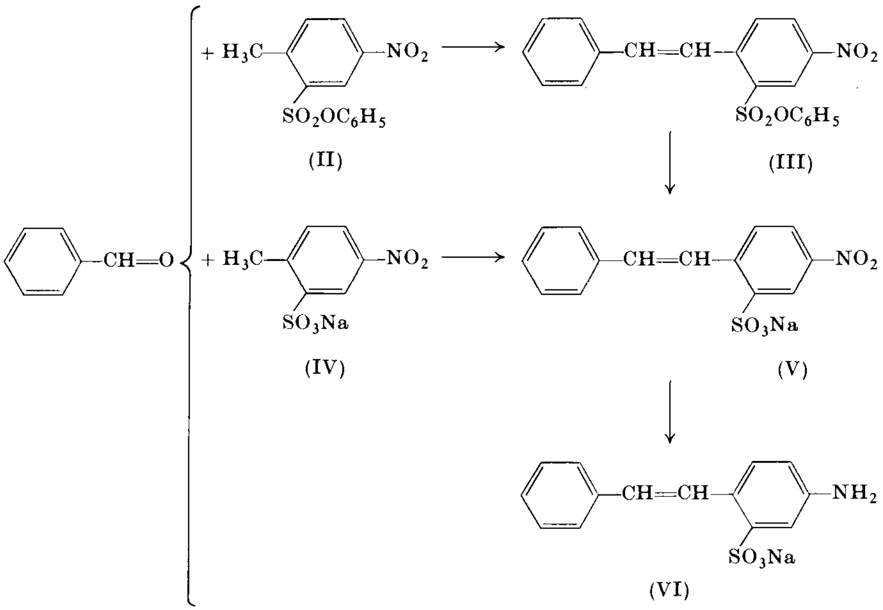
[25] G, *USP* 3,332,981; J. Pirkl, *CzechP* 87,680; *CA* 54, 9312c (1960).

[26] CI, fluorescent brightening agent No. 46; Gy, *USP* 2,713,057; 2,784,184; *DBP* 942,395.



(I)

fastness properties, this important compound possesses an excellent resistance to sodium hypochlorite and a good affinity from alkaline wash liquors on cotton and polyamides (nylon). The synthesis of Tinopal RBS (I) is based on 4-aminostilbene-2-sulfonic acid (VI), which is obtained from sodium 4-nitrotoluene-2-sulfonate (IV) and benzaldehyde in a manner similar to a Knoevenagel condensation, and subsequent reduction of the nitro compound (V).

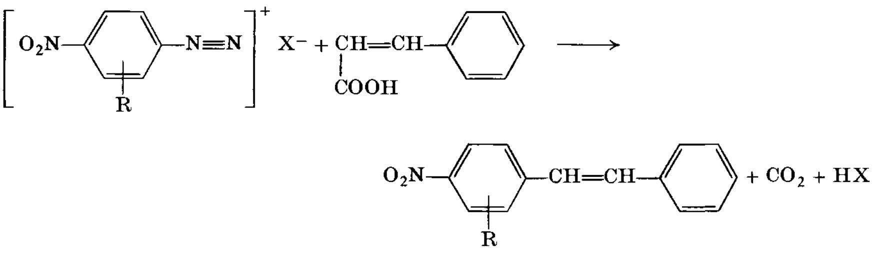


The initial difficulties experienced in carrying out this condensation reaction were overcome by introduction of the easier condensation of benzaldehyde with 4-nitrotoluene-2-phenylsulfonate (II) to give (III).[27] It was later found that under certain conditions benzaldehyde can also be condensed with (IV).[28]

[27] Gy, *DBP* 846,849.

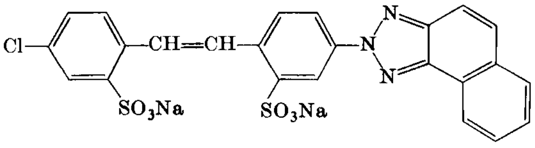
[28] Gy, *DBP* 1,065,838; see also G, *USP* 2,821,550.

Continual attempts have been made in various quarters to utilize the Meerwein arylation reaction[29] of cinnamic acid for the synthesis of 4-nitrostilbene and its substitution products (VII)[30]



(VII)

although yields exceeding 60% are never attained. No experimental difficulties are encountered in substituting by a Sandmeyer reaction a Cl atom for the NH_2 group of the readily accessible 4-nitro-4′-aminostilbene-2,2′-disulfonic acid[31] but the Rylux (VIII)[32] obtained from 4-amino-4′-chlorostilbene-2,2′-disulfonic acid is coloristically less valuable.



(VIII)

In addition to Tinopal RBS (I), the firm of Geigy has developed further interesting fluorescent brightening agents of 4-naphthotriazolyl-(2)-stilbene type, the most important commercial products of which are shown in Table V.[26, 33–37] Among these, the fluorescent brightening agents (IX)[34] and (XII)[36] are particularly interesting from a technical standpoint since they are suitable for the fluorescent brightening of polyester fibers and plastics. The synthesis of (IX) is simplified by the

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[29] H. Meerwein, E. Büchner, and K. van Emster, *J. Prakt Chem.* [2] **152**, 237 (1939); C. S. Rondestvedt, Jr., *Org. Reactions* **11**, 189 (1960) (the Meerwein-arylation reaction).

[30] "Houben-Weyl," 4th ed., Vol. 10, Part 3, p. 171. Thieme, Stuttgart, 1965.

[31] J. Dobas and J. Pirkl, *CzechP* 90,124; *CA* **54**, 25858e (1960); see also R. R. Davies and H. H. Hodgson, *J. Soc. Chem. Ind.* **62**, Trans. 90 (1943).

[32] V. Hanousek, J. Pirkl, and J. Dobas, *CzechP* 89,439/1962; *CA* **59**, 11707e (1963).

[33] Gy, *GB* 717,889.

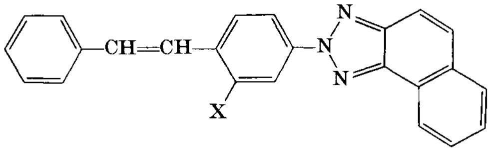
[34] Gy, *USP* 2,713,057.

[35] See also G, *DBP* 1,220,381; FW, *DBP* 1,209,119.

[36] Gy, *USP* 2,970,611; *DBP* 1,052,405.

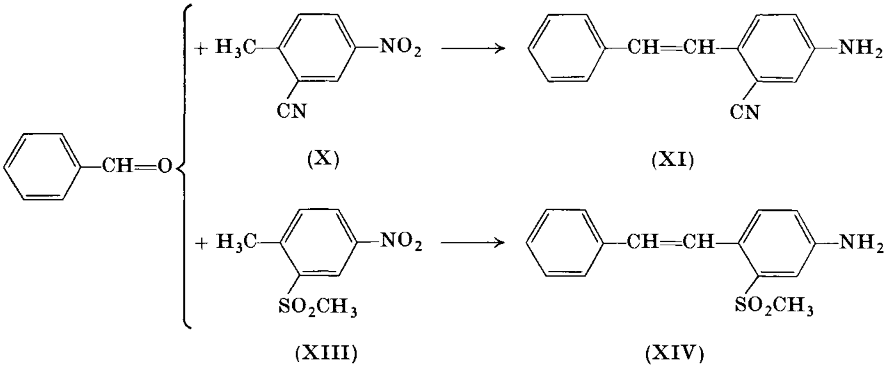
[37] Gy, *BeP* 532,585.

TABLE V



			Absorption maxima			
X	m.p. (°C)	*Solvent*	λ_{max} (nm)	$\tilde{\nu}$ (cm^{-1})	*nH* $\tilde{\nu}$ (cm^{-1})	*References*
(I) SO_3Na	—	Water	370	27.000	1760	26
(IX) $SO_2NHC_2H_5$	203	DMF	367	27.250	1800	33, 34
(XII) CN	226–228	DMF	369	27.100	1750	35, 36
(XV) SO_2CH_3	141–143	DMF	366	27.300	1750	37

fact that Tinopal RBS (I) is easily converted into the sulfonyl chloride, which can be reacted with ethylamine. For the preparation of the fluorescent brightening agents (XII) and (XV), the 4-aminostilbene compounds (XI)[38] and (XIV) must be produced by condensation of benzaldehyde with 4-nitro-2-cyanotoluene (X)[39] or 2-methylsulfonyl-4-nitrotoluene (XIII)[22] and subsequent reduction.



The triazolation of *o*-aminoazo dyes[40] has proved the best method of producing arylotriazolyl compounds since the selection of the diazotizable aromatic amines allows of many variations. The oxidation of

[38] G, *DBP* 1,218,436.

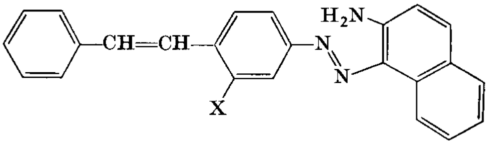
[39] F. Ullmann and M. Gschwind, *Ber.* **41**, 2296 (1908).

[40] "Houben-Weyl," 4th ed., Vol. 10, Part 3, p. 425. Thieme, Stuttgart, 1965.

o-aminoazo dyes, which are freely soluble in water, by heating briefly to 95–100° with an ammoniacal copper sulfate solution[41] is an extremely smooth reaction.[42]

$$o\text{-Aminoazo dyes} + 2Cu^{2+} \rightarrow \text{Triazole} + 2Cu^{+} + 2H^{+}$$

In the case of *o*-aminoazo dyes of type (XVI) which are sparingly soluble or insoluble in water this reaction with copper salts is more difficult. It can be facilitated by addition of pyridine or by use of pyridine as a solvent.[43] In certain cases, the triazolation gives satisfactory results when carried out with an aqueous ammoniacal copper sulfate solution at a temperature of 120° in a digester.[44] A further triazolating agent which can be generally used for *o*-aminoazo dyes is sodium hypochlorite (approx. 12%). Even *o*-aminoazo dyes which are insoluble in water can be oxidized in aqueous suspension with sodium hypochlorite.[45] The oxidation must take place in an alkaline medium to avoid chlorination. This method offers an advantage where the removal of the copper from the oxidation solutions is costly. For the production of the above-mentioned Tinopal types this method is of the utmost importance. Pirkl[46] describes for the dyestuff (XVI; $X = SO_3C_6H_5$) a method of air oxidation in boiling chlorobenzene in the presence of pyridine and copper powder. Moreover, in the presence of 1–5 mole % Cu compounds or Cu powder, aqueous solutions of *o*-aminoazo dyes can be oxidized at 75–100° in air to give arylotriazoles.[47]



(XVI)

A remarkable triazolation reaction is the treatment of *o*-aminoazo dyes with thionyl chloride. According to the investigations of

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[41] IG, *DRP* 695,404.

[42] Concerning the kinetics of the copper oxidation, see I. Cepcinasky, V. Slavik, L. Nemac, H. Fingerova, and I. Nameth, *Collect. Czech. Chem. Commun.* **33**, 100 (1968).

[43] M. P. Schmidt and A. Hagenböcker, *Ber.* **54**, 2199 (1921).

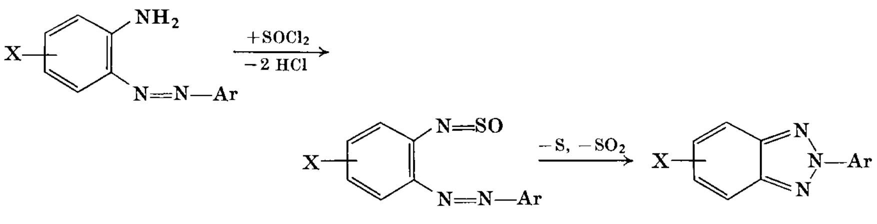
[44] K, *DRP* 338,926.

[45] FW, *DBP* 1,209,119.

[46] J. Pirkl, *CzechP* 102,169; *CA* **59**, 792a (1963).

[47] J. Dobas, *CzechP* 88,252; *CA* **55**, 7856g (1964).

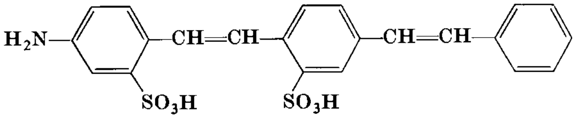
Michaelis *et al.*,[48] the *o*-aminoazo dye forms with $SOCl_2$ a thionyl compound (XVII) which is converted on application of heat into the triazole, releasing S and SO_2.



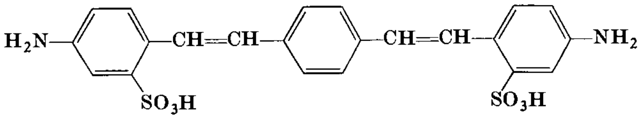
(XVII)

3. *4-Styryl Substitution Products*

By reacting diazotized 4-amino-4′-nitrostilbene-2,2′-disulfonic acid with cinnamic acid in a similar manner to a Meerwein arylation reaction and by condensation of terephthalaldehyde with 4-nitrotoluene-2-sulfonic acid the firm of Geigy produced the styrylstilbenes (XVIII)[49] and (XIX).[50]



(XVIII)



(XIX)

The shifting of the UV absorption of the stilbene system to longer wavelengths by introduction of the fluorophorous styryl substituent did not lead to the formation of useful fluorescent brightening agents; but the naphthotriazolyl-(2) substitution products are yellow dyes.

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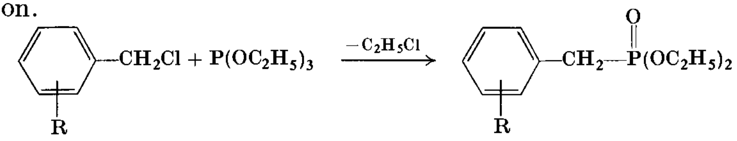
[48] A. Michaelis and H. Schumacher, *Ann. Chem.* **274**, 251 (1893); A. Michaelis and G. Erdmann, *Ber.* **28**, 2192 (1895); O. N. Witt and G. Schmitt, *ibid.* **27**, 2374 (1894); K. von Auwers, *ibid.* **71**, 604 (1938).

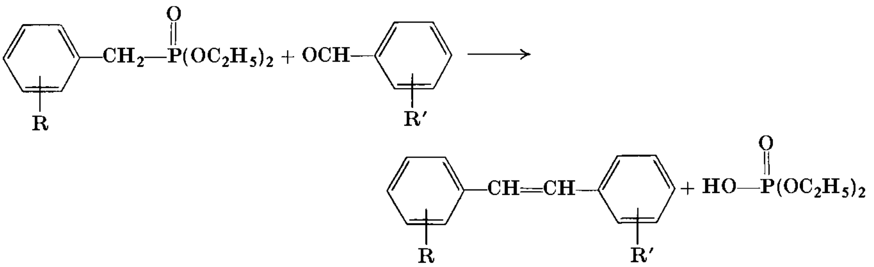
[49] Gy, *SP* 272,221.

[50] Gy, *DBP* 836,642; *USP* 2,547,910; 2,657,225; see also *FP* 993,307.

On the other hand, W. Stilz and H. Pommer[51] succeeded in introducing a new process, similar to a Wittig-Schöllkopf reaction but modified for simplicity,[52] for the industrial production of styrylstilbenes.[53] This process consists in reacting a benzyl chloride with an ester of phosphorous acid, preferably the ethyl ester $P(OC_2H_5)_3$, to form benzyl phosphonate (XX). This is then reacted in a solvent, preferably DMF, and in the presence of a proton acceptor (NaOH, $NaOCH_3$) with an aromatic aldehyde; the stilbene compound (XXI) is formed in an exothermic reaction.

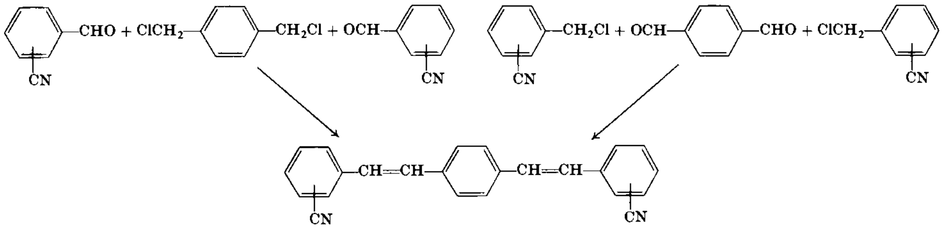


(XX)



(XXI)

For the Palanil Whites (XXII) of BASF[54] it is unimportant whether the starting components are *p*-xylylene dichloride and cyanobenzaldehyde[55] or cyanobenzyl chloride and terephthaldialdehyde.[54] These



(XXII)

a, 4,4′-CN
b, 2,2′-CN

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[51] BASF, *DBP* 1,108,219.

[52] U. Schöllkopf, *Angew. Chem.* **71**, 260 (1959); A. Maerker, *Org. Reactions* **14**, 270 (1964) (the Wittig reaction).

[53] T. W. Campbell and R. N. McDonald, *J. Org. Chem.* **24**, 1251 (1959).

[54] BASF, *DBP* 1,112,072.

[55] BASF, *DBP* 1,108,219.

products have an outstanding effect in the fluorescent brightening of polyester fibers.[56] According to the fluorescence maxima calculated with the aid of the Pestemer rule, a greenish fluorescent brightening effect is to be expected in the optical brightening agent (XXIIa) and a reddish effect in (XXIIb). (See Table Va.)

TABLE Va

PALANIL WHITES

	Absorption max.				*Fluorescence maxima* (calculated)	
	λ (nm)	$\tilde{\nu}$ (cm^{-1})	ϵ_{max}	*nH* $\tilde{\nu}$ (cm^{-1})	λ (nm)	$\tilde{\nu}$ (cm^{-1})
(XXIIa) 4,4′-CN	374	26.700	72.500	1850	452	22.100
(XXIIb) 2,2′-CN	365	27.400	57.000	1950	443	22.535

In the production of monosubstituted stilbene compounds the selection from among the possible syntheses plays a much greater part than in the case of 4,4′-disubstituted stilbene compounds. The synthesis of the latter, which are generally of symmetrical construction, is brought about throughout by dehydrogenation of the respective toluenes with a suitable agent (air, sodium hypochlorite, sulfur). In the methods described in the previous sections for the production of fluorescent brightening agents which are monosubstitution products of stilbene, use is made of the Meerwein arylation reaction, of the condensation of aromatic aldehydes with reactive toluenes in the manner of a Knoevenagel condensation, and of the carbonyl olefination according to Wittig-Schöllkopf. The most important of these are the condensation reactions of aromatic aldehydes. They always proceed smoothly where the reactant possesses sufficient reactivity. This is the case for 4-nitrotoluenes, phenylacetic acids,[57] benzyl cyanides, benzyl magnesium halides, benzyl triphenyl phosphonium chlorides,[58] or benzyl diethyl phosphonates.[51]

In the anil synthesis, Siegrist[59,60] has discovered a process which

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[56] See also Pilot Chem., *BP* 1,043,501.

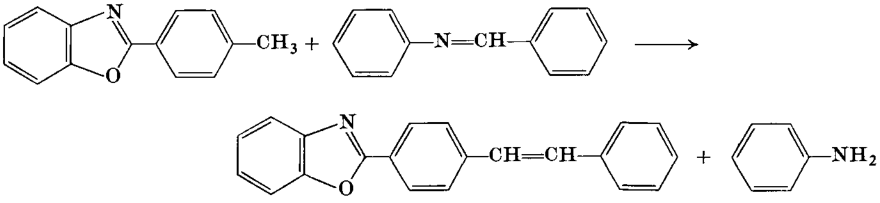
[57] See also Perkin's coumarin synthesis (III, A), *in* "Houben-Weyl," 4th ed., Vol. 6, Part 2, p. 639. Thieme, Stuttgart, 1963.

[58] G. Drefahl, G. Plötner, and A. Ziegler, *Chem. Ber.* **96**, 2775 (1962).

[59] A. E. Siegrist, *Helv. Chim. Acta* **50**, 906 (1967).

[60] CIBA, *Neth. Appl.* 6,615,211.

considerably improves the difficult condensation of *p*-tolyl-substituted heterocycles with aromatic aldehydes, the reaction being carried out with benzalanils under specific conditions, e.g.,



It proceeds with the participation of the DMF used as solvent at 40–60° and occurs best in the presence of pulverized KOH. As *p*-tolyl-substituted heterocycles, all those products can be used whose CH_3 group stands in the *p*-position to a $-CH{=}N-$ or $-N{=}CH-$ group of the heterocycle; the reactant must not contain any group which leads to secondary reactions or binds the KOH. Compared with other stilbene syntheses, an interesting advantage of the Siegrist anil synthesis is that the thermodynamically more stable *trans*-stilbenes are formed almost exclusively.

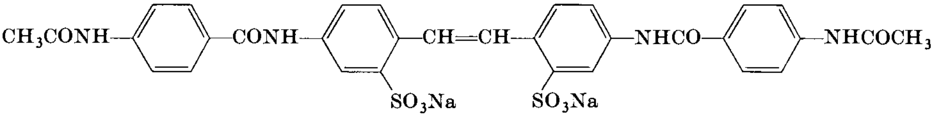
B. Disubstitution Products of Stilbene

To utilize the stilbene system in the synthesis of fluorescent brightening agents, a monosubstitution in the 4-position led to a satisfactory result only when a substitution by the strongly fluorophorous arylotriazolyl-(2) radical occurred; an acylamino group as a substituent is not sufficient for the formation of a fluorescent brightening agent. Substitution in the 4 and 4′ positions of stilbene now permits a wide range of variations, since the bis-carboxyamino stilbene compounds (Section II,B,1,*a*) can be used as fluorescent brightening agents. The bis-triazinylamino stilbene compounds (II,B,1,*b*), in the range of the bis-acylamino substitution products (II,B,1), produce an optimum effect.

The bis-naphthotriazolyl stilbene compounds (e.g., Blankophor G) corresponding to Tinopal RBS can absorb in the visible range to such an extent that they produce a greenish effect as fluorescent brightening agents. In the range of heterocyclic substitution products of stilbene (Section II,B,2), *C*-linked (IIB,2,*a*) and *N*-linked (II,B,2,*b*) heterocyclic substitution products have been developed as fluorescent brightening agents in recent years by Ciba and Farbenfabriken Bayer, respectively. These products produce the blue fluorescence required for fluorescent brightening agents.

1. *Bis-Acylamino Substitution Products*

It was first observed by IG-Farbenindustrie (1939) that derivatives of 4,4′-diaminostilbene-2,2′-disulfonic acid (DAS) can be used as fluorescent brightening agents for textiles made from cellulosic materials and for paper.[61] This firm also introduced two acylation products of DAS under the trade name Blankophor R and Blankophor B.[62] Although ICI had already pointed out in a patent applied for in 1934[63] that undyed, bleached cotton textiles which were treated with bisbenzoyl derivatives of DAS produced fluorescence when irradiated with UV, a fluorescent brightening agent of this range with the constitution[64]



was marketed under the designation Solium only after World War II.

DAS is a readily accessible dyestuff intermediate[65] obtained from 4-nitrotoluene-2-sulfonic acid. Solutions of its salts in water possess an absorption maximum at 340 nm and already show a visible fluorescence. A systematic comparison has shown that through an acylation the position of the UV absorption maximum (λ_{max}), the molar extinction coefficient (ϵ) and the shape of the absorption curve (characterized by the low-frequency half-value width) of the products can be adjusted in such a manner that fluorescent brightening agents with optimum properties are obtained.

a. Biscarboxyamino Substitution Products. The ability observed by ICI of the bisbenzoyl derivatives of DAS to produce fluorescence on cotton and the marketing of Solium started an intensive development, which was undertaken in Europe by the firms of Geigy,[66] Sandoz,[67] and Unilever[68] and in the United States by American Cyanamid,[69] General Aniline,[70] du Pont,[71] and Procter & Gamble.[72] The results of the work

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[61] At that time the principles of fluorescent brightening agents were already understood [see S. Petersen, *Angew. Chem.* **61**, 17 (1949); H. Gold, *SVF* (*Schweiz Ver. Faerbereifachleuten*) *Fachorgan Textilveredlung* **19**, 416 (1964)].

[62] See *CSD I*, pp. 635–636; CI, fluorescent brightening agent No. 30; CI, fluorescent brightening agent No. 32.

[63] ICI, *USP* 2,089,413.

[64] Lever Brothers & Unilever, *USP* 2,528,323; *BP* 596,524.

[65] Preparation, see *CSD I*, p. 628.

[66] Gy, *USP* 2,521,665.

[67] S, *SP* 318,441.

[68] Unilever, *USP* 2,643,197/9.

[69] CCC, *USP* 2,468,431; 2,671,790; 2,580,234.

[70] G, *USP* 2,581,059.

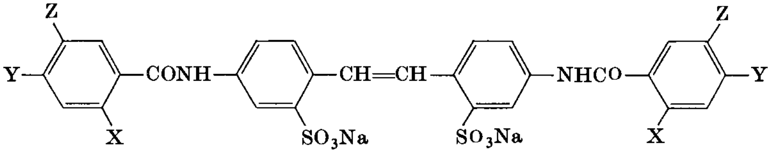
[71] DuP, *USP* 2,626,926; 2,635,113; 2,581,057.

[72] Proctor & Gamble, *BP* 663,919.

undertaken and concluded between 1946 and 1957 can be summarized as follows:

(a) The effectiveness of the sodium salts of bisbenzoyl-DAS as fluorescent brightening agents is influenced considerably by the introduction of substituents into the benzoyl groups. Table VI shows that the fluorescent brightening effect (determined by the amount required to achieve a certain degree of whiteness) is increased by the number and position of OCH_3 groups; the OCH_3 group is most effective in the 2-position.

TABLE VI



X	Y	Z	*Required amount for a specified degree of white* (wt.)
H	CH_3	H	100
H	OCH_3	H	46
H	OCH_3	OCH_3	36
OCH_3	H	OCH_3	32
OCH_3	OCH_3	H	25
OCH_3	OCH_3	OCH_3	18

Table VIIa, which includes the most important fluorescent brightening agents of the group of biscarboxyamino-substituted stilbenes (Section II,B,2,*a*), shows that by the introduction of OCH_3 groups the absorption maximum of benzoyl-DAS experiences a bathochromic shift, if only slight (Tinopal SP), which is increased by a further OCH_3 group in the *p*-position. 4,4′-Bis(2,4-dimethoxybenzoylamino)stilbene-2,2′-disulfonic acid is also for technical reasons a fluorescent brightening agent with optimum properties which is marketed under the name Calcofluor White 2GT or Pontamin White 2GT.[73]

The introduction of Cl atoms into the 5,5′-positions of the 4,4′-bis(benzamido)stilbene-2,2′-disulfonic acids results in a shift of the absorption maximum to shorter wavelengths [compounds (A) and (B) in Table VIIb]; the color sensation produced by the fluorescent light is

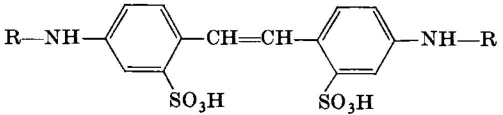
---

[73] CI, fluorescent brightening agent No. 34; DuP, *USP* 2,643,187/8.

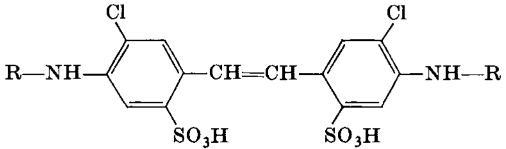
TABLE VII

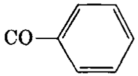
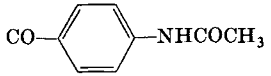
4,4′-Bis(benzamido)stilbene-2,2′-disulfonic Acids

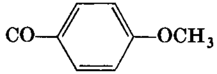
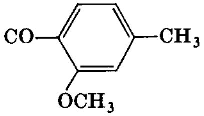
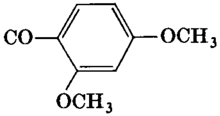
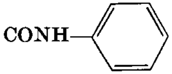
(Part a)



(Part b)



R	Trade name	Absorption maxima λ (nm)	Absorption maxima $\tilde{\nu}$ (cm^{-1})	nH $\tilde{\nu}$ (cm^{-1})	Compound	Absorption maxima λ (nm)	Absorption maxima $\tilde{\nu}$ (cm^{-1})
H	DAS	340	29.300	2300		340	29.300
$COCH_3$	—	328	30.350	2350		—	—
	—	335	29.600	2350	(A)	322	31.000
	Solium	340	29.400	2400		—	—

	—	338	29.500	—	(B)	322	31.000
	Tinopal SP	342	29.300	2830	(C)	381	26.200
	Pontaminwhite 2GT	345	29.000	2350	(D)	387	25.800
	Blankophor R	338	29.600	2230		—	—

redder. The analogous introduction of a Cl atom into the 6- and 6′-position, on the other hand, reduces the substantivity of the bis(benzamido)stilbene compounds and weakens the fluorescence; the 6,6′-dichloro compounds are of no practical interest. The slight bathochromic shift of the absorption maximum of the 4,4′-bis(benzamido)-stilbene-2,2′-disulfonic acids caused by OCH_3 groups in the *o*-position of the benzoyl groups (see Table VIIa) increases to 40 nm [compounds (C) and (D) in Table VIIb] in the case of the 4,4′-bis(benzamido)-5,5′-dichlorostilbene-2,2′-disulfonic acids, despite the hyposchromic effect of the Cl atoms. Because of the marked green shift, the sodium salt of 4,4′ - bis(2,4 - dimethoxybenzoylamino) - 5,5′ - dichlorostilbene -2,2′-disulfonic acid (D) is unsuitable as a fluorescent brightening agent (see Fig. 11).[74]

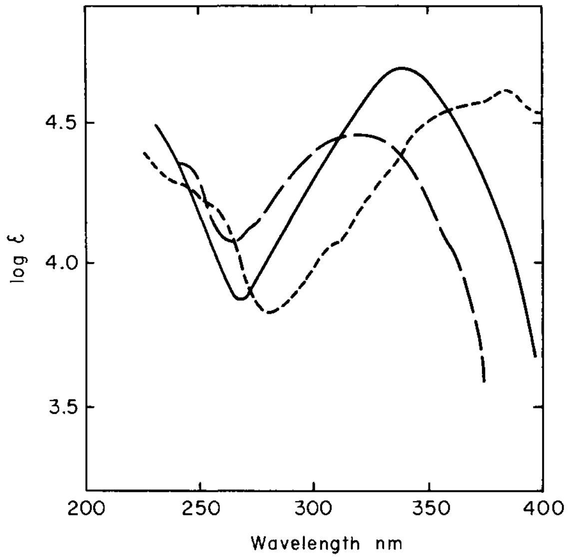
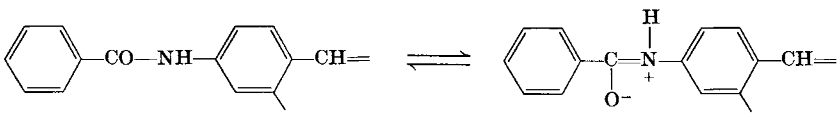


FIG. 11. UV absorption of *o*-$C_2H_5OC_6H_4CO$-derivatives of (———) DAS; (——), (6,6′-dichloro-DAS); (– – –), 5,5′-dichloro-DAS.

The marked effects of the *o*-substitution can be explained by its influence on the amide resonance and therefore on the length of the conjugate system.[75]



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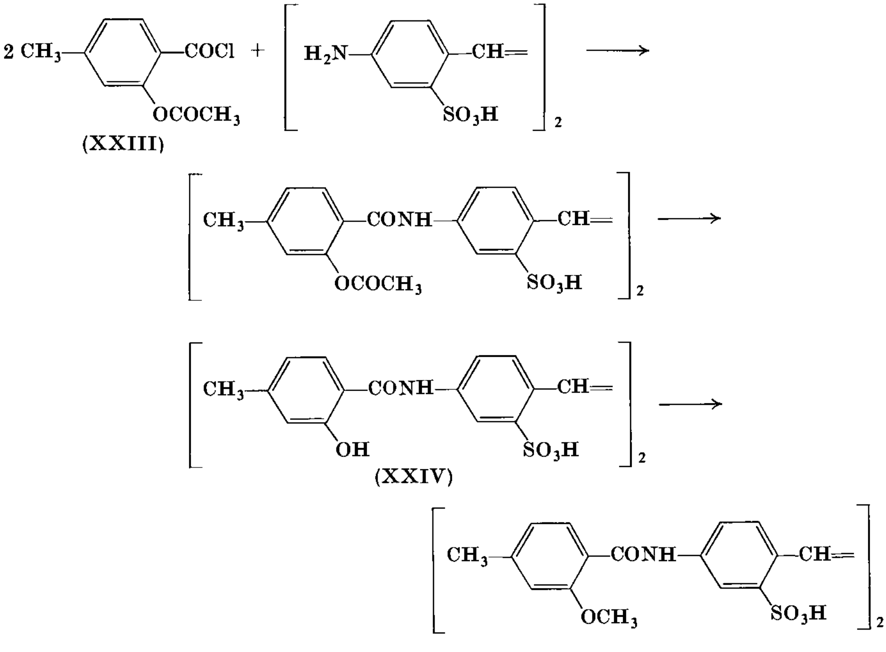
[74] R. S. Long, *Proc. Perkin Centennial* 1845–1956 (H. F. White Jr., ed.) p. 416 (1956).

[75] D. W. Hein and E. S. Pierce, *J. Am. Chem. Soc.* **76**, 2725 (1925); *USP* 2,681,926; 2,688,617.

(b) The bisbenzoyl-DAS compounds are suitable as fluorescent brightening agents for cotton and polyamide textiles, particularly in combination with detergents.[76] Their high affinity for cellulose is due to the extended conjugation and to the formation of hydrogen bonds. The stability of the fluorescent brightening effects to hypochlorite (as a chemical bleaching agent) is moderate. Although bis-benzoyl-DAS compounds derived from 5,5′-dichloro- and 6,6′-dichloro-DAS[74] possess a higher resistance to hypochlorite, these products are of no interest as fluorescent brightening agents because of their unsatisfactory optical performance.

The production of the benzoyl-DAS compounds is accomplished by reacting DAS with the respective substituted benzoyl chlorides in water or water–acetone and water–benzene mixtures. Since the acid chlorides of 2-methoxybenzoic acid (salicylic acid methyl ether) and of 2-methoxy-4-methylbenzoic acid (*m*-cresotinic acid methyl ether) are very susceptible to hydrolysis, acylation is carried out with *o*-acetyl salicyl chloride or acetyl cresotinic chloride (XXIII); the acetyl group is split off in an alkaline reaction and the resulting *o*-hydroxybenzamide (XXIV) alkylated. The production of Tinopal SP proceeds according to the following reaction pattern[77]:



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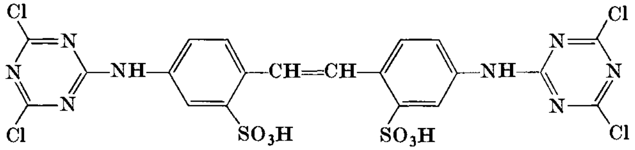
[76] O. Uhl, *Fette, Seifen, Anstrichmittel* **53**, 545 (1951).

[77] Gy, *DBP* 825,404.

b. Bistriazinylamino Substitution Products. Among the acylation products of DAS, the bistriazinyl derivatives have proved the most important and successful group of fluorescent brightening agents for substrates made from cellulosic materials and polyamides.[78] There were various reasons for this development:

(a) The triazinylaminostilbene fluorescent brightening agents possess medium coloristic fastness properties, well adapted to one another. With an adequate fastness to light of about 4 in most cases, a high maximum white can be obtained on paper and textiles made from cellulosic materials and polyamides (nylon, Perlon, Dederon). It is higher than that which can be achieved with the dibenzoyl-DAS compounds (Section B,2,*a*).

(b) An almost infinite number of variations is possible by interaction of the Cl atoms of 4,4′-bis(2,4-dichloro-1,3,5-triazinyl-6-amino)stilbene-2,2′-disulfonic acid with virtually all primary and secondary amines, alcohols, mercaptans, and phenols, as well as their substitution products.



(c) DAS and cyanuric chloride are two inexpensive industrial intermediates, the latter playing an important part in the field of reactive dyestuffs and also in that of plant protective agents (e.g., Simazin, produced by Geigy).

The bis-triazinyl-DAS compounds which are interesting from an industrial standpoint are shown in Table VIII. Largely independent of the amine and alcohol components, they possess a UV absorption band at 350 nm + 3 nm; the calculated fluorescence maximum is between 442 and 432 nm, in the range of a blue fluorescent light. The fluorescence intensities are practically equal.[79] The salient feature of these compounds as fluorescent brightening agents is their performance on the substrates with regard to affinity and substantivity (see Section *b. i.*) and also the level attained by their fastness properties.

There have been numerous attempts to employ substitution products of DAS, but without much progress being made. In addition to dichloro-DAS (XXV), investigated by D. W. Hein and E. S. Pierce, 5-alkoxy-5′-chloro-DAS (XXVI) obtained by reacting 5,5′-dichloro-DAS with

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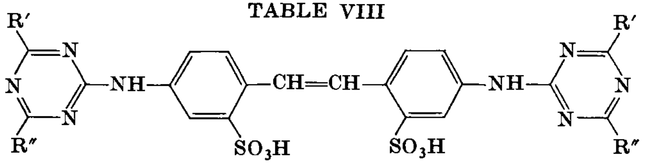
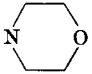
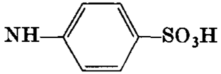
[78] IG, *DRP* 731,558; *BeP* 440,622; CIBA, *DBP* 870,146; 882,704.

[79] A. Yabe and M. Hayashi, *Kogyo Kagaku Zasshi* **63**, 987 (1960); *CA* **60**, 10860d (1904).

TABLE VIII



	R′	R″	Absorption maxima[b] λ (nm)	Absorption maxima[b] $\tilde{\nu}$ (cm^{-1})	nH $\tilde{\nu}$ (cm^{-1})	Fluorescence max., calc. λ (nm)	Fluorescence max., calc. $\tilde{\nu}$ (cm^{-1})
DEA-Cl	$N(CH_2CH_2OH)_2$	Cl	347	28.800	2450	441	22.680
MEA-Am	$NHCH_2CH_2OH$	NH_2	347	28.800	2250	432	23.170
A-Am	NHC_6H_5	NH_2	344	29.000	2350	432	23.125
A-DEA	NHC_6H_5	$N(CH_2CH_2OH)_2$	352	28.410	2170	435	22.980
A-M	NHC_6H_5		349	28.650	2400	442	22.650
A-A[a]	NHC_6H_5	NHC_6H_5	358	27.900	2300	452	22.150
A-Me	NHC_6H_5	OCH_3	350	28.530	2290	432	23.130
A-MEA	NHC_6H_5	$NHCH_2CH_2OH$	346	28.900	2350	434	23.025
A-MeMPA	NHC_6H_5	$NHCH_2CH_2CH_2OCH_3$	347	28.800	2400	439	22.800
A-MMEA	NHC_6H_5	$N(CH_3)CH_2CH_2OH$	349	28.500	2300	440	22.750
S-DEA		$N(CH_2CH_2OH)_2$	350	28.530	2290	438	22.810

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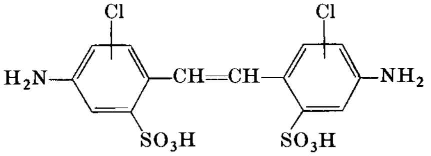
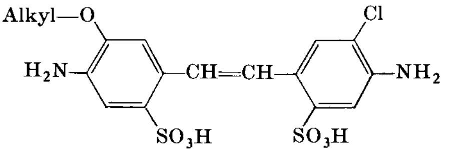
[a] Determined in DMF. [b] Determined in water.

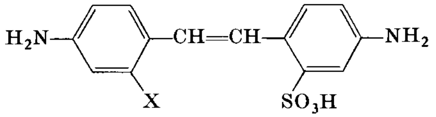
alcoholates[80] was proposed by R. S. Long.[80a] The benzoyl and triazinyl derivatives of 2-alkyl- and 2-alkoxy-4,4′-diaminostilbene-2′-sulfonic acids described by Geigy (XXVII)[81] produce a marked green fluorescent brightening effect and are therefore less interesting. Although 4,4′-diaminostilbene-3,3′-disulfonic acid (XXVIII), produced by Tyman,[82] yields *N*,*N*′-dibenzoyl compounds which are more substantive than *N*,*N*′-dibenzoyl-DAS (Table VII), this acid is only of theoretical interest up to the present because of the difficulty of producing 4-nitrotoluene-3-sulfonic acid.[83]



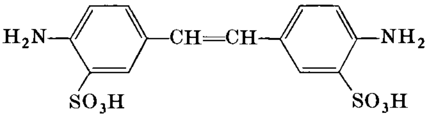
(XXV)



(XXVI)



(XXVII)



(XXVIII)

X = Alkyl, Alkoxy

The production of the sodium salts of 4,4′-bis(1,3,5-triazinyl-6-amino)stilbene-2,2′-disulfonic acids (Table VIII) is carried out by condensation of cyanuric chloride with DAS and amines, alcohols, phenols or mercaptans in any desired sequence in an aqueous or water–acetone medium in the presence of an acid-binding agent. From a technical standpoint it is interesting that the condensation sequence is carried out in a "one-step process" without any separation of the intermediate stages.

In this connection three fundamental points require particular attention:

(1) The replacement of a chlorine atom in cyanuric chloride by basic groups is greatly facilitated by the ring nitrogen atoms of the symmetrically built triazine nucleus. At 0° cyanuric chloride is therefore already susceptible to alcoholysis and aminolysis, as well as to hydrolysis. The

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[80] The second Cl atom cannot be substituted even with a larger excess.

[80a] CCC, *USP* 2,841,613.

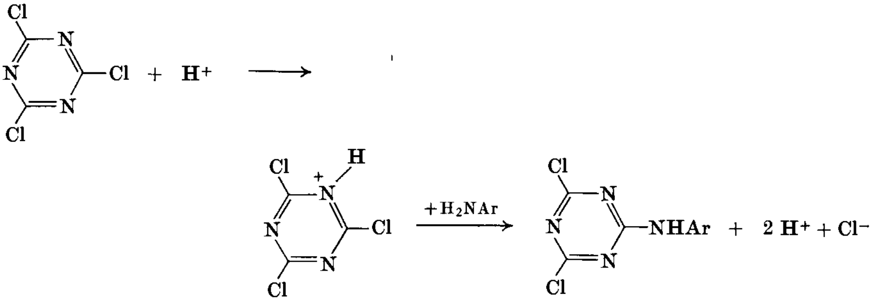
[81] Gy, *USP* 2,762,802; *DBP* 1,001,273.

[82] J. H. P. Tyman, *J. Soc. Dyers Colourists* **82**, 102 (1966); see also Gy, *BP* 1,031,750.

[83] S. Coffey, *J. Chem. Soc.* p. 3221 (1926).

course of the substitution reactions is determined not only by the nucleophilicity of the basic reactant, but also by the electrophilic character of the triazine ring.

As discovered by Banks,[84] these substitution reactions can be catalyzed by acids; the more electrophilic triazonium ion (XXIX) is, in fact, more reactive than cyanuric chloride itself.[85] An acid catalysis is also possible in aqueous reaction media, provided that the nucleophilic reactant does not prevent protonation of the triazine ring. The self-catalyzed hydrolysis of cyanuric chloride is an example of this. For this reason, the reactions of cyanuric chloride with alcohols and with aromatic amines, in particular, can be catalyzed by acids. Formation of the arylaminodichlorotriazines will therefore proceed the more quickly the fewer protons the aromatic amines require. By contrast, in the reaction of cyanuric chloride with aliphatic amines the course of the reaction is determined to a large extent by the nucleophilic character of the amine, since a protonation of the triazine ring according to Banks can hardly be possible.



(XXIX)

To prevent a possible acid catalysis in the substitution of a chlorine atom in cyanuric chloride by OH,[86] OCH_3, or OC_2H_5 [87] to give hydroxy- and alkoxydichlorotriazines, the reaction is best carried out in the presence of an acid-binding medium, preferably $NaHCO_3$.

(2) In its reactions with amines at 0° and below, cyanuric chloride is, in general, a monofunctional acid chloride. Since a slight bifunctionality of cyanuric chloride cannot quite be suppressed, the formation of varying amounts of higher molecular weight chlorotriazinylaminostilbenedisulfonic acids must be expected under any conditions in the reaction of cyanuric chloride with the bifunctional DAS. These lead in further

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[84] C. K. Banks, *J. Am. Chem. Soc.* **66**, 1127 and 1771 (1941); **68**, 944 (1946).

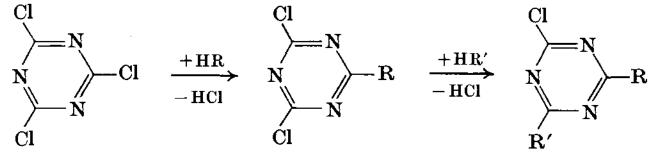
[85] H. Zollinger, *Angew. Chem.* **73**, 132 (1961).

[86] CIBA, *FP* 1,229,750.

[87] J. R. Dudley, J. T. Thurston, F. C. Schaefer, and D. Hom-Hansen, *J. Am. Chem. Soc.* **73**, 2989 (1951).

condensation reactions to the formation of by-products which cannot usually be separated and whose own fluorescence may interfere with the fluorescent brightening effect.

(3) The 2-monosubstituted 4,6-dichloro-1,3,5-triazines (XXX) obtained by reacting cyanuric chloride with amines, alcohols, or phenols possess in further reactions as acid chlorides a specific reactivity which is less catalyzed by acids. It is dependent mainly on the substituent R.



(XXX) (XXXI)

Since the reactivity of a chlorine atom is determined in the chlorotriazines (XXX) by the electron attraction of the adjacent ring nitrogen atoms, which is itself controlled by the substituent R, it decreases in the sequence

$$R = C_6H_5O > CH_3O > C_2H_5O > C_6H_5NH > NH_2 > CH_3NH > C_2H_5NH > (CH_3)_2N > OH$$

The reactivity of the chlorine atom in the 2,4-disubstituted 6-chloro-1,3,5-triazines (XXXI) shows the same gradation. It decreases in such a manner that, for example, 2,4-dimethoxy-6-chloro-1,3,5-triazine reacts as an acylating agent at medium temperatures, while 2,4-bis(dimethylamino)-6-chloro-1,3,5-triazine does so only at temperatures exceeding 100°.

For these reasons, the suggestion has been made in various quarters that the primary reaction of DAS with cyanuric chloride should be avoided. The arbitrary sequence often referred to in the patent literature shows clearly that the acylation of DAS should be carried out with a chlorotriazine compound which is less polyfunctional than cyanuric chloride. Suggested products are 2-methoxy-4,6-dichloro-1,3,5-triazine,[88] 2-phenylamino-4,6-dichloro-1,3,5-triazine,[89] 2-(4-sulfophenylamino)-4,6-dichloro-1,3,5-triazine,[90] and 2-(dimethylamino)-4,6-dichloro-1,3,5-triazine, the reactivity of these products decreases in the stated sequence from the 2-methoxy to the 2-(dimethylamino) substitution product. In none of the specified acylating agents could the slightest trace of a condensation product which had been formed by the reaction of both Cl atoms with DAS be found.

i. Coloristic properties. From the range of CC/DAS fluorescent brightening agents about 50 chemically different members have been

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[88] FW, *BP* 943,639.

[89] FBy, *DBP* 1,250,830.

[90] Gy, *DBP* 1,207,296; R. Meckel, *Textil-Praxis* **16**, 737 and 1032 (1961).

marketed; Table VIII gives only a small selection of the most important commercial products. In this range no marked changes are obtained in the UV absorption (347–352 nm) by variation of the substituents R′ and R″ and, therefore, only slight shifts in the fluorescence maximum (432–442 nm) (see Table II). To a much larger extent the substituents R′ and R″ exert an influence on the coloristic performance of CC/DAS fluorescent brightening agents. The considerable amount of experimental material available permits adjustment to a determined coloristic behavior by a selection of the substituents R′ and R″.

CC/DAS fluorescent brightening agents which contain as substituents only NH_2 groups or secondary tertiary aliphatic amino groups are extremely suitable for the fluorescent brightening of paper pulps, cotton at low temperatures, or spinning compounds made from regenerated cellulose; they are notable for their good leveling capacity. CC/DAS fluorescent brightening agents containing anilino groups ($R' = NHC_6H_5$) as substituents possess a marked affinity for cellulose.[91] In this connection, when R″ stands for NH_2 or secondary or tertiary aliphatic or aromatic amino groups, they determine the leveling capacity, solubility, and affinity for cellulose or polyamide fibers, depending on temperature and pH value of the liquor. They are generally used as fluorescent brightening agents in wide temperature ranges in combination with detergents. A special position is occupied by those CC/DAS fluorescent brightening agents which contain four anilino groups bound as substituents, such as fluorescent brightening agent A-A. In addition to their affinity for cotton, they possess in alkaline liquors a marked affinity for polyamide fibers.[92] Table IX gives a summary of the most important CC/DAS fluorescent brightening agents for application in the washing process.[93]

The solubility and acid resistance of CC/DAS fluorescent brightening agents are improved by the introduction of further SO_3H groups into aniline or the aliphatic amine (S-DEA, Table VIII). These fluorescent brightening agents are suitable for the optical brightening of acidic papers and of polyamide fibers from acid liquors. Moreover, those fluorescent brightening agents of the CC/DAS range in which R″ stands for alkoxy substituents are very resistant to acids. Because of its high affinity and acid resistance the fluorescent brightening agent A-Me in Table VIII is suitable for many fields of application, e.g., the optical brightening of polyamide fibers, cotton in the creaseproof process (synthetic resin finish), and paper.

[91] M. Hayashi and A. Yabe, *Kogyo Kagaku Zasshi* **63**, 991 (1960); *CA* **60**, 12138h (1964).

[92] FBy, *DBP* 1,100,583.

[93] P. S. Stensby, *Soap Chem. Specialties* **43**, April 4 (1967).

The stability of CC/DAS fluorescent brightening agents to perborate, persulfate, hydrosulfites, and bisulfites is so good that no decrease of fluorescence is observed when they are used in combination. However, the stability is only moderate and extremely variable in combination with hypochlorite and *N*-chlorocyanurates, since the presence of NH groups on the triazine ring is responsible for the susceptibility to decomposition by agents which liberate chlorine.

(a) The disodium salt of 4,4′-bis(2,4-dimorpholino-1,3,5-triazinyl-6-amino)stilbene-2,2′-disulfonic acid (A-M), which contains only one NH group bound to the triazine ring is the most stable.

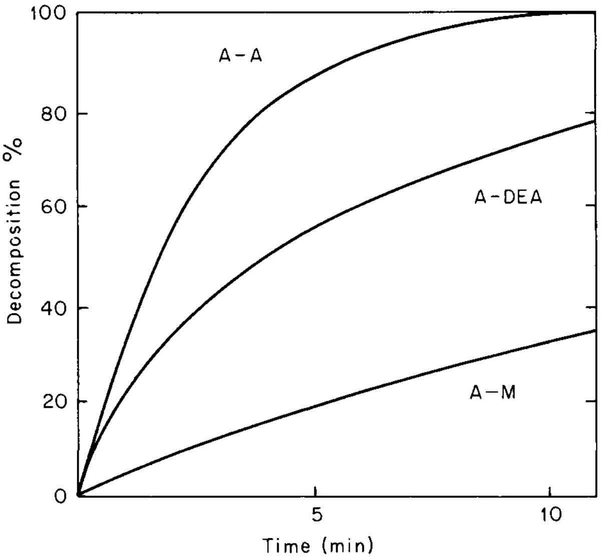

FIG. 12. Decomposition of triazinyl-DAS fluorescent brightning agents (Table VIII) by sodium hypochlorite.

(b) The most unstable is the fluorescent brightening agent A-Am, which contains two NH groups and an NH_2 substituent bound to the triazine ring.

(c) A medium stability to hypochlorite is shown by those fluorescent brightening agents which are built up from aniline and primary or secondary amines (A-DEA, A-A, A-MEA, A-M) and which contain two or three NH groups bound to a triazine ring.

The rate of decomposition of CC/DAS fluorescent brightening agents with hypochlorite is shown diagrammatically in Fig. 12.[94] On the other

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[94] J. G. Villaume, *Soap Chem. Specialties* **44**, 70 (1968).

hand, the resistance to chlorine of the fluorescent brightening effects obtained with these products is evaluated good to moderate (see Table IX).

ii. Cis–trans isomerism in DAS fluorescent brightening agents. As in the case of all substituted ethylenes, the stilbene compounds show cis–trans isomerism; the isomers can be transformed into each other under the influence of short-wave radiation.[95] This isomerism in the DAS fluorescent brightening agents has been investigated very carefully since it is highly important for the brightening effect and for analytical examinations.[96] The supposition expressed by Lewis[95] that the cis forms of DAS fluorescent brightening agents cannot fluoresce was confirmed by Bocharov[97] and by H. Walz[98] by measurement of the absorption bands of dilute solutions (5 ppm) of a DAS fluorescent brightening agent on exposure to UV radiation. Figure 13 shows the absorption curves of an unexposed solution of the fluorescent brightening agent (D) (Table X) (a), and after various exposure times (b and c) with a UV lamp (HQV 500 Osram). The extinction of the absorption band at 365 nm, which is responsible for the effect of the fluorescent brightening agent, diminishes

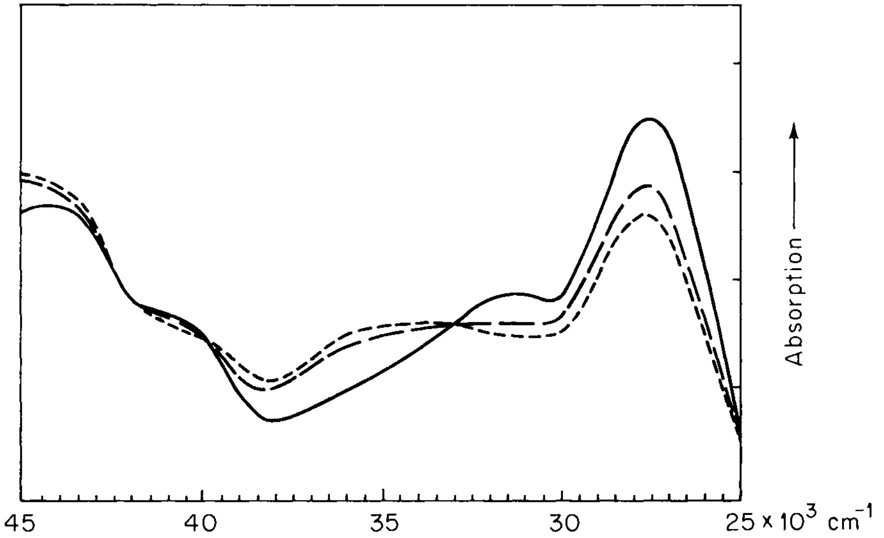

Fig. 13. *Cis-trans* isomerization of fluorescent brightening agent (D) (Table X): (a) ———; (b) — — —; (c) - - -.

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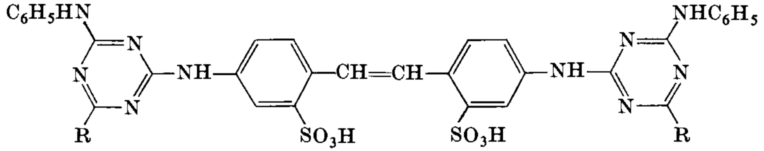
[95] G. N. Lewis, T. T. Masel, and D. Lipkin, *J. Am. Chem. Soc.* **62**, 2973 (1940).

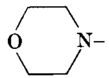
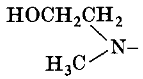
[96] H. Theidel, *Melliand Textilber.* 514 (1964).

[97] V. G. Bocharov, *Zavodsk. Lab.* **28**, 1454 (1962); *CA* **59**, 9470g (1963).

[98] See Theidel.[96]

TABLE IX



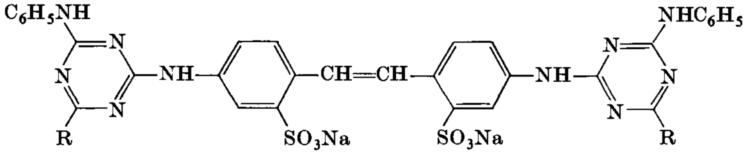
	R	*Relative solubility in water*	*Fiber affinity*	*Relative bleach stab. (chlorine)*	*Recom. for temp. range*
A-A	C_6H_5HN–	Low Low–medium	Cellulosics Polyamide	Medium	Above 110°F
A-M		Medium–high Low–medium	Cellulosics	Good	Best above 110°F
A—MMEA		Medium–high	Cellulosics	Good	All temp.
A-DEA	$(HOCH_2CH_2)_2N$–	High	Cellulosics	Good–medium	All temp.

more and more, while an absorption band at 278 nm is intensified simultaneously; the system of curves has three isosbestic points in common which are typical of the transposition.

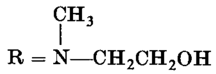
The cis–trans isomer pairs obtained by irradiation of the solution of a DAS fluorescent brightening agent can be separated by chromatographing in darkness, for example, with the carrier–flow-promoting agent system paper-pyridine, butanol, Kolthof buffer (pH 11) 4:1:3.[96,99] The cis isomer can be rendered visible by transformation into the fluorescent trans isomer by irradiation of the chromatogram.

The trans isomers of DAS fluorescent brightening agents are substantive and fluorescent; the cis isomers are freely soluble and for this reason are not found in the isolated solid powders. Formation of the cis isomer is promoted only in very dilute solutions. Treatment liquors set with fluorescent brightening agents must therefore be protected against light containing UV radiation. More concentrated stock solution are faster to light because of the UV filter effect of their surfaces.[100]

iii. Crystal forms in CC/DAS fluorescent brightening agents. Various crystal forms are known in those CC/DAS fluorescent brightening agents with formula (XXXII) which are commercially interesting for combination with detergent powders.

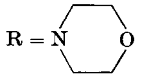


(XXXII)



$R = N(CH_3)\text{—}CH_2CH_2OH$ 101

$R = NHC_6H_5$ 102



103

The fluorescent brightening agents obtained by conventional methods at a temperature up to 100° consist of an "unstable" crystal modification which tends to yellowness and amorphism, conferring a yellowish appearance on detergent powders. At temperatures above 100° in water in the presence of alkalis or organic bases in a closed vessel, these fluorescent brightening agents form "thermostable" crystal modifications. They are

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[99] Y. Sayato, *Shokuhin Eiseigaku Zasshi* **2**, 56 (1961); *CA* **56**, 878d (1962).

[100] A. Wagner, *SVF* (*Schweiz. Ver. Faerbereifachleuten*) *Fachorgan Textilveredlung* **19**, 466 (1964).

therefore of greater technical interest because they are white and the detergent powders into which they are incorporated do not undergo a change of shade. The crystal modifications show characteristic differences in their X-ray spectra. Figure 14 shows the X-ray diffraction pattern of the unstable (yellow) modification of the fluorescent brightening agent [XXXII; R = $N(CH_3)CH_2CH_2OH$] and that of the stable (white) α-modification, which were obtained by use of the powders.[101, 104] The *d* values generally used for definition of the peaks are calculated from the angles plotted on the abscissa

$$d = \frac{\lambda}{2.\sin\delta}$$

where λ is the X-ray wavelength, $\lambda_{\mathrm{CuKx}} = 1.5418$ Å.

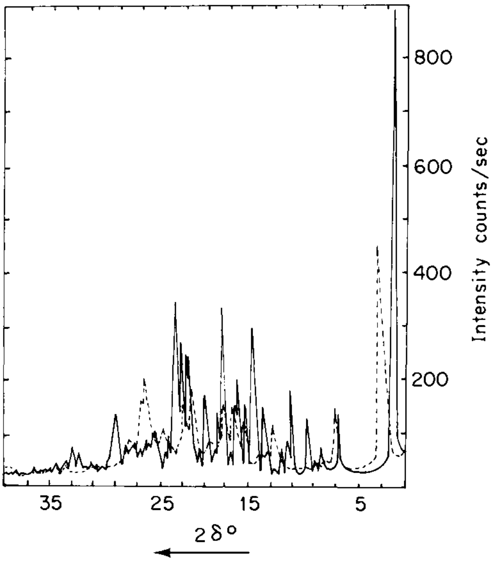


FIG. 14. X-Ray diffraction pattern. (———), α-Modification; (– – –), starting material.

2. *Heterocyclic Substitution Products*

Among the stilbene compounds substituted in the 4,4′-position by heterocyclic systems,[105] products of particular interest are those in which the heterocyclic substituent contains three hetero atoms: three N atoms,

[101] Gy, *BP* 1,116,619.

[102] Gy, *DBP* 1,219,940.

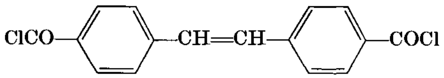
[103] Sterling Drug Inc. *BeP* 680,847.

[104] H. P. Klug and L. E. Alexander, "X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials," p. 235 ff. Wiley, New York, 1954.

[105] The arylooxazolyl-(2)- and aryloimidazolyl-(2)stilbene compounds are discussed in Section VI,C,4.

or two N atoms and one O atom. The following division into Section II,B,2,*a* (*C*-heterocyclic substitution products) and II,B,2,*b* (*N*-heterocyclic substitution products) has been selected according to whether the type of bond linking the heterocycle to the stilbene system is formed by a C or an N atom, since from the experimental-chemical standpoint the fluorescent brightening agents of group II,B,2,*a* can be built up from stilbene-4,4′-dicarboxylic acid and those of group II,B,2,*b* from 4,4′-diaminostilbene compounds. In their effect as fluorescent brightening agents those of the II,B,2,*b* group are more comparable with the aryltriazolyl-(2) (II,A,2) and the styryl substitution products (II,A,3), because in a similar manner to these they are built up from fluorophores without linking groups of atoms which may interrupt a conjugation. Because of the extensive conjugate system they show a longer-wave absorption but a narrower absorption curve and a favorable fluorescence maximum (see the Tinopal RBS types in Table V).

a. 4,4′-C-Heterocyclic Substitution Products. Up to the present, only those fluorescent brightening agents of this group which are free from solubilizing groups are known. The fluorescent brightening agents (A) and (B) (Table X) are two typical members. The starting product for their manufacture is stilbene-4,4′-dicarboxylic acid,[24] which is easily formed from *p*-toluic acid in a sulfur melt and is separated as an acid potassium salt. It can be converted without difficulty into stilbene-4,4′-dicarbonyl chloride (XXXIII).[106]



(XXXIII)

According to the conversion reaction of aromatic acid chlorides with nitriles investigated by Eitner,[107] (XXXIII) reacts with at least 4 moles of benzonitrile in the presence of 2 moles of $AlCl_3$ at 120–130° in an inert nonpolar solvent (*o*-dichlorobenzene), forming in good yield bis-*N*-acylacylnitrilium chloroaluminate (XXXIV), which cyclizes with ammonium chloride to 4,4′-bis[2-diphenyl-1,3,5-triazinyl-(6)]stilbene [fluorescent brightening agent (A), Table X].[108] An alternative course for the

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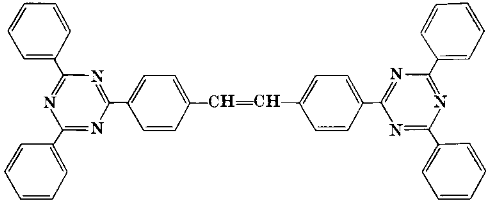
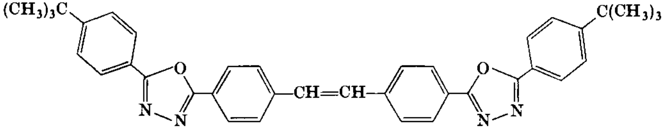
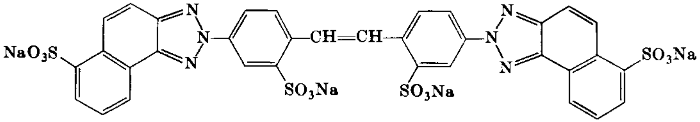
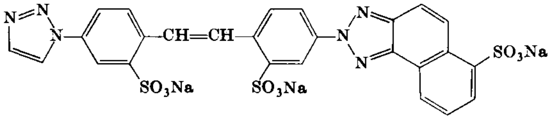
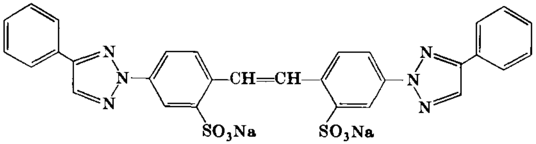
[106] F. Bell and D. H. Waring, *J. Chem. Soc.* p. 1025 (1948).

[107] P. Eitner and F. Krafft, *Ber.* **25**, 2266 (1892); H. Meerwein, P. Laasch, R. Mersch, and J. Spille, *ibid.* **89**, 219 (1956); see also E. Smolin and L. Rapoport, *in* "The Chemistry of Heterocyclic Compounds: *s*-Triazine," (A. Weissberger, ed.), p. 156 ff. Wiley (Interscience), New York, 1959.

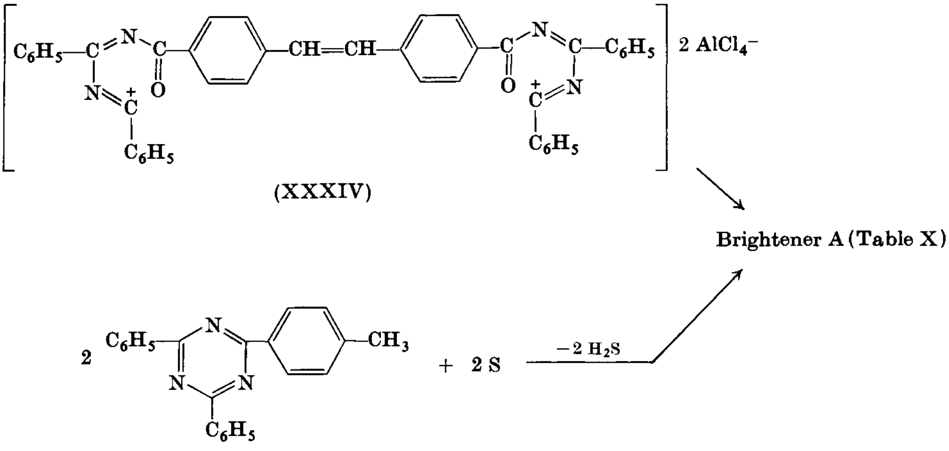
[108] CIBA, *FP* 1,456,944.

TABLE X

STILBENES SUBSTITUTED BY HETEROCYCLES

				Absorption maxima			Fluorescence maxima	
		M.p. (°C)	*Solv.*	λ (nm)	$\tilde{\nu}$ (cm^{-1})	*nH*	λ (nm)	$\tilde{\nu}$ (cm^{-1})
(A)		390	DMF	370	27.000	1850	446	32.402
(B)		350	DMF	363	27.500	1850	436	22.923
(C)		—	Water	375	26.600	1800	451	22.187
(D)		—	Water	365	27.300	1850	439	22.773
(E)		—	Water	370	27.000	1700	439	22.777

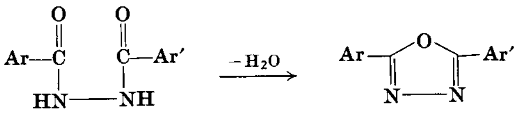
synthesis of fluorescent brightening agent (A) consists in the *S*-dehydration of 2,4-diphenyl-6-(*p*-tolyl)-1,3,5-triazine (XXXV), which can be produced from 4-methylbenzoyl chloride, benzonitrile, and $AlCl_3$, with subsequent cyclization with ammonium chloride.


(XXXIV)

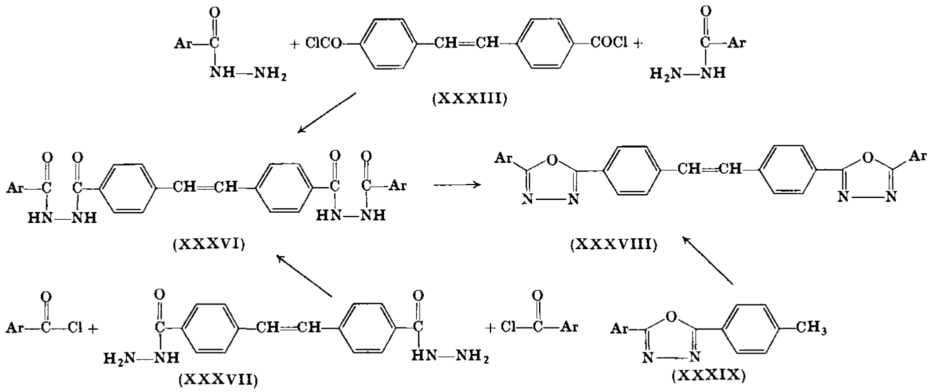
Brightener A (Table X)

(XXXV)

The dehydration of *N*,*N*′-diacylhydrazines by heating or with the aid of dehydrating agents ($SOCl_2$, PCl_5, $ClSO_3H$, oleum) is a long-known method for the production of 2,5-diaryloxadiazoles.[109]



The application of this reaction to the dehydration of the bis diacylhydrazines of stilbenedicarboxylic acid (XXXVI) leads to a group of


(XXXIII)

(XXXVI)

(XXXVIII)

(XXXVII)

(XXXIX)

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[109] R. Stollé, *Ber.* **32**, 797 (1899); *J. Prakt. Chem.* [2] **68**, 130 (1903); see FBy, *DBP* 825,111; CIBA, *DBP* 932,184.

fluorescent brightening agents (XXXVIII), among which 4,4′-bis[5-(*p*-*tert*-butylphenyl)-1,3,4-oxadiazolyl-(2)]stilbene [fluorescent brightening agent (B), Table X][110] is interesting from a commercial standpoint because of its good emulsifiability and high affinity for polyester. The bisdiacylhydrazine compounds (XXXVI) are produced by reacting the bisacylhydrazides (XXXVII) of stilbenedicarboxylic acid with the chloride of an aromatic acid or from (XXXIII) with an aromatic acylhydrazine in pyridine at 90–95°. As an alternative course in this series, the *S*-dehydration of the 2-aryl-5-(4-methylphenyl)-1,3,4-oxdiazole compounds (XXXIX) is also available.

Owing to their high melting points, fluorescent brightening agent (A) and its alkyl, alkoxy, and chlorine substitution products, which can be produced from the respective substituted benzonitriles, and also fluorescent brightening agent (B), are particularly suitable for the optical brightening of polyester, polyamide, and polypropylene spinning melts.

*b. 4,4′-*N*-Heterocyclic Substitution Products.* Starting from DAS by tetrazotization, coupling of the tetrazo compound with 2-naphthylamine-5-sulfonic acid, and triazolation of the resulting *o*-aminoazo dyestuff,[111] a chlorine-resistant, substantive fluorescent brightening agent was discovered in Blankophor G[112] [fluorescent brightening agent (C), Table X)] by Farbenfabriken Bayer. In high concentrations Blankophor G gives a marked green-blue fluorescence; the calculated maximum is at 450 nm (see Table II). Of the attempts to syntheisze from DAS *N*-heterocyclic substitution products with a blue fluorescence, only those concerned with the production of 1,2,3-triazoles were successful.[113, 114] The fluorescent brightening agents (D) and (E) are typical examples. The reactions in Chart 2 are used in the production of these fluorescent brightening agents. The production of 1-aryl-1,2,3-triazole compounds is experimentally a smooth reaction which can also be carried out on an industrial scale. In the case of the fluorescent brightening agent (D), it consists in the diazotization of 4-nitro-4-aminostilbene-2,2′-disulfonic acid (XL), reaction of the resulting diazonium salt with the amide of an aromatic sulfonic acid,[115] and treatment of the resulting azido compound (XLI) with acetylene.[116] The addition of acetylene to

[110] CIBA, *FP* 1,445,769.

[111] See also NSK, *JP* 3134/64; *CA* **61**, 8449b (1964).

[112] CI, fluorescent brightening agent No. 40.

[113] FBy, *DBP* 1,008,248.

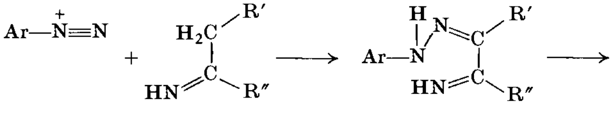
[114] FBy, *FP* 1,480,699.

[115] "Houben-Weyl," 4th ed., Vol. 9, p. 312. Thieme, Stuttgart, 1955; H. Bretschneider and H. Rager, *Monatsh. Chem.* **81**, 970 (1950).

[116] "Houben-Weyl," 4th ed., Vol. 10, Part 3, p. 817. Thieme, Stuttgart, 1965.

azido compounds proceeds uniformly and with sufficient velocity in aqueous DMF as solvent; it can be easily followed analytically since azido compounds show in the IR an isolated and characteristic band at 4.7 μ. The amine (XLIII) obtained from (XLII) by reduction yields the fluorescent brightening agent (D) in the usual reaction sequence: diazotization, coupling with 2-naphthylamine-5-sulfonic acid, and triazolation.[40]

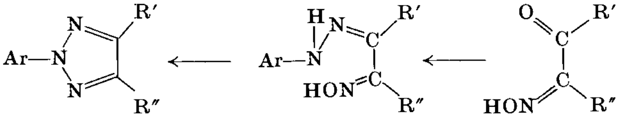
In principle, 1,2,3-triazolyl-(2) substitution products (XLVIII) are obtained by triazolation of the glyoxaliminoarylhydrazones (XLVII)[117] corresponding to the *o*-aminoazo dyes or by dehydration of the α-oximinoarylhydrazone compounds (XLIX). Selection of the method depends upon the availability of the hydrazones (XLVII) or (XLIX). For the production of the fluorescent brightening agent (E) (Chart 2), the dehydratization of α-oximinohydrazone (XLVI) obtained from 4,4′-dihydrazinostilbene-2,2′-disulfonic acid (XLV) and oximinoacetophenone has been selected. This is carried out with acetic anhydride in the presence of a little DMF.



(XLVII)

$R' = NO_2, COOR, CONH_2, CN, COR, C_6H_5$

$R'' = CH_3, C_6H_5$



(XLVIII) (XLIX)

$R' = H$, Alkyl

$R'' =$ Alkyl, Aryl

As in the case of Tinopal RBS and GS, fluorescent brightening agents (C), (D), and (E) are chlorine-resistant optical brighteners for cotton and for polyamide fibers (from acid liquors).

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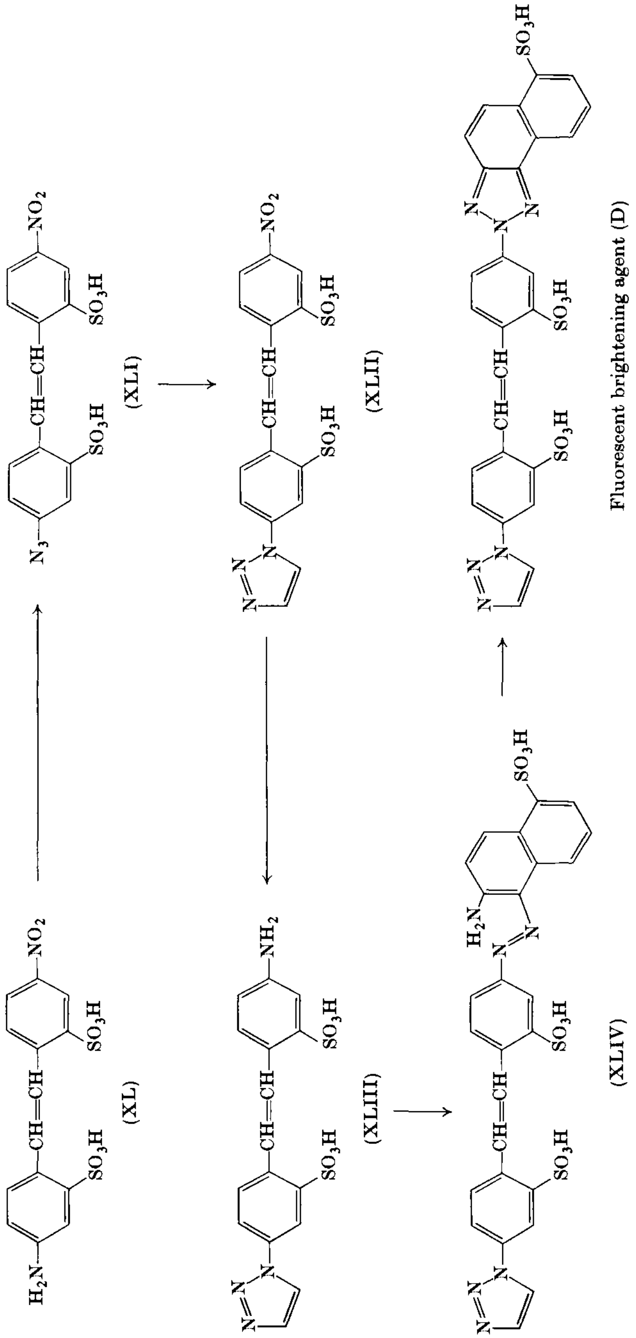
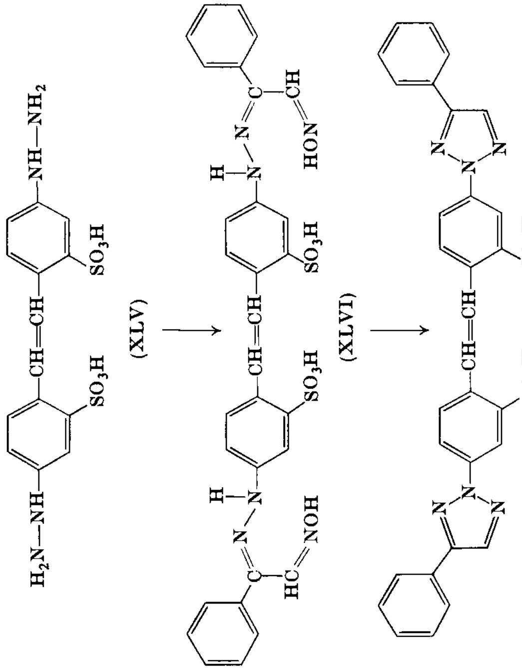
[117] "Houben-Weyl," 4th ed., Vol. 10, Part 3, p. 490. Thieme, Stuttgart, 1965; Isis-Chemie K.G., *DBP* 1,226,591.

CHART 2



(XL) (XLI) (XLII) (XLIII) (XLIV)

Fluorescent brightening agent (D)



Fluorescent brightening agent (E)

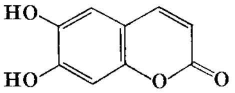
III. Coumarin and Carbostyril Compounds

A. Coumarin Compounds

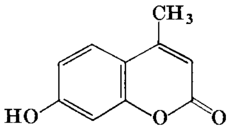
In 1911 Kopp and Joseph[118] described UV-absorbing light filters containing coumarin derivatives, in which the absorption band of coumarin at 311 nm was shifted bathochromically by one or several auxochromic groups (OH, NH_2, COOH, C_6H_5) in the 3- or 7-position. Among those mentioned were, for example, esculetin (L), daphnetin, and methylumbelliferone (7-hydroxy-4-methylcoumarin) (LI), which possesses a long-wave absorption band at 322 nm.[119] Eighteen years later, in the glucoside of esculetin (L), esculin, also known to be fluorescent, Krais[120] was the first to conceive of the possibility of fluorescent brightening with colorless fluorescent substances, thus discovering a "new white."

Brightening effects similar to those of esculin are also shown by 7-hydroxy-4-methylcoumarin (LI)[121] and 7-hydroxy-4-carboxymethylcoumarin (LII), subsequently marketed as Ultralin by Ultrazell.[122]

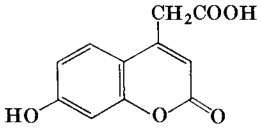
While the nonsubstantive hydroxycoumarin compounds can be applied only from alkaline baths and in the presence of starch,[123] good optical brightening effects are obtained on wool and synthetic fibers



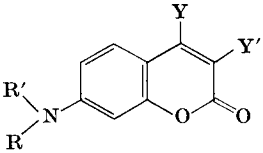
(L)



(LI)



(LII)



(LIII)

Y and Y′ = H, Alkyl,
Aralkyl, Aryl,
CH_2COOAlkyl, COOAlkyl

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[118] *DRP* 253,334.

[119] R. S. Shah and S. L. Bafna, *Indian J. Chem.* **1**, 400 (1963).

[120] P. Krais, *Melliand Textilber.* **10**, 468 (1929).

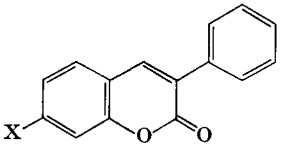
[121] H. von Pechmann and C. Duisberg, *Ber.* **16**, 2119 (1883).

[122] *BP* 472,473.

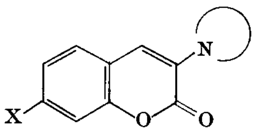
[123] See, for example, H. Meyer, *BP* 522,672; Lever Brothers & Unilever, *BP* 566,810; 567,716; Proctor & Gamble Comp., *USP* 2,673,186.

when the 7-aminocoumarin compounds (LIII)[124] are applied in aqueous solution in the form of water-soluble salts or as water-soluble derivatives. Strongly fluorescent optical brightening agents with valuable coloristic effects are those derivatives of the 7-hydroxy- and 7-aminocoumarins which contain a phenyl or *N*-heterocyclic radical in the 3-position. The 3-phenyl- (LIV) and 3-*N*-heterocyclic coumarin derivatives (LV) are important intermediates for this application.

Since 3-phenylcoumarin is constitutionally similar to stilbene, 7-*H*-3-phenylcoumarin derivatives which have an NH_2 or COOH group in the 4-position of the phenyl radical [3-(4′-aminophenyl)- and 3-(4′-carboxyphenyl)coumarin (LVI)] are also intermediates for the production of fluorescent brightening agents comparable with 4-aminostilbene[125] and stilbene-4-carboxylic acid.[126] In comparable ranges for both stilbene and 3-phenylcoumarin, valuable fluorescent brightening agents can be found among the *N*- and *C*-linked azoles. Petrovich[127] has investigated the quantum yields of the fluorescence of 14 coumarins which show their main fluorescence at 400–500 nm and ascertained that the most interesting products are 3-phenyl-7-aminocoumarin and its derivatives. The derivatives of 7-aminocoumarin are of the highest importance as fluorescent brightening agents. Table XI shows the influence of substituents on the UV absorption of 3-phenylcoumarin.

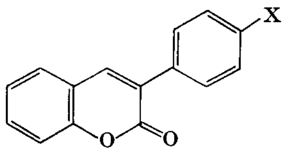


(LIV)



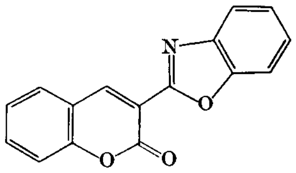
(LV)

$X = OH, NH_2, COOH$



(LVI)

$X = NH_2, COOH$



(LVII)

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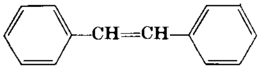
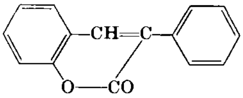
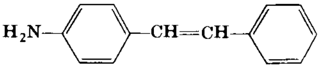
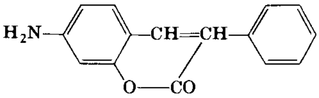
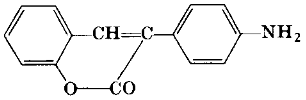
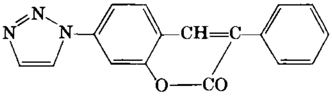
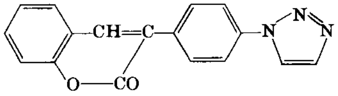
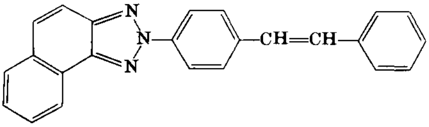
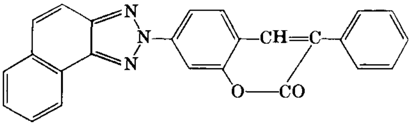
[124] CIBA, *USP* 2,610,152; S, *USP* 2,791,564; *FP* 1,025,467.

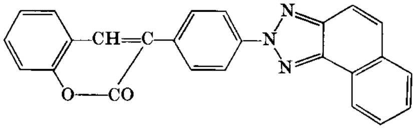
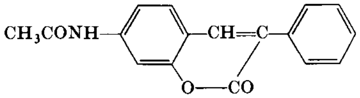
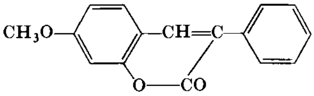
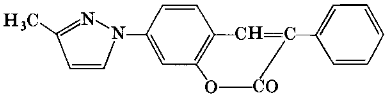
[125] See Section II,A.

[126] See Section VI,B,3.

[127] P. I. Petrovich, *Izv. Akad. Nauk SSSR, Ser. Fiz.* **27**, 703 (1963); *CA* **59**, 9477h (1963).

TABLE XI
UV Absorption of 3-Phenylcoumarins

	Absorption maxima[a]			
	λ (nm)	$\tilde{\nu}$ (cm^{-1})	$\epsilon \times 10^{-4}$	nH
	298 310.5 324	33.550 28.900 30.900	2.82 2.89 1.81	— — —
	325	30.800	1.47	—
	356.5	28.050	2.20	2450
	380	26.300	2.20	1750
	375	26.650	1.47	2350
	338	29.600	2.78	1950
	328	30.450	2.05	2300
	367	27.100	—	1750
	374	26.700	5.25	1650

	360	27.750	4.87	1600
	350	28.550	2.70	1900
	343	29.200	2.22	2000
	351	28.500	3.23	1950

[a] Determined in DMF.

The replacement of 3-phenyl in (LVI) by the stronger fluorophore, benzoxazolyl-(2) radical, leads to 3-benzoxazolyl-(2)-coumarin (LVII),[128] which is a good fluorescent brightening agent for polyacrylonitrile and polyester fibers. An additional auxochromic amino group shifts the absorption into the visible range; the benzazoles obtained from 7-diethylaminocoumarin-3-carboxylic acid are yellow-green fluorescent dyestuffs.[129]

1. *3-Substituted Coumarins*

Of the coumarin derivatives which bear no substituent in the 7-position only two types, (LVIII) and (LIX), are technically interesting as fluorescent brightening agents.

a. 5,6-Benzocoumarin-3-carboxylic Acid Derivatives. Ethyl 5,6-benzocoumarin-3-carboxylate (LVIII; $R = COOC_2H_5$)[130] is obtained by condensation of 2-hydroxy-1-naphthaldehyde with malonic ester in the

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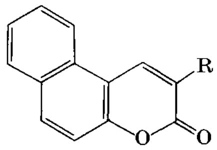
[128] CIBA, *BP* 914,719; *DBP* 1,222,014.

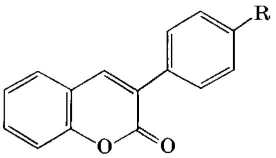
[129] Gy, *DBP* 1,098,115; *USP* 3,014,041; Ilford, *BP* 867,592.

[130] "Beilsteins Handbuch der organischen Chemie," 4th ed., Vol. 18, p. 438; see, for example, E. Knoevenagel and F. Schröter, *Ber.* **37**, 4484–4496 (1904).



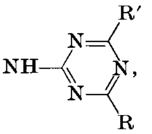
(LVIII)

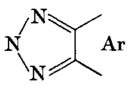
R = COOAlkyl, CONHAlkyl, CN



(LIX)

R = NH—Acyl,





presence of piperidine,[131] preferably in the presence of morpholine[132] as a catalyst. It gives fluorescent brightening effects with medium coloristic properties on fibers made from polyester, polyurethane, polyacrylonitrile, and cellulose esters, as well as on polyamides. With regard to the further derivatives of 5,6-benzocoumarin-3-carboxylic acid,[133] attention is drawn, in particular, to the amides.[134]

b. 3-Phenylcoumarins

3-(4-Aminophenyl)coumarin (LIX; R = NH_2)[135] was first proposed by du Pont[136] as a starting material for the production of fluorescent brightening agents. This 3-phenylcoumarin compound, which is obtained by condensation of salicylaldehyde with 4-nitrobenzyl cyanide and subsequent reduction of the NO_2 group, is also readily available on an industrial scale.

Owing to the pharmacological importance of the coumarins, the reactions leading to 3-phenylcoumarins were soon under investigation. Since the fluorescent brightening agents derived from 3-phenylcoumarins substituted in the 7-position (Section III,A,2,*b*) are also of great industrial interest, the methods used in the production of 3-phenylcoumarins will be discussed here.

(1) The condensation of salicylaldehyde with benzyl cyanide (p. 596) with separation of water takes place on heating to 200°[137]; it is facilitated by use of NaOH[138] or piperidine[139] in the manner of the Knoevenagel

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[131] FBy, *DBP* 1,090,624; *USP* 2,878,138.

[132] P. I. Petrovich, *RP* 165,750; *CA* **62**, 10417a (1965).

[133] See also BASF, *DBP* 1,275,983.

[134] FBy, *DBP* 1,205,941; *USP* 3,075,996.

[135] "Beilsteins Hanbduch der organischen Chemie," 4th ed., Vol. 17, pp. 374.

[136] *USP* 2,702,296.

[137] R. von Walter, *J. Prakt. Chem.* [2] **61**, 194 (1900).

[138] W. Borsche and F. Streitberg, *Ber.* **37**, 3156 (1904).

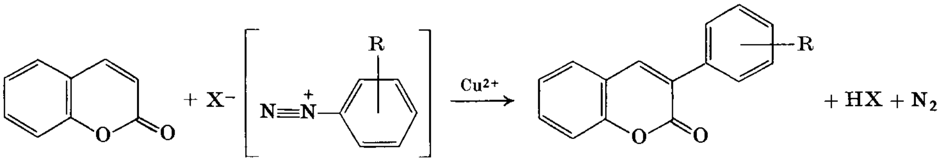
[139] K. Brand and O. Loehr, *J. Prakt. Chem.* [2] **109**, 375 (1925).

reaction.[140] This does not result in the 2-hydroxy-α-phenylcinnamonitrile (LX)[141] at first formed, but in the ring–chain tautomers, 3-phenylcoumarinimine (LXI), which on treatment with aqueous hydrochloric acid is saponified to 3-phenylcoumarin (LXIII); in methanolic hydrochloric acid the acetal (LXII) is formed as a separable intermediate.[141a]

A smoother reaction is the condensation of 2-methoxybenzaldehyde with benzyl cyanide similar to the Knoevenagel reaction and cyclization of the resulting 2-methoxy-α-phenylcinnamic nitrile (LXV) by heating briefly with pyridine hydrochloride.[142]

(2) Perkin[143] had already obtained 3-phenylcoumarin by condensation of salicylaldehyde with phenylacetic acid in acetic anhydride (and sodium acetate). The moderate yields were improved by Oglialoro[144] by use of sodium phenylacetate.[145] The condensation of salicylaldehyde with 4-nitrophenylacetic acid in the presence of triethylamine or tripropyl amine under the conditions of the Knoevenagel reaction gives 3-(4-nitrophenyl)coumarin with a 78% yield.[146]

(3) In addition to the 3-phenylcoumarin syntheses according to Knoevenagel,[147] and Perkin-Oglialoro, the Meerwein reaction of arylating α,β-unsaturated aldehydes, ketones, and carboxylic acids with aryldiazonium compounds in the presence of cupric salts is of interest in the case of coumarin. The yield of 3-phenylcoumarin derivatives depends on the substituents in the aryldiazonium compounds. It increases for R in the sequence 2-NO_2 (11%) < H (18%) < CH_3CONH



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[140] *Org. Reactions* **1**, 226 and 233 (1942); *Chem. Rev.* **36**, 4 (1945).

[141] R. Kuhn and D. Weiser, *Ann. Chem.* **600**, 144 (1956).

[141a] *Angew. Chem.* **69**, 371 (1957).

[142] N. P. Buu-Hoi, *J. Chem. Soc.* p. 2130 (1950).

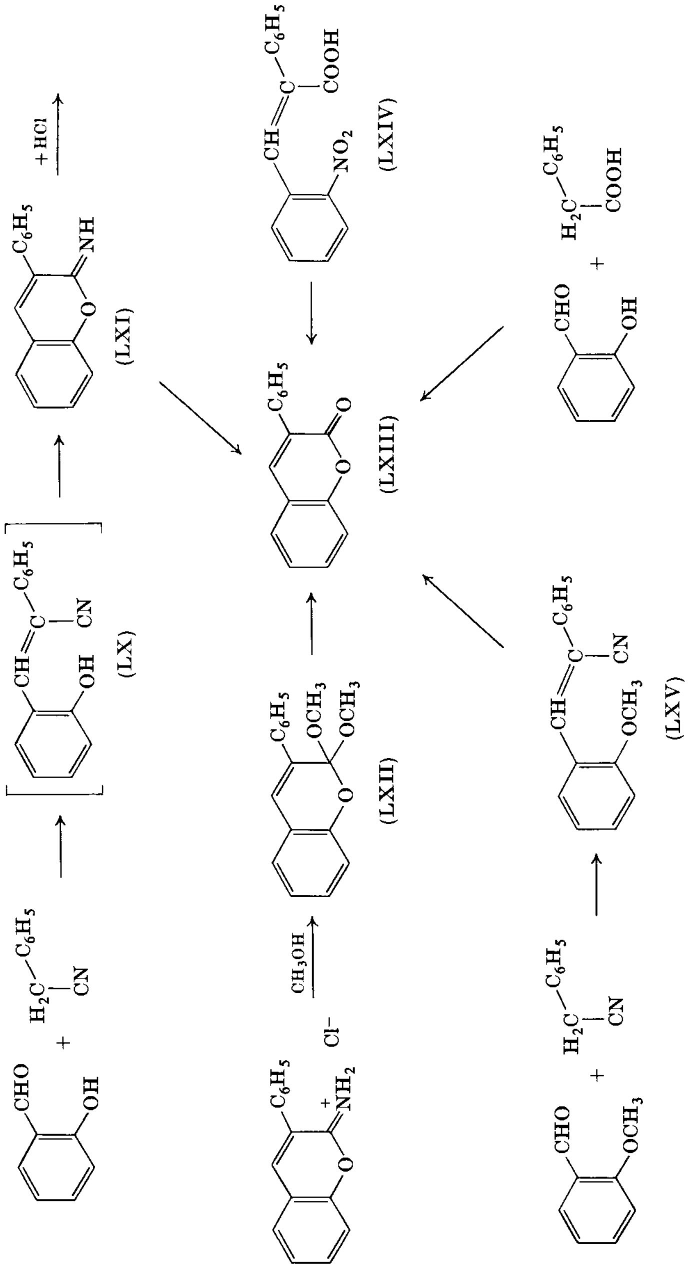
[143] W. H. Perkin, *J. Chem. Soc.* **21**, 53 and 181 (1868).

[144] A. Oglialoro, *Gazz. Chim. Ital.* **9**, 428 and 533 (1879); **20**, 396 (1890); *Chem. Zentr.* pp. 132 and 230 (1880); p. 553 (1890).

[145] Concerning the Oglialoro modification of the Perkin reaction, see J. R. Johnson, *Org. Reactions* **1**, 210 (1942); M. Crawford and J. A. M. Shaw, *J. Chem. Soc.* p. 3435 (1953).

[146] W. Vorsche, *Chem. Ber.* **42**, 3596 (1909); R. E. Buckles, *J. Am. Chem. Soc.* **70**, 415 (1948); **73**, 4972 (1951).

[147] E. Knoevenagel, in "Houben-Weyl," 4th ed., Vol. 6, Part 2, p. 640. Thieme, Stuttgart, 1963.


(LX)
(LXI)
+HCl
(LXII)
CH₃OH
Cl⁻
(LXIII)
(LXIV)
(LXV)

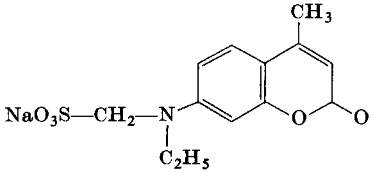
(26%) < OCH_3 (35%) < SO_3H (43%) < 4-Cl (46%) < 4-NO_2 (50%) < 4-COOH (52%).[148] The Meerwein reaction is therefore also a suitable method for the production of 3-(4-nitrophenyl)coumarin.

(4) An interesting method for the production of 3-phenylcoumarin is the cyclization of 2-nitro-α-phenylcinnamic acid (LXIV) in quinoline with Gattermann copper at 260°.[149]

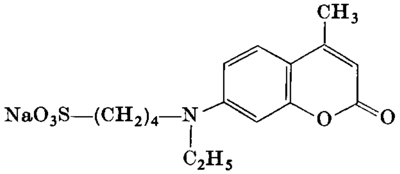
The 3-(4-aminophenyl)coumarin (LVI; $X = NH_2$) required as an intermediate for fluorescent brightening agents of the 3-phenylcoumarin series (LIX) (Table XII)[135, 151–154] has been produced both according to Knoevenagel (von Walter) and Perkin-Oglialoro, and also according to Meerwein.[150] Important fluorescent brightening agents are obtained from this amine by acylation with methoxybenzoic acid, chlorocarbonic esters, carbamic chlorides, and chlorotriazinyl compounds, e.g., 2-diethylamino-4,6-dichlorotriazine, and also by attachment of the NH_2 group to an aryltriazole nucleus in the 2-position. The isomers of 3-phenylcoumarin substituted in the 7-position (Section III,A,2,*b*) are more interesting and more important fluorescent brightening agents.

2. *7-Aminocoumarins*

a. 4-Alkyl-7-aminocoumarins. Coumarins substituted in the 7-position by an amino or an alkylamino group are notable for the strong blue fluorescence of their solutions. 7-Amino- and 7-alkylamino-4-methylcoumarins, as well as their water-soluble salts (see Table XIII) and their derivatives solubilized by reaction with aldehydes and $NaHSO_3$ (LXVI),[155] with chloroacetic acid, or by sulfonation were marketed by Ciba and Sandoz. A fluorescent brightening agent (LXVII) obtained by



(LXVI)



(LXVII)

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[148] H. Meerwein, E. Büchner, and K. van Emster, *J. Prakt. Chem.* [2] **152,** 189 (1939); Schering-Kahlbaum, *BP* 480,617; *DRP* 714,573; C. S. Rondestvedt, *Org. Reactions* **11,** 189 (1960); *in* "Houben-Weyl," 4th ed., Vol. 10, Part 3, p. 171. Thieme, Stuttgart, 1965.

[149] N. Oda, *Yakugaku Zasshi* **82,** 1185 (1962); *CA* **59,** 566d (1963).

[150] S. Kumar, J. L. Bose, and S. Siddiqui, *J. Sci. Ind. Res.* (*India*) **11B,** 81 (1952).

[151] DuP, *USP* 2,701,357; 2,701,296.

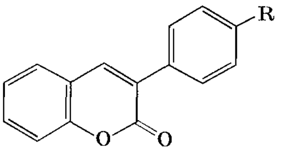
[152] FBy, *DBP* 1,089,357; *USP* 3,074,963.

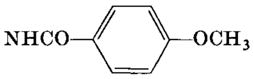
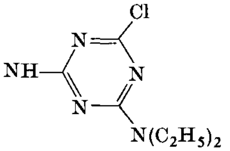
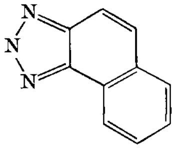
[153] FBy, *DBP* 1,249,211; *USP* 3,184,459.

[154] S, *SP* 441,347; *USP* 3,288,804.

[155] CIBA, *SP* 265,707/8; 265,713.

TABLE XII



R	*M.p.* (°C)		*References*
NH_2	177–178		135
	—	Paper, textiles	151
$NHCOOCH_3$	152–154	Synthetic fibers, particularly those made from polyamides, polyacrylonitrile from an aqueous bath	152
	218	Plastic and synthetic fibers in the mass	153
	250–255	Organic materials, particularly polyesters	154

reaction of 7-ethylamino-4-methylcoumarin with butanesultone has been recommended by Farbenfabriken Bayer[156] for the fluorescent brightening of wool.

The Pechmann coumarin synthesis[157] can be applied generally for the production of the 7-aminocoumarin and 7-hydroxycoumarin derivatives (Section III,A,3). It consists in the condensation of phenols with β-ketocarboxylic esters or nitriles in the presence of ionizing catalysts: HCl, H_2SO_4, H_3PO_4, $POCl_3$, $AlCl_3$, $ZnCl_2$, $SnCl_4$; and it proceeds so easily when the reactive *m*-alkylaminophenols and resorcinol are used

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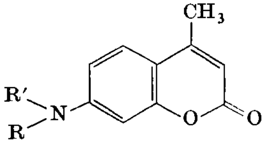
[156] *DBP* 946,449.

[157] "Houben-Weyl," 4th ed., Vol. 6, Part 2, p. 641. Thieme, Stuttgart, 1963.

that ion-exchange resins are effective as catalysts. The 7-amino-4-methylcoumarins which are commercial fluorescent brightening agents are summarized in Table XIII.

TABLE XIII



R	R'	M.p. (°C)	References[a]
H	H	—	1
CH_3	H	123	2
CH_3	CH_3	145	3
C_2H_5	H	151	4
C_2H_5	C_2H_5	73	5

[a] Key to references:

1. H. von Pechmann and O. Schwab, *Chem. Ber.* **32**, 3693 (1899); CCC, *USP* 3,008,969.
2. H. von Pechmann and O. Schwab, *Chem. Ber.* **32**, 3696 (1899).
3. CIBA, *DRP* 923,422; 963,268; *BP* 735,395; CCC, *USP* 2,844,599; 2,903,430; Pro-Nyl-Chem., *USP* 2,692,238; S. Pressner, *USP* 2,915,472.
4. S, *SP* 285,144; *CA* **47**, 11763f (1953).
5. CIBA, *DRP* 842,074; *BP* 741,959; S, *SP* 307,298; *BP* 741,959; *DRP* 1,070,133; S. Pressner, *USP* 2,730,503; Saul & Co., *USP* 2,791,564; Nippon Kagaku Co., *JP* 2680; *CA 54*, 12605g (1960); Warwick Chemical, *BP* 911,104; CCC, *USP* 2,844,539; G, *USP* 2,791,563; Gevaert Photo Prod. N.V., *BP* 1,052,692.

In the condensation of *m*-aminophenol with acetoacetic ester under the conditions of the Pechmann coumarin synthesis,[158] 7-amino-4-methylcoumarin is formed only in a low yield, together with 7-hydroxy-4-methylcarbostyril, in the manner of the Knorr quinoline synthesis.[159] On the other hand, according to a patent of American Cyanamid,[160] 7-amino-4-methylcoumarin can be produced in good yield from *m*-hydroxyphenyl ethyl carbamate.

The 7-alkylamino-4-methylcoumarin compounds are produced by use of ethyl acetoacetate and $ZnCl_2$ as catalyst in alcohol.[161] The important commercial product 7-diethylamino-4-methylcoumarin is obtained with

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[158] H. von Pechmann and O. Schwab, *Ber.* **32**, 3696 (1899).

[159] F. W. Bergmann, *Chem. Rev.* **35**, 157 (1944).

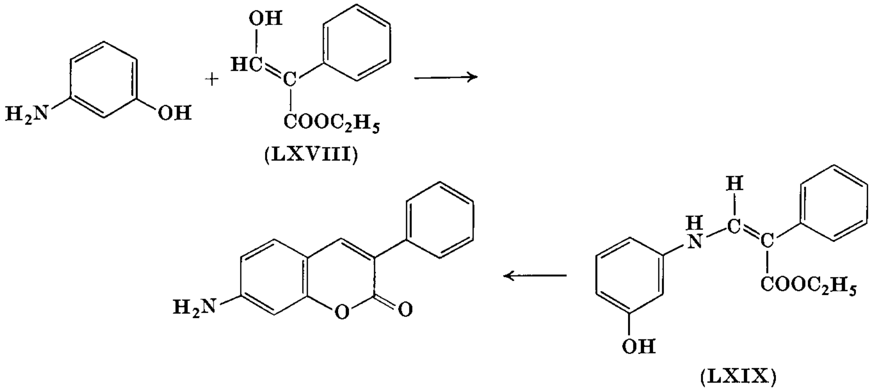
[160] CCC, *USP* 3,008,969.

[161] V. L. Plakidin *et al.*, *RP* 182,730; *CA* **66**, 10847e (1967).

a better yield by heating *m*-diethylaminophenol (stabilized with $SnCl_2$) with excess ethyl acetoacetate in the presence of $ZnCl_2$ for 8–12 hours at 102–108°.

The 7-alkylamino-4-methylcoumarins offer the advantage as fluorescent brightening agents that they can be applied to textiles, preferably cellulose acetate and nylon, in the scouring operation[162] from organic solvents or from neutral and acid baths. For this reason commercial brands of these products are in most cases prepared accordingly (Table XIV). Although the fastness properties of their fluorescent brightening effects do not meet high requirements, the alkylamino-4-methylcoumarins continue to be recommended.[163] They show a high yield, a high degree of whiteness, and are readily available on an industrial scale.

b. 3-Phenyl-7-aminocoumarins. The most important fluorescent brightening agents of the coumarin range are derived from 3-phenyl-7-aminocoumarin. Its production is therefore of particular interest. In principle, it can be produced according to the Pechmann coumarin synthesis (see preceding section) by using as the β-ketocarboxylic acid derivative ethyl 3-hydroxy-2-phenylacrylate or 3-hydroxy-2-phenylacrylonitrile (formyl benzyl cyanide) [e.g., (LXVIII)].[164]



(LXVIII)

(LXIX)

The reaction with *m*-aminophenol proceeds in an inert solvent (nitrobenzene) in the presence of Lewis catalysts ($AlCl_3$ or BF_3) at 100–130° with a 50% yield, without the necessity of protecting the NH_2 group of the *m*-aminophenol. Ethyl 3-(3-hydroxyphenylamino)-2-phenylacrylate

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[162] CIBA, *DBP* 963,268.

[163] *SVF* (*Schweiz. Ver. Faerbereifachleuten*) *Fachorgan Textilveredlung* **18**, 175 and 693 (1963) (Uvitex WGS); M. Hayashi, *Kaseigaku Zasshi* **11**, 252 (1960); **13**, 136 (1961); *CA* **55**, 22834h (1961).

[164] Gy, *USP* 3,322,794.

TABLE XIV

APPLICATION OF 7-ALKYLAMINO-4-METHYLCOUMARINS

With compounding agents	*References*[a]
Acids	
Solid, water-soluble inorganic acids, e.g., sodium hydrogen sulfate	1
Organic acids, e.g., tartaric acid, oxalic acid, maleic acid, fumaric acid (possibly + dispersing agent)	2
Solid, water-soluble sulfonic acids, e.g., naphthalene-1,5-disulfonic acid	3
Benzylphosphonic acid	4
Surface-active agents	
Ionic agents:	
Soap, oleylsulfonate, condensation products formed from naphthalenesulfonic acids and formaldehyde	5
Isobutylphenoxypentaethoxysulfate	6
Sulfonates of higher synthetic alcohols	7
Nonionic agents:	
Oxyalkylated fatty amines	
Isooctylphenoxydeca(penta)ethoxyethanol	8
Mixtures	
Turpentine, surfactant compounds, or emulsifiers (polyethylene laurate)	9
Formaldehyde-urea	10

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[a] Key to references:

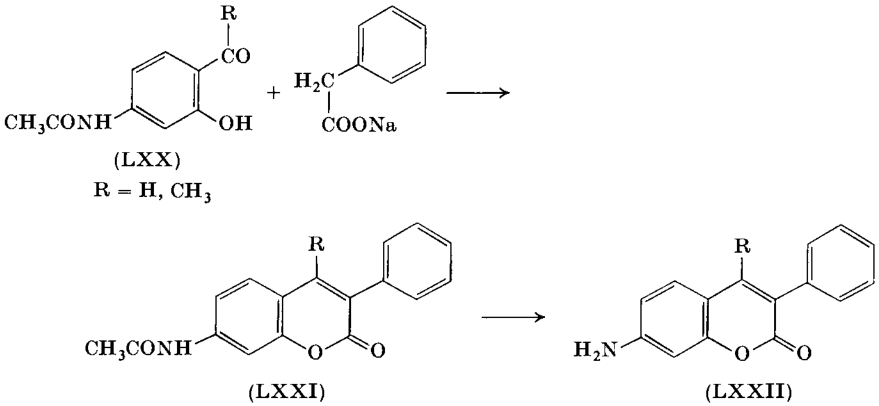
1. G, *USP* 2,791,563; Nisso Chem. Ind. Co., *JP* 14,929; CIBA, *DRP* 923,422.
2. CIBA, *SP* 320,749; CCC, *USP* 2,844,539; Nihon Kagaku, *JP* 342,680.
3. G, *DRP* 1,151,259; *BP* 735,395.
4. CCC, *USP* 2,844,539; Nihon Kagaku, *JP* 342,680.
5. Sandoz, *BP* 741,959; *SP* 307,298.
6. S. Pressner, *USP* 2,730,503.
7. Warwick Chemical, *BP* 911,104.
8. S. Pressner, *USP* 2,730,503.
9. S. Pressner, *USP* 2,915,472; Pro-Nyl, *USP* 2,763,618; 2,692,328; CCC, *USP* 2,903,430.
10. Mitsubishi Rayon, *JP* 3150/58.

(LXIX), which is formed from *m*-aminophenol and ethyl 3-hydroxy-2-phenylacrylate in boiling toluene under azeotropic conditions with an 80% yield, can be converted in a simplified procedure without use of Lewis catalysts and without solvent in the presence of aromatic amines (aniline, *m*-aminophenol, nitroaniline, anisidine) at 150–200° into 3-phenyl-7-aminocoumarin.[165] The yields do not exceed 60%.

The methods described in Section III,A,1 for the production of 3-phenylcoumarin using the Knoevenagel, Perkin-Oglialoro, and Meerwein reactions, are also suitable for the production of 3-phenyl-7-aminocoumarins. A most important consideration in the selection of the method is the availability of the starting products.

The Meerwein reaction can be carried out in the case of 7-dialkylamino-4-methylcoumarins[166] and 7-nitrocoumarin,[167] but 7-dialkylamino-3-phenylcoumarins are very greenish fluorescent brightening agents and 7-nitrocoumarin is not easy to obtain.

By the Perkin-Oglialoro reaction, on the other hand, 7-acetamido-(LXXI) and 7-amino-3-phenylcoumarin (LXXII) are readily available, using aromatic carbonyl compounds (LXX) which have an OH group in the 2-position and an acetylamino group in the 4-position, with sodium phenylacetate.[168]



(LXX)
R = H, CH_3

(LXXI)

(LXXII)

This reaction is facilitated when 2-hydroxy-4-acetylamidobenzaldehyde (LXX; R = H) is replaced by its anil.[169] By use of the Knoevenagel reaction in the condensation of 2-methoxy-4-acetamidobenzaldehyde

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[165] Gy, *USP* 3,356,689.

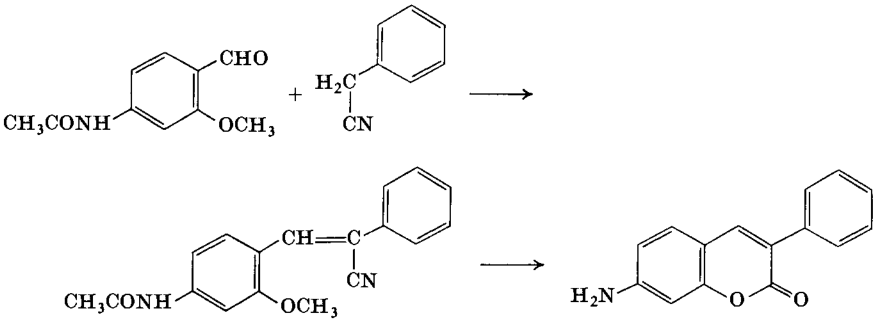
[166] CCC, *USP* 2,844,594.

[167] Showa Chem. Ind., *JP* 18,632/65; *CA* **65**, 7329h (1966).

[168] N. V. Subba Rao and V. Sundaramurthy, *Proc. Indian Acad. Sci.* **A42**, 249 (1955); *CA* **50**, 7797a (1956).

[169] FBy, *FP* 1,425,950; 3,352,885.

with benzyl cyanide,[170] 7-amino-3-phenylcoumarin can be produced with a total yield of 75–90% according to the following reaction scheme[171]:



As in the case of 3-(4-aminophenyl)coumarins, the most important and most valuable fluorescent brightening agents are to be found among the *N*-acyl compounds of 3-phenyl-7-aminocoumarin, particularly among the *N*-triazinyl compounds (see Table XV).

3. *7-Hydroxy- and 7-Alkoxycoumarins*

a. 7-Hydroxycoumarins. The 7-hydroxycoumarins which have a substituent in the 4- or 3-position are easily obtained by the Pechmann coumarin synthesis from resorcinol and β-ketocarboxylates in the presence of conc. H_2SO_4.[172] Despite the moderate coloristic fastness properties of 7-hydroxy-4-methylcoumarin (methylumbelliferone), which can be produced easily and cheaply from resorcinol and acetoacetic ester, this product[173] and the more fluorescent 3-benzyl derivatives[174] continue to be recommended as fluorescent brightening agents (Blankan, Dragolux).

b. 7-Hydroxy- and 7-Alkoxy-3-phenylcoumarins. By application of the Oglialoro variant of the Perkin reaction to the condensation of resorcylaldehyde with phenylacetic acid, Bargellini[175] obtained 7-acetoxy-3-phenylcoumarin (LXXIII), which can be saponified to the 7-hydroxy compound (LXXIV), and which gives on methylation 7-methoxy-3-phenylcoumarin (LXXV). In comparison with methylumbelliferone,

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[170] See Buu-Hoi.[142]

[171] Gy, *DBP* 1,020,636; *USP* 2,881,186; 2,929,822.

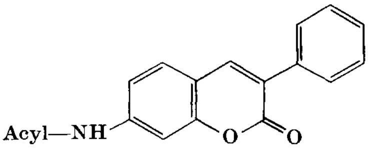
[172] See von Pechmann and Duisberg.[121]

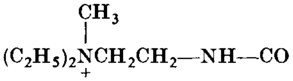
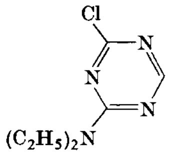
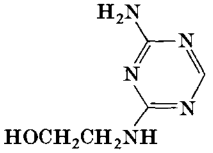
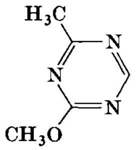
[173] Chadeloid Corp., *USP* 2,855,369; BASF, *BeP* 620,722; N. A. Pater, *Nuovo Cimento* [10] **5**, 526 (1957).

[174] Davies-Young Soap, *USP* 2,710,285.

[175] G. Bargellini, *Gazz. Chim. Ital.* **57**, 457 (1927); *CA* **21**, 2193 (1927); *Atti Accad. Nazl. Lincei* [6] **8**, 394 (1928).

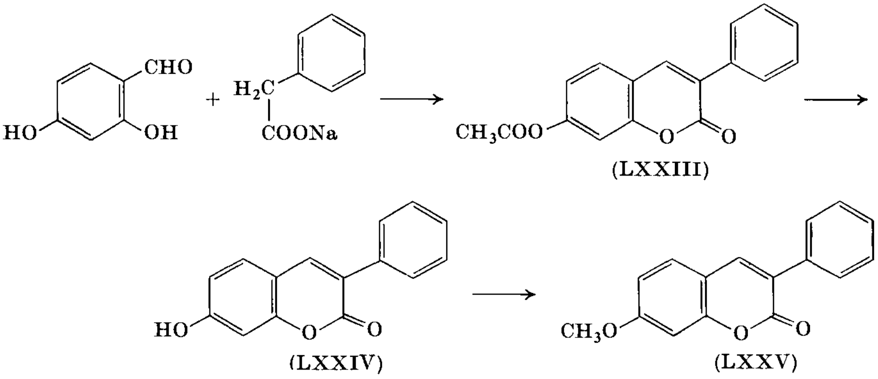
TABLE XV



Acyl	*M.p.* (°C)	*Application*	*References*[a]
$C_2H_5O—CO$	260	Nylon, acetate filament	1
$HOCH_2CH_2—NH—CO$	218–219	Wool, nylon, acetate filament	1
 $(C_2H_5)_2\underset{+}{\overset{CH_3}{N}}CH_2CH_2—NH—CO$	163–167	Photographic coatings	2
	199–200	Plastics vinyl polymers (PVC)	3
	220–221	Polyacrylonitrile cellulose acetate (wool, polyamide)	3
	221	Polyester, plastics	4

[a] Key to references:

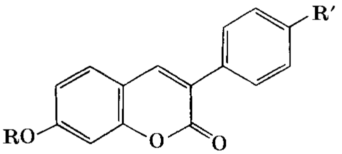
1. Reference 171.
2. E. Kobayashi and T. Suzuki, *JP* 11,956/65; *CA*. **63**, 16511e (1965); Eastman Kodak, *FP* 1,443,030.
3. Gy, *DRP* 1,096,909; *USP* 2,945,033.
4. FBy, *DRP* 1,245,306; *USP* 3,242,177.



(LXXIII) (LXXIV) (LXXV)

(LXXV) possesses improved fluorescent brightening effects and improved coloristic fastness properties.[176] The properties of the fluorescent brightening agents of this group of compounds are summarized in Table XVI.

TABLE XVI



R	R′	M.p. (°C)	*Application*	*References*
H	H	206–208	Cellulose acetate	175, 176
CH_3CO	H	182–184	Polyamide	175, 176
CH_3	H	125–126	Polyacrylonitrile	175
CH_3	$COOCH_3$	233–234	Polyester	176
CH_3	Cl	184–185	Cellulose acetate	176
CH_3	CH_3	146–147	Polyacrylonitrile	176
C_2H_5	H	164–165	Polyester	175, 176

c. 7-Alkoxy-3-heterylcoumarins. The *N*-heterylacetic acids and their nitriles, particularly those which are derived from nitrogen heterocycles with two and three N atoms, such as 1,2,3-triazolyl-(1)-acetonitrile (LXXVII) and 1,2,4-triazolyl-(1)-acetic acid, can be reacted with

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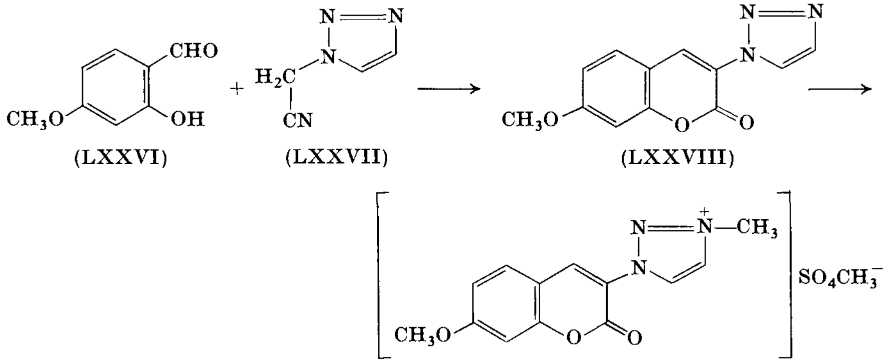
[176] FBy, *DBP* 1,102,694; *USP* 3,351,482.

2-hydroxy-4-methoxybenzaldehyde (LXXVI), using the Knoevenagel or the Perkin-Oglialoro procedures, to form 3-*N*-heteryl-7-methoxycoumarin compounds.[177] The 7-alkoxy-3-*N*-heterylcoumarins, which



(LXXVI) (LXXVII) (LXXVIII)

(LXXIX)

are formed in good yields, can be converted without any difficulty by alkylating agents (dimethyl sulfate) into cycloammonium salts. The ammonium salt (LXXIX) obtained from 3-[1,2,3-triazolyl-(1)]-7-methoxycoumarin (LXXVIII) is a good fluorescent brightening agent for polyacrylonitrile fibers.

4. *7-N-Heterylcoumarins*

The derivatives of 7-amino-3-phenyl- and 7-amino-3-*N*-heterylcoumarins in which the N atom of the NH_2 group is built into a five-membered heterocycle with two or three N atoms are of particular technical and coloristic interest. The methods used to obtain these derivatives from 7-aminocoumarins are essentially the same as those adopted in the production of *N*-heterylstilbenes from aminostilbenes (see Sections II,A,2 and II,B,2,*b*). The most important fluorescent brightening agents of this group are summarized in Table XVII. Their syntheses are summarized in Chart 3.

The starting material best used in manufacturing processes for the fluorescent brightening agents (A) to (F) (Table XVII) is generally 7-amino-3-phenylcoumarin. The processes start with diazotization of the hydrochloride in glacial acetic acid suspension or in sulfuric acid solution. The acid solutions or suspensions of the 3-phenylcoumarinyl-(7)-diazonium salts can be used directly for coupling with 2-naphthylamine-1-sulfonic acid or with 4-amino-2-butoxytoluene; triazolation of

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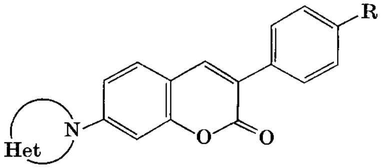
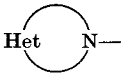
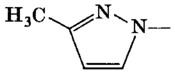
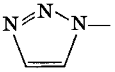
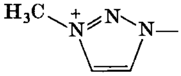
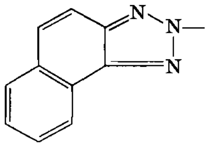
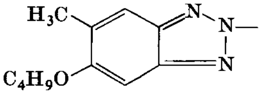
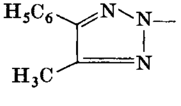
[177] FBy, *USP* 3,271,412.

TABLE XVII



		R	*M.p.* (°C)	*Application*	*References*[a]
(A)		H	216–217	Fibers made from polyester, acetylcellulose, nylon 66, Perlon, nylon 6	1
(B)		H	143–146	Fibers made from polyester	2
(C)		CH_3	252–253	Fibers made from polyacrylonitrile	3
(D)		H	250	Fibers made from polyester (Terylene, Dacron) in presence of carriers. Plastic compositions and spinning compounds	4
(E)		H	188–190	Migration-resistant fluorescent brightening of polyvinyl chloride	5
(F)		H	162	Fibers made from polyester, plastics, polyester spinning compounds	6

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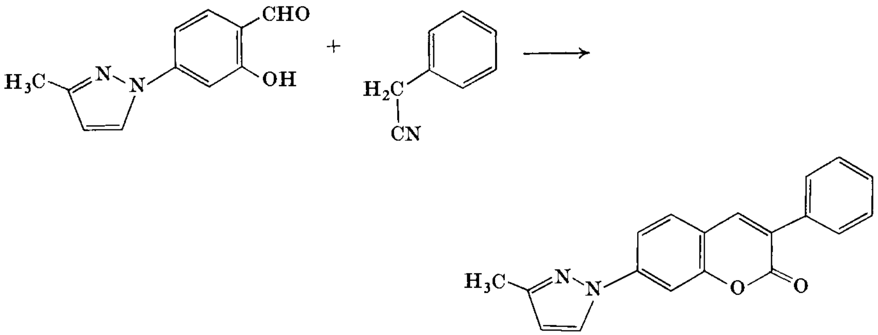
[a] Key to references:
1. Gy, *SP* 405,327; 419,146; *USP* 3,123,617.
2. FBy, *BP* 1,049,149.
3. FBy, *BP* 1,049,149.
4. S, *FP* 1,358,820.
5. FBy, *FP* 1,487,745.
6. FBy, *BP* 1,113,918; S, NE. 6800021.

the resulting *o*-aminoazo dyestuff to the fluorescent brightening agents (D) and (E) is carried out according to the triazolation process described in Section II,A,2,[40] preferably with copper acetate in pyridine at 75°.

For the production of 3-phenyl-7-hydrazinocoumarin (LXXX), 3-phenylcoumarinyl-(7)-diazonium chloride formed in water is reduced with sodium sulfite. (LXXX) reacts with 1,3-diketones according to the Knorr pyrazole synthesis,[178] forming 3-phenyl-7-pyrazolylcoumarins: for the fluorescent brightening agent (A), (LXXX) is reacted with β-ketobutyraldehyde dimethylacetal in neutral solution. The reaction of (LXXX) with α-oximinopropiophenone and subsequent cyclodehydration with acetic anhydride and pyridine gives the fluorescent brightening agent (F). A reaction which proceeds quantitatively is the action of sodium azide on 3-phenylcoumarinyl-(7)-diazonium salts. Dissolved in DMF, the resulting 3-phenyl-7-azidocoumarin reacts quantitatively with acetylene, practically without pressure, forming 3-phenyl-7-triazolylcoumarin [fluorescent brightening agent (B)].

The synthesis of the 7-pyrazolyl- and 7-triazolyl-3-phenylcoumarins from 4-pyrazolyl-2-hydroxybenzaldehyde[179] and 4-triazolyl-(1)-2-hydroxybenzaldehyde[180] with benzyl cyanide or phenylacetic acid is also possible, e.g.,



B. Carbostyril Compounds

7-Aminocarbostyril compounds whose cyclic amide nitrogen is alkylated must be considered as isologs of the 7-aminocoumarins. The replacement of the O atom in coumarin by an *N*-alkyl group is associated with a marked hypsochromic shift of the UV absorption. Although 7-aminocarbostyril (LXXXI; $R = R' = H$) offers certain

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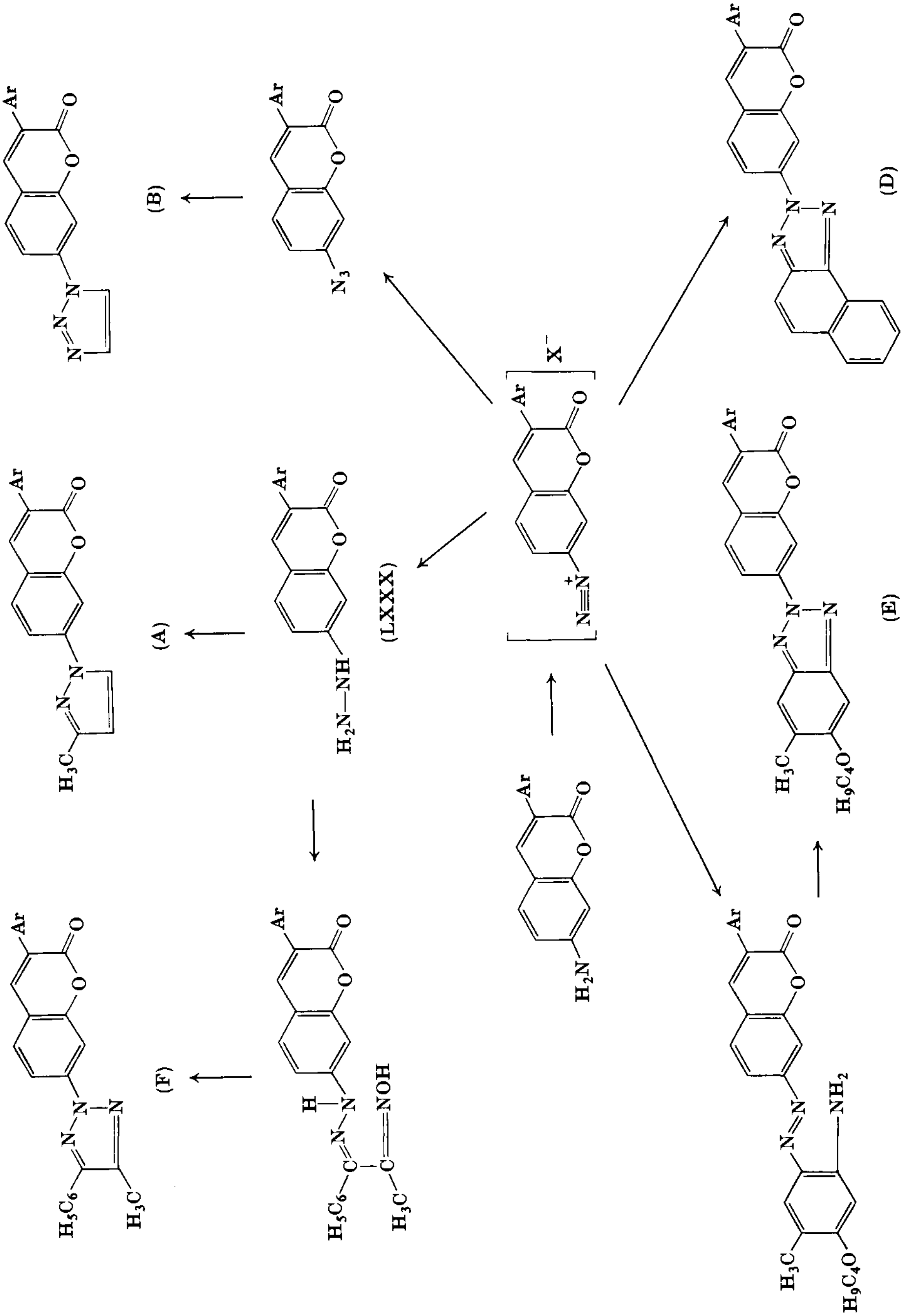
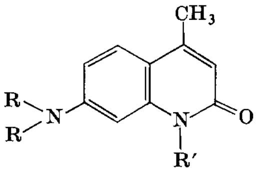
[178] H. Henecka, "Chemie der β-Dicarbonylverbindungen," p. 331. Springer, Berlin, 1950.

[179] Gy, *FP* 1,320,597.

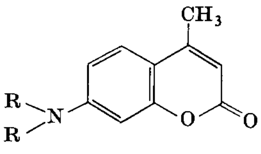
[180] FBy, *FP* 1,388,469.

CHART 3

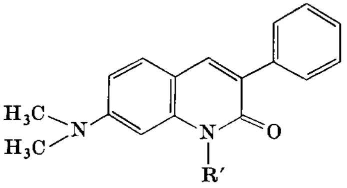




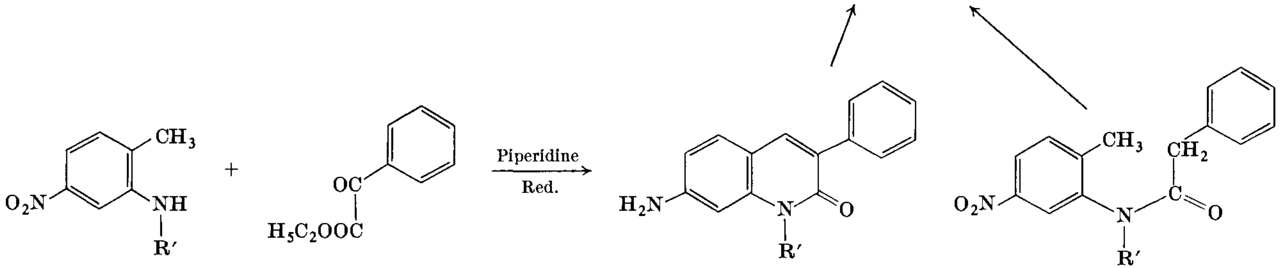
(LXXXI)



(LXXXII)



(LXXXIII)



(LXXXIV) (LXXXV) (LXXXVI)

advantages over 7-hydroxy-4-methylcoumarin (methylumbelliferone) as a fluorescent brightening agent,[181] its fluorescence, in contrast to the 7-aminocoumarins (LXXXII), is weaker and redder. Its *N*-substitution products are also less suitable as fluorescent brightening agents. For this reason, the 3-phenyl-7-dimethylaminocarbostyril derivatives (LXXXIII) possess a bluer fluorescence than the 7-dialkylamino-3-phenylcoumarins; the compounds (LXXXIII) are strong fluorescent optical brightening agents for wool, synthetic polyamides, acetylcellulosics, and polyvinyl chloride.[182] They possess a high affinity for polyamides from alkaline wash liquors.

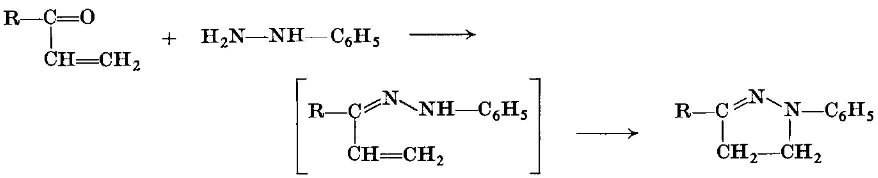
They are best produced by condensation of a 4-nitro-2-alkylaminotoluene (LXXXIV) with ethyl glyoxylate in the presence of piperidine, reduction of the resulting 3-phenyl-7-nitrocarbostyril derivatives, and methylation of the 3-phenyl-7-aminocarbostyril compounds (LXXXV) according to Leuckart.

An elegant process for the production of (LXXXIII) consists in the reduction of the 2-(*N*-phenylacetyl-*N*-alkylamino)-4-nitrotoluenes (LXXXVI) with alkali polysulfides in aqueous alcohol.[183]

IV. 1,3-Diphenylpyrazolines

Similar to the 4-styryl derivatives of stilbene (see Section II,A,3), 1,3-diphenyl-Δ^2-pyrazoline is a pronounced fluorophore. The discovery of the group of pyrazoline compounds dates back to the research on pyrazoles carried out by Knorr.[184] By the reduction with sodium in alcohol of the pyrazoles obtained from 1,3-dicarbonyl compounds and hydrazines, dihydropyrazoles (pyrazolines) were formed, some of which produce a blue fluorescence in solution.

A convenient method for the production of pyrazolines consists in the reaction of α,β-unsaturated carbonyl compounds with phenylhydrazine, without the expected hydrazone being detectable.[185] In this connection,



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[181] Proctor & Gamble, *USP* 2,616,855; *BP* 661,023.

[182] FBy, *BP* 1,087,375.

[183] FBy, *BP* 1,103,531.

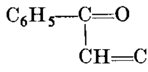
[184] L. Knorr, *Ann. Chem.* **238**, 137 (1887).

[185] E. Fischer and E. Knoevenagel, *Ann. Chem.* **239**, 194 (1887).

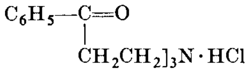
it is immaterial whether the reaction takes place in the presence or absence of acetic acid. The stability of the hydrazone intermediate stage depends entirely on the reactivity of the $CH{=}CH_2$ group and therefore on the nature of the substituent R. As might be expected, it then increases in the sequence

$$R = CH_3 < (CH_3)_2CH < (CH_3)_3C < C_6H_5 < C_6H_4CH = CH_2.^{186}$$

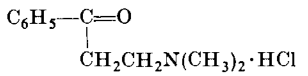
The phenylhydrazone of dibenzalacetone can be isolated, but is then cyclized by heating in glacial acetic acid. The strong blue fluorescence which Knorr observed[187] is limited to the 1,3-diphenyl-Δ^2-pyrazolines; 1-phenyl-3-alkyl-Δ^2-pyrazolines do not fluoresce.[188] Although fluorescence is present in 1,5-diphenyl-3-methyl-Δ^2-pyrazoline, it is so weak that a maximum at 358 nm cannot be measured. In the production of 1,3-diphenyl-Δ^2-pyrazolines,[189] which are interesting as fluorescent brightening agents, use is made almost exclusively of the Fischer-Knoevenagel synthesis. Since, owing to the poor stability of the vinyl ketones, the reaction of phenylhydrazine with phenyl vinyl ketone[190] gives rise to difficulties, more valuable reactants with phenylhydrazine are tris(β-benzoylethyl)amine hydrochloride,[191] β-benzoylethyldimethylamine[192] (the Mannich base from acetophenone, formaldehyde, and methylamine), and β-chloropropiophenone.[193]



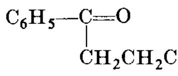
$$C_6H_5{-}\underset{\displaystyle CH{=}CH_2}{\underset{|}{C}}{=}O$$



$$C_6H_5{-}\underset{\displaystyle CH_2CH_2]_3N\cdot HCl}{\underset{|}{C}}{=}O$$



$$C_6H_5{-}\underset{\displaystyle CH_2CH_2N(CH_3)_2\cdot HCl}{\underset{|}{C}}{=}O$$



$$C_6H_5{-}\underset{\displaystyle CH_2CH_2Cl}{\underset{|}{C}}{=}O$$

In the production of 1,3,5-triphenyl-Δ^2-pyrazoline, benzalacetophenone is a stable vinyl ketone.

In the previously discussed fluorophorous systems—the stilbenes, styrylstilbenes, and 3-phenylcoumarins—the absorption of light quanta in the range of 350–400 nm through the presence of a resonance system was pointed out.[194] In the 1,3-diphenyl-Δ^2-pyrazolines a resonance

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[186] K. von Auwers *et al.*, *Ber.* **41**, 4230 (1908); **42**, 4411 (1909).

[187] L. Knorr and P. Duden, *Ber.* **26**, 115 (1893).

[188] F. Straus, *Ber.* **51**, 1457 (1918).

[189] H. Chase and J. M. Evans, *J. Chem. Soc.* p. 4825 (1964); A. Wagner, C.-W. Schellhammer, and S. Petersen, *Angew. Chem.* **78**, 769 (1966).

[190] E. P. Kohler, *Am. Chem. J.* **42**, 387 (1909).

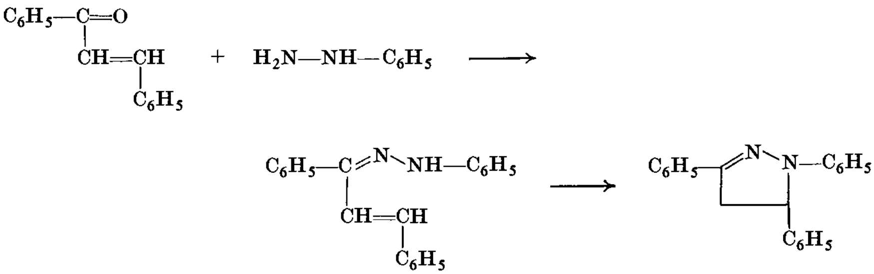
[191] H. Schäfer and B. Tollens, *Ber.* **39**, 2186 and 2188 (1906).

[192] B. Mannich, *Ber.* **55**, 3510 (1922); see *Org. Reactions* **1**, 303 (1942).

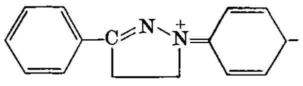
[193] K. von Auwers, *Ber.* **65**, 833 (1932).

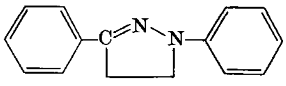
[194] *CSD I*, p. 344.

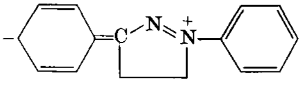
caused by a series of conjugate double bonds is not so clearly recognizable. Investigation of the action of the 1,3,5-triarylpyrazolines as scintillators[195] has nevertheless produced results which permit model demonstrations of the relation between the constitution of the pyrazoline molecule and the UV absorption.



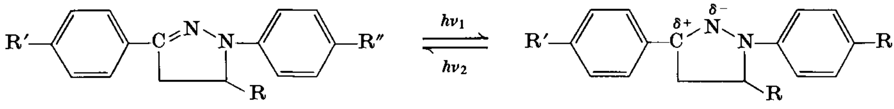
Neunhöfer and Rosahl[196] think it possible that a resonance may result from the absorption of the induction of the mesomeric limiting states (A′) and (A″) in the fluorescent 1,3-diphenyl-Δ^2-pyrazoline molecule.


(A′)


(A)


(A″)

Sandler and Tsou[197] describe the state of excitation of the 1,3-diphenyl-Δ^2-pyrazoline molecule (B) by the formula (B′). Electron-withdrawing



(B) (B′)

groups in the *p*-position of the 3-phenyl nucleus (R′) facilitate formation of the excitation state B′ by their action on δ^+; electron-donating groups in this position render formation of the excitation state B′ more difficult. According to the data in Table XVIII, it is noteworthy that the introduction of a Cl atom into the *p*-position of the 3-phenyl nucleus (R′)

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[195] R. H. Wiley, *J. Org. Chem.* **28**, 732 (1959).

[196] O. Neunhöffer and D. Rosahl, *Ber.* **88**, 1123 (1955); *Z. Elektrochem.* **57**, 81 (1953).

[197] S. R. Sandler and K. C. Tsou, *J. Chem. Phys.* **39**, 1062 (1963).

shifts the UV absorption (λ_{max}) by 6–9 nm to longer wavelengths (bathochromic shift); by contrast, a Cl atom in the *p*-position of the 1-phenyl nucleus (R″) is without any influence on the absorption maximum.

As a result of the proposal to use 1,3-diphenyl-Δ^2-pyrazoline, 1,3,5-triphenyl-Δ^2-pyrazoline, and their derivatives for the fluorescent brightening of natural and synthetic fiber materials and of films,[198] a large number of new fluorescent brightening agents were described: in particular, those which show an absorption maximum not exceeding 390 nm. They can be produced in all cases by reacting β-chloroethyl phenyl ketones,[193] Mannich bases from acetophenones,[192] and benzalacetophenones with phenylhydrazines.

The reaction of the chalcones obtained from benzaldehyde sulfonic acids and of phenylhydrazine sulfonic acids in these processes leads to the production of water-soluble fluorescent brightening agents which are marketed for the optical brightening of wool and synthetic polyamides.[199]

With onlya few exceptions, most of the fluorescent brightening agents of this group available on the market are substitution products of 1-phenyl-3-*p*-chlorophenyl-Δ^2-pyrazoline; sulfonyl groups (R″ = SO_2R; R = NH_2, alkyl) in the 4′-position of the 1-phenyl nucleus are responsible for the valuable colonistic properties, such as affinity for the fiber and substantivity, and therefore brilliance of the fluorescent brightening effect. A summary of the most important commercial products is given in Table XIX.[200–211]

In addition to those previously described, there are two further processes for the production of 1,3-diphenyl-Δ-^{2}pyrazolines, namely, the arylation of 1-phenyl-Δ^2-pyrazolines with diazonium salts in the 3-position[212] and the 1,3-dipolar addition of the component

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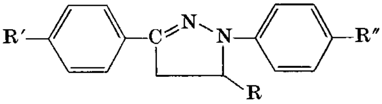
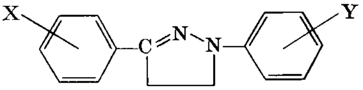
[198] Ilford, *BP* 669,589; 669,590; 669,591.
[199] Ilford, *DBP* 1,023,445.
[200] Gy, *AustP* 260,924.
[201] HWL, *FP* 1,453,061.
[202] FBy, *DBP* 1,104,483; *USP* 2,879,174.
[203] Unilever, *BP* 883,826.
[204] FBy, *DBP* 1,080,963.
[205] FBy, *USP* 3,135,742.
[206] FBy, *BP* 906,960; *USP* 3,131,079.
[207] Gy, *SP* 415,535.
[208] FBy, *BeP* 629,875.
[209] HWL, *BeP* 609,589.
[210] FH, *FP* 1,354,629.
[211] FH, *FP* 1,449,163.
[212] Ilford, *USP* 2,610,969; G. F. Duffin and D. Kendall, *J. Chem. Soc.* p. 408 (1954).

TABLE XVIII



R	R′	R″	M.p. (°C)	Absorption maxima λ (nm)	Absorption maxima ε	Fluorescence maxima λ (nm)	Fluorescence maxima ε
H	H	H	153	349	20.900	470	44.000
C_6H_5	H	H	135	356	19.000	470	—
H	Cl	H	130	364	27.550	475	72.000
H	H	Cl	136	356	26.700	468	65.000
H	Cl	Cl	175	363	29.100	471	94.000

TABLE XIX



X	Y	M.p. (°C)	Application	References
H	3-Cl	108	Polyamide, detergents	200
4-Cl	3-Cl	125	Polyamide, detergents	200
4-$NHCOCH_3$	3-Cl	320	Nylon, polyacrylonitrile	201
4-Cl	4-COOH	272	Polyacrylonitrile, soap	202
4-Cl	4-$COOCH_3$	112	Polyamide, detergents	203
4-Cl	4-SO_2NH_2	226	Polyacrylonitrile	204
4-Cl	4-$SO_2NH(CH_2)_3N(CH_3)_2$	—	Polyamide	205
4-Cl	4-$SO_2NH(CH_2)_3\overset{+}{N}(CH_3)_3$- $SO_4CH_3^-$	200	Polyacrylonitrile	206
4-Cl	4-SO_2CH_3	184	Polyacrylonitrile	207, 208 209
4-Cl	4-$SO_2CH_2CH_2OH$	222	Polyamide	209, 210
4-Cl	4-$SO_2CH_2CH_2$-SO_3H	—	Polyamide	210
4-Cl	4-$SO_2CH_2CH_2OCH(CH_3)$- $CH_2N(CH_3)_2$	132	Polyacrylonitrile	211

R′—C=N—N—R″ of the phenylhydrazones of aromatic aldehydes to olefins.[213] These processes are suitable for the introduction of specific substituents in the 3-phenyl nucleus (by selection of the diazonium compound) or in the 5-position of the pyrazoline (by selection of the olefin component). From a commercial standpoint these processes are not important.

The previously described pyrazoline derivatives are unstable to oxidizing agents. The nature of the resulting oxidation products depends to a large extent on the substituents in the aryl nuclei and on the oxidizing agent. As primary oxidation product, the corresponding pyrazole can be assumed, with an 89% yield in the oxidation of 1,3,5-triphenyl-Δ^2-pyrazoline with lead tetraacetate in methylene chloride at room temperature.[214] Also 5,5-dimethyl-substituted pyrazolines, whose oxidation to pyrazoles might not be possible, give pyrazoles under these conditions with migration of a CH_3 group. Other oxidizing agents, such as HgO, $Hg(OAc)_2$, Br_2, CrO_3, $AgNO_3$, and $KMnO_4$, give mixtures containing carbonyl compounds and amines with ring cleavage.[215, 216]

V. Naphthalimide Compounds

Among the naphthalimides, 4-alkoxy- and 4-acylamino substitution products are important from a commercial standpoint as fluorescent brightening agents.

Naphthalic acid (naphthalene-1,8-dicarboxylic acid) and its imide (1,3-dioxo-1,2,3-H-benz[*de*]isoquinoline) have long been known as fluorophores. They show a strong blue fluorescence when dissolved in concentrated sulfuric acid. Because of the importance of these compounds as dyestuff intermediates, the chemistry of naphthalic acid has been thoroughly investigated.

The starting product for naphthalic acid is acenaphthene, which gives naphthalic anhydride with a 60–70% yield when oxidized with CrO_3 or $Na_2Cr_2O_7 \cdot 2H_2O$ in glacial acetic acid or sulfuric acid. In aqueous suspension and in the presence of emulsifiers (naphthalene–formaldehyde condensation products), oxidation takes place with $Na_2Cr_2O_7$ at 190–195° almost quantitatively in 24 hours.[217] Although naphthalic acid is

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[213] R. Huisgen, *Tetrahedron Letters* **17**, 3 (1962).

[214] N. A. F. Gladstone and R. O. C. Norman, *J. Chem. Soc. C*, p. 1536 (1966).

[215] R. Loquin and R. Heilman, *Compt. Rend.* **185**, 1477 (1927); *Bull. Soc. Chim. France* **45**, 541 (1929).

[216] L. C. Raiford and E. L. Hill, *J. Am. Chem. Soc.* **55**, 1125 (1933).

[217] J. Arient, *CzechP* 114,790; *CA* **64**, 9655 (1966).

easily oxidized by $KMnO_4$ to hemimellitic acid, the $KMnO_4$-oxidation of acenaphthene in aqueous pyridine with formation of 78% naphthalic anhydride can also be successfully accomplished.[218] In a similar manner to acenaphthene, 5-sulfo-,[219] 5-nitro, 5-chloro-, and 5-bromoacenaphthene can also be oxidized to 4-sulfo-, 4-nitro, 4-chloro-, and 4-bromonaphthalic acid. The ease of conversion of the resulting acids to the anhydrides, which are important for the further reaction, depends on the nature of the substituents.[220]

	Anhydride after 7 days at 20° (%)
Naphthalic acid	10
4-Nitronaphthalic acid	15
4-Chloronaphthalic acid	45

In general, brief heating at 100° is sufficient to obtain a quantitative conversion; crystallization of the acids from glacial acetic acid and HNO_3 (density, 1.4) quickly gives the pure anhydrides.

1. *4-Acylaminonaphthalimides*

The production of naphthalimide and its *N*-substitution products from naphthalic acid or naphthalic anhydride with ammonia and amines is a reaction which proceeds smoothly and in good yield (75–80%).[222] The reactions are summarized in Chart 4.[221] Naphthalic acid or its sodium salt yields naphthalimide quantitatively with ammonia.[223] In the case of 4-substitution products of naphthalic anhydride, imide formation also first takes place in all cases before the further exchange of an SO_3H group,[224] of a halogen atom,[225] or of an NO_2 group is observed under more energetic conditions (170–180°). Although the conversion of naphthalic anhydride and its substitution products with aliphatic amines to the imide is a smooth reaction, for the formation of the *N*-alkylimides there is still the possibility of *N*-alkylation. The potassium salts of the naphthalimides, which are formed on boiling with a 5% caustic potash solution, can be converted with alkyl (ethyl, propyl, butyl, amyl) bromides almost quantitatively to the *N*-alkylnaphthalimides.[226]

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[218] M. Wolff, *Przemysl Chem.* **41**, 389 (1962); *CA* **58**, 2413d (1963).

[219] "Ullmann", Vol. 16, p. 591.

[220] M. M. Dashevshii, *Zh. Obshch. Khim.* **25**, 2485 (1955); *CA* **50**, 9356b (1956).

[221] M. Okazaki, *Yuki Gosei Kagaku Kyokai Shi* **14**, 355, 395, 455, 504, and 558 (1956); *CA* **51**, 8050h (1957).

[222] C. F. Allen, *J. Am. Chem. Soc.* **74**, 5801 (1952).

[223] Selden Comp. *USP* 1,919,889.

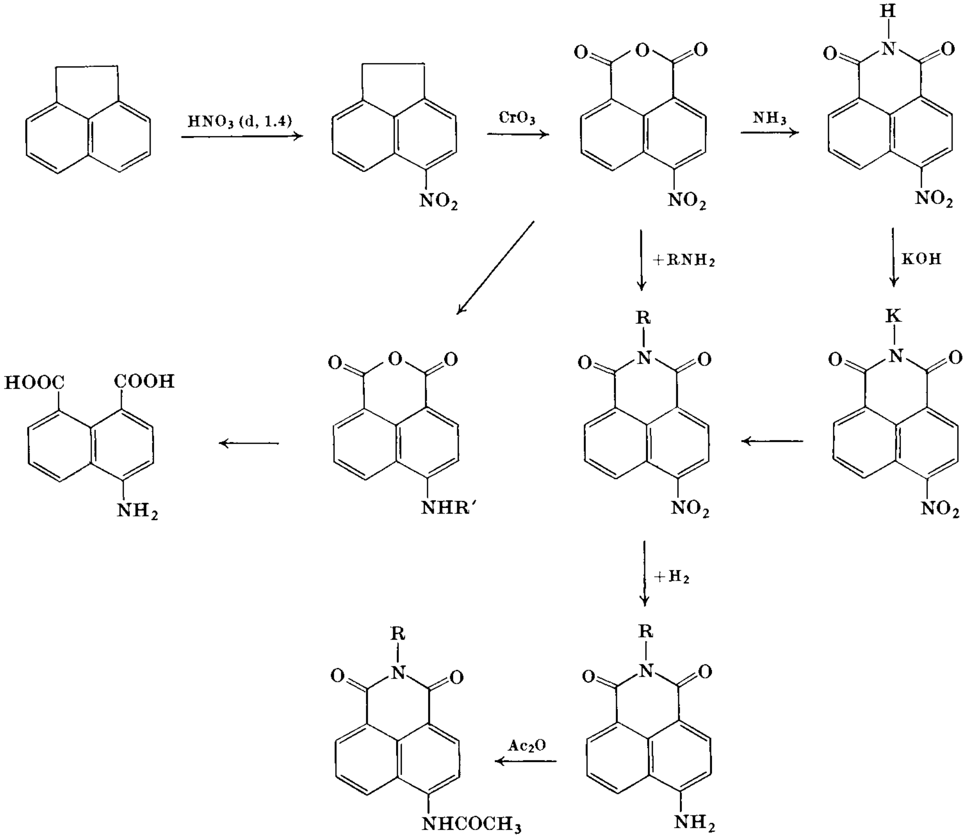
[224] IG, *DRP* 602,944; *BP* 402,309; G, *USP* 2,006,017.

[225] CCC, *USP* 2,415,373; G, *USP* 1,887,797.

[226] A. P. Kalishin, *Zh. Obshch. Khim.* **29**, 3048 (1959); *CA* **54**, 13073h (1960.)

CHART 4

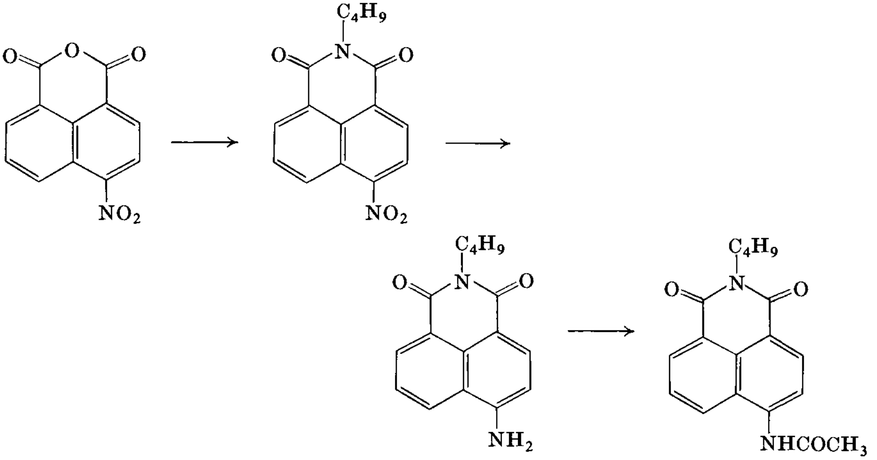
Reaction Pattern for the Production of 4-Aminonaphthalic Acid and 4-Aminonaphthalimides



4-Aminonaphthalimide and its *N*-alkylation products are yellow-green dyestuffs with a green fluorescence, they are suitable for the dyeing of acetate filament, wool, and synthetic polyamides.[227] The 4-acylaminonaphthalimide and its *N*-alkylation products are, however, more valuable, since they are only slightly colored and are soluble in organic solvents with a strong blue fluorescence. They are important as fluorescent brightening agents for surface-coating materials, resins, solvents, and synthetics (acetate filament, polyamides, polyester, polyvinyl

[227] G, *USP* 1,836,529; see also CCC.[225]

chloride).[228] The most important product of this range, 4-acetylamino-*N*-butylnaphthalimide, is best produced according to the following reaction pattern[229]:



2. *4-Alkoxynaphthalimides*

The most interesting fluorescent brightening agent of this group is 4-methoxy-*N*-methylnaphthalimide.[230] With this product, chlorite-resistant fluorescent brightening effects are obtained in the Thermosol dyeing process[231] on cellulose acetates, polyacrylonitrile, polyolefins, polyoxymethylene and, particularly, on polyester fibers.

Owing to the possibility of replacing by the OCH_3 group the substituents SO_3H, NO_2, Cl, and Br in the 4-position of naphthalic anhydride[232] and of the naphthalimides[233] in boiling methanolic NaOH, certain variants are suitable for the synthesis of this fluorescent brightening agent.[230, 234] Among these, the exchange of SO_3H or of a halogen atom in naphthalic anhydride for an alkoxy group is particularly recommended; the alkylation of 4-hydroxynaphthalic acid or of the 4-hydroxynaphthalimides is a reaction which proceeds less smoothly.

3. *Fluorescence of the Naphthalimides*

The fluorescence of the arylpyrazolines may be explained by resonance structures, and in addition the possibility of polarizability of the ring

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[228] G, *USP* 2,600,080; BASF, *DBP* 1,023,169.

[229] BASF, *DBP* 1,068,260; G, *USP* 2,600,080; see also BASF, *DBP* 1,005,971; 1,046,622.

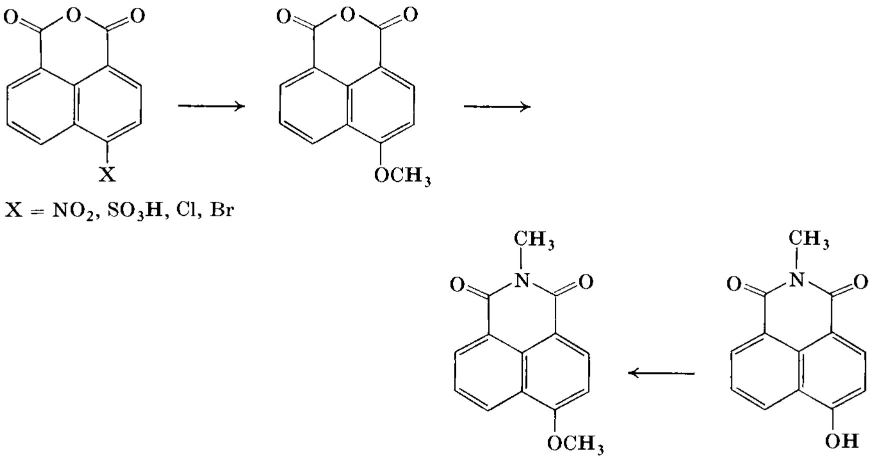
[230] T. Kasai, *BP* 1,003,083; *JP* 1,003,084; *USP* 3,310,564.

[231] MCI, *JP* 14,431/65; *CA* **64**, 2206c (1966).

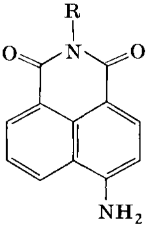
[232] W. Bradley and F. W. Pexton, *J. Chem. Soc.* p. 4432 (1954); see also Kusai.[230]

[233] MCI, *FP* 1,344,883.

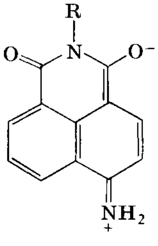
[234] MCI, *BP* 963,019.



-C=N- double bond in the 1,3-diphenyl-Δ^2-pyrazoline molecule by UV excitation can be considered. The IR spectra of the naphthalimides show two carbonyl bands at 1700–1720 cm^{-1} and 1600–1680 cm^{-1}[235] attributed to mesomeric and inductive effects of substituents, particularly of amino groups in the 4-position. This confirms the increase of the polarity of the CO group by electron-donating substituents in the naphthalene nucleus (A′).[236]



(A)



(A′)

VI. Aryloazolyl-(2) Compounds

Only a short time after the introduction of the first fluorescent brightening agents, Ciba succeeded in developing a new type of fluorescent brightener in the condensation products of 1,2-diaminobenzenes and of 2-aminophenols with maleic or fumaric acid, products which must be considered as isologs of stilbene[237] (see Table XX). Among these strongly fluorescent bis-benzazolylethylene compounds, the Uvitex type SIA as

[235] S. Nishizaki, *Nippon Kagaku Zasshi* **86**, 696 (1965); *CA* **64**, 3321e (1966).

[236] K. Yasuda, *Nippon Kagaku Zasshi* **80**, 960 (1959); *CA* **53**, 21165h (1959).

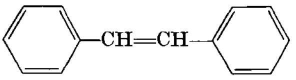
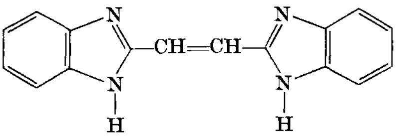
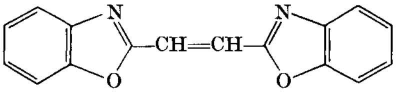
[237] CIBA, *DBP* 883,286; *BP* 588,792; 600,696; 623,428; *USP* 2,463,264; 2,488,289.

acid is also soluble in alkali with a strong greenish fluorescence and can be applied to cellulosic fibers. The Uvitex type ERN is practically insoluble in water.

The fluorescent brightening agents of the aryloazolyl-(2) group offer the advantage of producing a strong fluorescent brightening effect on polyester and polyolefin fibers from aqueous liquors. They are notable for a good heat stability, which renders them suitable for incorporation in spinning compositions and plastics. The fastness to light of certain members is evaluated as 7–8. Owing to the increasing interest shown in modern synthetic fibers, as well as the technical advantages in the application and fastness properties of the aryloazolyl-(2) fluorescent brightening agents, they have been marketed extensively. However, such compounds solubilized by sulfonic groups have aroused no technical interest up to the present.[238]

TABLE XX

COMPARISON OF UVITEX FLUORESCENT BRIGHTENERS WITH STILBENE

	Uvitex type	*Absorption maxima*		
		λ (nm)	$\tilde{\nu}$ (cm^{-1})	$\epsilon \times 10^{-4}$
	—	298	33.550	2.82
		310.5	32.300	2.89
		324	30.870	1.81
	SIA	348	28.800	2.10
		362	27.630	2.54
		381	26.250	1.79
	ERN	355	28.170	4.69

A. PRODUCTION OF ARYLOAZOLYL-(2) COMPOUNDS

(a) The reactions of aromatic 1,2-diamino, 1-amino-2-hydroxy, and 1-amino-2-mercapto compounds with mono- and dicarboxylic acids and their acid derivatives to form aryloazolyl-(2) compounds were investigated[239] many years ago by Ladenburg,[240] Walter and von Pulawski,[241]

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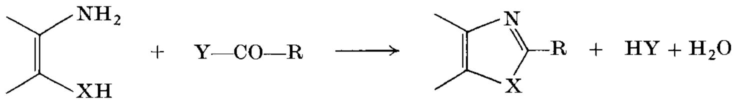
[238] A. Landolt, *Testil-Rundschau* **8**, 339 (1953).

[239] R. C. Elderfield, "Heterocyclic Compounds," Vol. 5, pp. 267, 420, and 506. Wiley, New York, 1957.

[240] A. Ladenburg, *Ber.* **8**, 677 (1875); **9**, 1525 (1876).

[241] R. Walter and T. von Pulawski, *J. Prakt. Chem.* [2] **59**, 251 (1899).



$X = N(R'), O, S$

Wheeler,[242] and Ransom.[243] Because of its technical importance, improved processes for the production of fluorescent brightening agents utilizing this reaction have been developed by several firms. Table XXI[265–275] gives a summary of the experimental possibilities which are available in the reaction of aromatic 1,2-diamino or 1-amino-2-hydroxy-(thio) compounds with carboxylic acids to form 2-aryloazolyl-(2) compounds.

TABLE XXI

Preparation of Aryloarolyl Compounds from Carboxylic Acids

Process	*Catalyst*	*Solvent*	*Temperature* (°C)	*References*
—	—	—	125–235	244, 246, 249, 250, 265
A	Boric acid	—	150–270	249, 266
B	Boric acid	Xylene	150–260	248, 271,
		1,2-Dichlorobenzene		258
		Trichlorobenzene		
		Diethylene glycol		267, 268
		Glycerin		
		Diglycol dibutyl ether		269, 270
C	5% H_2SO_4 15% HCl	—	100	272, 273
D	*p*-Toluenesulfonic acid	1,2-Dichlorobenzene	170	248, 274
E	Polyphosphoric acid (with 84% P_2O_5)	(Catalytic quantities of KI)	140–245	248, 252 262, 272
F	PCl_3(+HCl)	Xylene	210–250	273, 275
	$POCl_3$	Trichlorobenzene		
	PCl_5	Nitrobenzene		
G	$ZnCl_2$	+6% Water	150	260, 273
		Diethylene glycol		
H	$SnCl_2$	Glycol monomethyl ether	—	262

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[242] H. L. Wheeler, *Am. Chem. J.* **17**, 400 (1895).

[243] J. H. Ransom, *Am. Chem. J.* **23**, 17 (1900).

[244] W. O. Pool, H. J. Harwood, and A. W. Ralston, *J. Am. Chem. Soc.* **59**, 178 (1937).

Aromatic 1,2- diamino compounds react with aliphatic[244] or heterocyclic carboxylic acids (e.g., with 2-phenylfuran-5-carboxylic acid) without a catalyst in excess diamine or in boiling water under the catalytic action of mineral acids (C)[245]; and with unsaturated aliphatic or aromatic carboxylic acids only on fusion of the components in the presence of boric acid as catalyst[246] (Processes A and B) and at temperatures of 150–200° in an inert gas atmosphere (nitrogen) with formation of 2-substituted benzimidazoles.[247]

Aromatic 1-amino-2-hydroxy compounds are less reactive. Aryloazoles can no longer be formed with aliphatic carboxylic acids in aqueous acids. In the presence of acid catalysts,[248] particularly boric acid (B), the reaction temperature must be increased to 200–240°,[249–251] so that the

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[245] R. L. Shriner and R. W. Upson, *J. Am. Chem. Soc.* **63**, 2277 (1941); M. A. Phillips, *J. Chem. Soc.* p. 2393 (1928).

[246] CIBA, *USP* 2,488,094.

[247] J. B. Wright, *Chem. Rev.* 48, 398 (1951).

[248] CIBA, *DBP* 1,238,873.

[249] CIBA, *DBP* 1,166,197.

[250] L. C. Galatis, *J. Am. Chem. Soc.* **70**, 1967 (1948).

[251] CIBA, *DBP* 1,044,555.

[252] F. Uhlig, *Angew. Chem.* **66**, 435 (1954); CCC, *USP* 2,985,661.

[253] CIBA, *DBP* 1,040,555.

[254] R. A. B. Copland and A. R. Day, *J. Am. Chem. Soc.* **65**, 1072 (1943); BASF, *DBP* 1,201,354; *FP* 1,361,778.

[255] FH, *FP* 1,358,895.

[256] See, e.g., Naukai Kaken Kogyo, *JP* 9791/67; *CA* **68**, 31051a (1968); CIBA, *USP* 3,268,543; *SP* 437,314.

[257] CCC, *BeP* 656, 224.

[258] CIBA, *DBP* 1,281,385; 1,238,431; CCC, *USP* 3,158,610.

[259] MDW, *JP* 29,450/64; *CA* **62**, 14866g (1965); *FP* 1,336,949.

[260] CIBA, *DBP* 1,051,855; 1,119,865.

[261] FH, *FP* 1,444,004.

[262] NSK, *FP* 1,411,999.

[263] CIBA, *DBP* 1,232,932; FH, *FP* 1,358,895.

[264] See also Tables 21, 22, and 23.

[265] CFM, *DBP* 893,792.

[266] CIBA, *DBP* 841,752; 883,286; 1,109,177.

[267] Toyo Rayon, *JP* Publ. No. 18,406/67; Appl. No. 37,545/62. 5.3.62./22.9.62.

[268] CIBA, *DBP* 1,086,237.

[269] CIBA, *DBP* 1,268,097.

[270] CIBA, *FP* 1,467,750.

[271] CIBA, *Neth. Appl.* 6,511,364.

[272] CIBA, *DBP* 1,039,064.

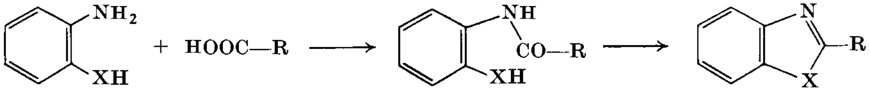
[273] MDW, *JP* 10,512/66; *CA* **66**, 11875c (1967).

[274] CIBA, *DBP* 1,117,125.

[275] Eastman Kodak, *BeP* 648,984; *SP* 421,964.

reaction, particularly when carried out in a polar solvent, does not remain at the stage of the difficultly cyclized 2-hydroxyarylamides. As in the case of the aromatic 1,2-diamino compounds, the ease of reaction of the aromatic 1-amino-2-hydroxy compounds with carboxylic acids decreases in the sequence aliphatic, heterocyclic, aromatic, unsaturated aliphatic carboxylic acids. From 2-aminophenols and maleic or fumaric acid, bis-benzoxazolylethylene compounds in a yield of only 15–20% are also obtained in the presence of the extremely effective boric acid and in a CO_2 atmosphere at 200° (B). Although polyphosphoric acid (E)[252] is more effective as a catalyst than boric acid, when used on an industrial scale it corrodes the materials of all apparatus at temperatures exceeding 200°.

The formation of the 2-substituted aryloazolyl compounds from aromatic 1,2-diamino- or 1-amino-2-hydroxy compounds takes place in two steps. In the first part of the reaction carboxylic arylides (LXXXVII) are formed and this reaction may be catalyzed by heavy metal salts. In the second part of the reaction, cyclization to the aryloazolyl-(2) compounds (LXXXVIII) takes place with separation of water by heating at higher temperatures[253] under vacuum; this reaction is facilitated by the acid catalysts used.

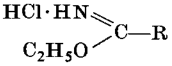
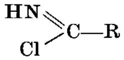
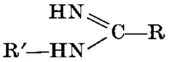


X = NH, O (LXXXVII) (LXXXVIII)

Higher yields and a smoother aryloazole formation can therefore be achieved if the carboxylic acids are replaced by derivatives which are better acylating agents. Table XXII[276–288] contains a summary of those carboxylic acid derivatives from which a selection was suggested for the production of aryloazolyl compounds. In this connection, carboxylic esters (K) and carboxylic amides (L) are more reactive than nitriles (M); ethyl cyanoacetate yields with 2-aminophenols exclusively 2-cyanomethylbenzoxazole.[254] The method often used is to react 1,2-diamino- and 1-amino-2-hydroxy compounds with the acid chloride (see Process J), mainly in chlorobenzene, in such a manner that the arylides are formed and then cyclized by heating[255] alone in a solvent (trichlorobenzene), preferably in the presence of dehydrating agents.[256] Suitable dehydrating agents are acid catalysts, such as toluenesulfonic acid[257] (in *o*-dichlorobenzene), pyrophosphoric acid/polyphosphoric acid (P_2O_5 in phosphoric acid), boric acid[258] (in diglycol, diethyl, or dibutyl ether) and phosphorusoxychloride,[259] as well as zinc chloride[260] (in a little water, glycol, or

TABLE XXII

Preparation of Aryloazolyl Compounds from Carboxylic Acid Derivatives

Process	*Acid derivative*	*Condensing agent (temperature)*	*References*
I	$O(CO—R)_2$	Boric acid + $ZnCl_2$ in diglycol (160–165°)	276–279
J	ClCO—R	Trichlorobenzene (215°)	239, 265
	(+HCl)	Nitrobenzene, xylene, toluene 1,2-Dichlorobenzene $ZnCl_2$ (H_2O, glycol)	280, 281
K	$C_2H_5OCO—R$	Boric acid	282, 283
		Toluenesulfonic acid in aromatic hydrocarbons	284
L	$H_2NCO—R$	Polyphosphoric acid (220°)	241
		$ZnCl_2$ (+H_2O) in glycerol, glycol (160–200°)	
M	NC—R	Polyphosphoric acid (220°)	241, 285, 286
N	 $\mathrm{HCl{\cdot}HN{=}C(R)OC_2H_5}$	—	241, 287
O	 $\mathrm{HN{=}C(R)Cl}$	Hydrochloric acid	288
P	 $\mathrm{HN{=}C(R)NH{—}R'}$	Hydrochloric acid	288

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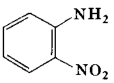
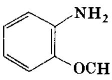
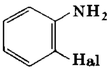
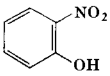
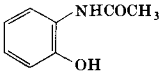
[276] W. Theilacker, *J. Prakt. Chem.* [2] **153**, 54 (1939).
[277] Nisso Chem. Ind., *JP* 24,643/64; *CA* **63**, 11566h (1965).
[278] Intermediate & Dyes Res. Inst., *RP* 186,489; *CA* **66**, 115,702k (1967).
[279] CIBA, *BeP* 559,677.
[280] CFM, *DBP* 893,792; 855,404.
[281] MDW, *JP* 7257/67; *CA* **67**, 55171v (1967).
[282] CIBA, *DBP* 1,134,989.
[283] MDW, *JP* 5180/64; *CA* **61**, 16210c (1964).
[284] Osaka Seika, *JP* 7258/67; *CA* **67**, 55172w (1967).
[285] E. C. Wagner, *J. Org. Chem.* **9**, 31 (1944).
[286] CIBA, *BeP* 611,489.
[287] Kodak-Pathé, *FP* 1,378,455.
[288] E. C. Wagner, *J. Org. Chem.* **5**, 133 (1940).

halobenzenes)[261] and tin(II) chloride[262] (in glycol monomethyl ether) and also mixtures of, e.g., zinc chloride and boric acid in glycol ethers.[263, 264]

(b) With the processes outlined in Table XXIII (Q to U)[289–298] it is possible first to carry out the definite production of the arylide (Processes Q to S) or of the phenol ester (processes T and U) by blocking one of the reactive groups (NH_2 or OH), and subsequently to cyclize these products. The 2-nitroarylides obtained in Process Q often lead on

TABLE XXIII

PREPARATION OF ARYLOAZOLYL COMPOUNDS IN TWO STEPS

Process	*Production of the arylides or phenol esters with Cl—CO—R*			*Cyclization of the arylides or phenol esters*	*References*
	Starting material	*Solvent*	*Temp.*		
Q		Chlorobenzene	70–120°	Sn/HCl $SnCl_2$/HCl Catalytic hydrogenation (H_3BO_3, H_2SO_4) Reduction (heating)	246, 263, 266, 289, 290, 291
R		Chlorobenzene	120°	Polyphosphoric acid $ZnCl_2$ (+ 6% H_2O) Glycol, glycerol (200° NaCl + $AlCl_3$, 200–250°)	292 262, 263, 280
S		Pyridine	100°	$NaHCO_3$ + Cu powder (240°) $NaOCOCH_3$ + CuCl, CuO in nitrobenzene 200°/1 hr	293 294
T		Xylene	120°	Sn/HCl $SnCl_2$/HCl in glycol monomethyl ether (110°) Zinc dust reduction ($ZnCl_2 \cdot HCl$, $POCl_3$, P_2O_5)	295, 296 297
U		Chlorobenzene	120°	$ZnCl_2$ (+ 6% H_2O) $ZnCl_2$ in glycol 170–180° under vacuum/3 hr	298

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[289] H. Green and A. R. Day, *J. Am. Chem. Soc.* **64**, 1167 (1942).

[290] C. Kelley and A. R. Day, *J. Am. Chem. Soc.* **67**, 1074 (1945).

[291] Sterling Drug, *USP* 2,937,148.

[292] NSK, *BeP* 653,181.

[293] CCC, *Neth. Appl.* 6,413,676.

[294] HCC, *JP* Publ. No. 6233/64; 27.3.62/2.5.64; no Appl. No.; *USP* 3,147,253.

[295] C. Kelley and A. R. Day, *J. Am. Chem. Soc.* **67**, 1074 (1945).

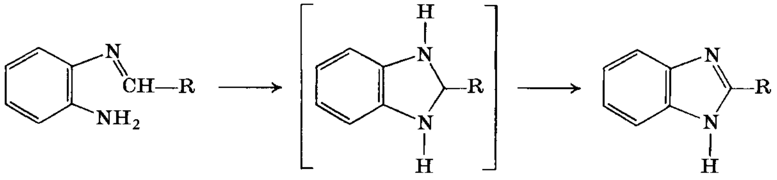
[296] CIBA, *DBP* 1,205,970; 1,232,922.

[297] MDW, *JP* 13,504/65; *CA* **64**, 9858b (1966).

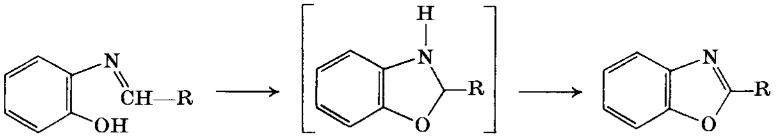
[298] Osaka Seika Ind., *JP* 2630/64; *CA* **61**, 3242d (1964).

reduction directly to imidazoles, but a subsequent cyclization is usually required. The 2-aminophenol esters obtained in Processes T and U can be cyclized under mild conditions.

(c) In addition to the cyclization of 2-hydroxy- and 2-aminoarylides, the benzazoles (XCI) and (XCIV) can be produced by the oxidative cyclization of the Schiff bases of aromatic 1,2-diamines [e.g. (LXXXIX)], and 1-amino-2-hydroxy compounds [e.g., (XCII)]. In this reaction acetal-type structures, (XC) and (XCIII), are possible transition stages.



(LXXXIX) (XC) (XCI)



(XCII) (XCIII) (XCIV)

As oxidizing agents, ferric chloride, lead tetraacetate, chloranil, sulfuryl chloride, benzoyl chloride, and *N*-bromosuccinimide,[299, 300] as well as nitrobenzene[301, 302] and nitrous acid[303] have been suggested.

Table XXIV contains a summary of typical 2-substituted benzazoles synthesized from benzoic acid (discussed in Section VI,B,1), cinnamic acid (VI,B,2), stilbene-4-carboxylic acid (VI,B,3), thiophene-2-carboxylic acid (VI,B,4), fumaric acid (VI,C,1), terephthalic acid (VI,C,2), 4-carboxycinnamic acid (VI,C,3), stilbene-4,4′-dicarboxylic acid (VI,C,4), *p*-phenylenebis(acrylic acid) (VI,C,5), and thiophene-1,5-dicarboxylic acid (VI,C,6). A comparison of the UV absorption, which is of primary importance for the color of the fluorescent brightening effect attained, shows relationships with the constitution of the acid used. It is related in the aryloazolyl-(2) compounds derived from monocarboxylic acids

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[299] F. F. Stephens and J. F. Bower, *J. Chem. Soc.* p. 1722 (1950).

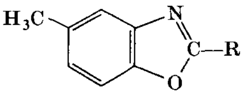
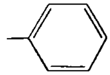
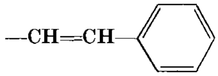
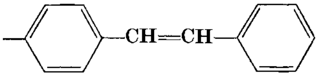
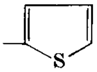
[300] See also W. Traube and W. Nithaek, *Chem. Ber.* **39**, 229 (1906).

[301] H. Green and A. R. Day, *J. Am. Chem. Soc.* **64**, 1169 (1942).

[302] Meisei Kagaku, *JP* 18,530/61; *CA* **57**, 9858e (1962).

[303] CCC, *USP* **3,341,529**.

TABLE XXIV

From Monocarboxylic Acids				
		*Absorption maxima*[a]		
		λ (nm)	$\tilde{\nu}$ (cm^{-1})	$\epsilon \times 10^{-4}$
—		—	—	—
R =  (VI,B,1)[b]	(XCV)	305	32.790	2.4
R =  (VI,B,2)	(XCVI)	345	28.990	3.0
R =  (VI,B,3)	(XCVII)	353	28.330	5.8
—		—	—	—
R =  (VI,B,4)	(XCVIII)	311	32.150	2.3

[a] Determined in DMF.

(Section VI,B) to the substituents in the 2-position, and in those from dicarboxylic acids to the group linking the benzoxazole nuclei.[304] Extension of the conjugation of the substituent in the transition from

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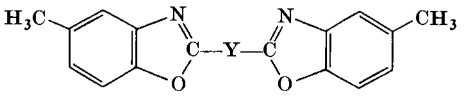
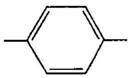
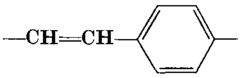
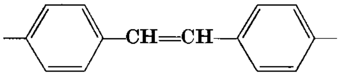
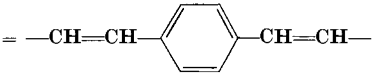
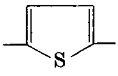
[304] T. Maruyama, *Bull. Univ. Osaka Prefect.*, **A13**, 75 (1964).

2-Substituted Benzazoles

From Dicarboxylic Acids

		*Absorption maxima*[a]		
		λ (nm)	$\tilde{\nu}$ (cm^{-1})	$\epsilon \times 10^{-4}$
Y = —CH=CH— (VI,C,1)	(XCIX)	363	27.550	4.30
Y =  (VI,C,2)	(C)	347	28.820	5.18
Y =  (VI,C,3)	(CI)	372	26.880	5.40
Y =  (VI,C,4)	(CII)	379	26.390	7.3
Y =  (VI,C,5)	(CIII)	391	25.580	7.82
				5
Y =  (VI,C,6)	(CIV)	395 375 358	25.320 26.670 27.930	3.0 4.9 4.2

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[b] Number of the section in which these compounds are discussed.

the phenyl in (XCV) to the styryl group in (XCVI) produces a bathochromic shift of the UV absorption by 40 nm, and in the transition to the stilbyl-(4) group in (XCVII) by 8 nm. The bathochromic shift caused by extension of the conjugation of the linking units in the compounds derived from dicarboxylic acids takes place through –CH=CH– groups and p-phenylene groups. In the series (XCIX) to (CIII) (Table XXIV; see also Table XXIX), the bathochromic shift of the absorption maximum through –CH═CH– amounts in each case to 24 nm and that taking place through p-phenylene to 8 nm. The substitution of the p-phenylene group in (C) by –CH═CH– produces, on the same principle, a bathochromic shift of the UV absorption by 16 (=24 – 8) nm.

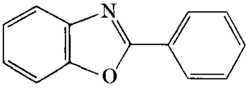
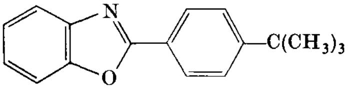
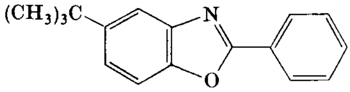
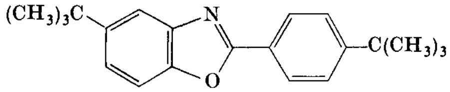
B. Aryloazolyl-(2) Compounds from Monocarboxylic Acids

1. *From Benzoic Acids*

The 2-phenylbenzazoles (CV) obtained from the reaction of 1,2-diaminobenzenes[305] and 2-aminophenols[306] with benzoic acids show a UV absorption at 300–310 nm. They are used as UV-absorbers for this

TABLE XXV[a]

2-Phenylbenzazoles

	Absorption maxima[b]		
	λ (nm)	$\tilde{\nu}$ (cm^{-1})	$\epsilon \times 10^{-4}$
	298.5	33.500	2.35
	302.0	33.100	3.14
	305.0	32.780	2.42
	308.0	32.470	2.90

[a] Reference 306.

[b] The bathochromic shift of the absorption maximum through a $(CH_3)_3C$ group in the 5-position is twice as high as that in the 4′-position; on the other hand, the extinction coefficient is increased by alkylation in the 4′-position.

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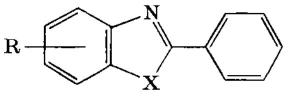
[305] IG, *DRP* 676,103; 2-Phenylbenzimidazole-5-sulfonic acid is the UV-absorber in "Delial."

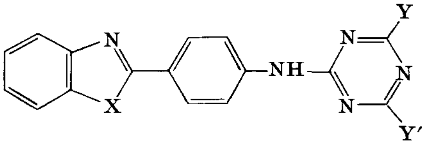
[306] CIBA, *DBP* 1,201,953; *FP* 1,228,524.

spectral range (Table XXV).[307] By introduction of amino[308] (Table XXVI), acylamino, or triazinylamino (CVI) groups[309] as auxochromic groups into the phenyl and benzo nuclei the absorption undergoes a bathochromic shift of 35–40 nm, entering the absorption range of the fluorescent brightening agents. Nevertheless, triazinylaminophenylbenzazoles are not fluorescent brightening agents with optimum properties.[310] Strongly fluorescent products are obtained only by the substitution of the 2-phenylbenzazoles (CV) by fluorophores such as arylotriazolyl-(2), benzoxazolyl-(2), or stilbenyl-(4) groups.

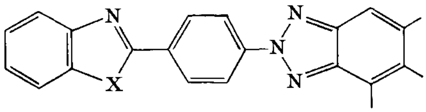


(CV)

X = O, S, NR



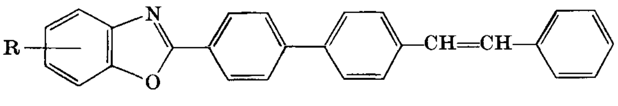
(CVI)



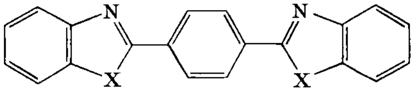
(CVII)

X = O, S, NR

2-[4′-Arylotriazolyl-(2)]- (CVII),[311] 2-[4′-stilbyl-(4)]- (CVIII),[312] and 2-[4′-aryloazolyl-(2)]-phenylbenzazoles (CIX)[313] are commercially interesting fluorescent brightening agents.



(CVIII)



(CIX)

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[307] See also FH, *FP* 1,506,801; CIBA, *FP* 1,511,691.

[308] CCC, *USP* 2,793,192.

[309] S. Bartkowicz, *Zeszyty Nauk. Politech. Lodz Chem.* **4**, 83 (1956); *CA* **51**, 1613f (1957).

[310] CIBA, *DBP* 1,205,970; CCC, *USP* 3,183,231; 3,167,563.

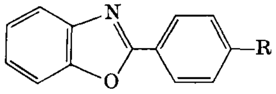
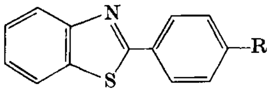
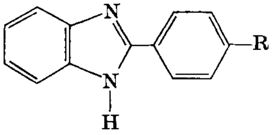
[311] FBy, *DBP* 911,368; Daito Chem. Ind., *JP* 26,489/63; *CA* **60**, 16030f (1964); DuP, *USP* 2,713,054/6; 2,720,528; 2,733,247; 2,700,044.

[312] CIBA, *BP* 1,115,274.

[313] These compounds are described in Section VI,C,2.

TABLE XXVI

2-(4-Substituted Phenyl) Azolyl Compounds

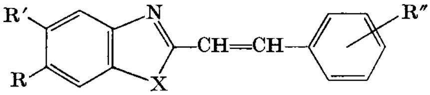
	Absorption maxima								
	R = H			R = NH_2			R = $NHCOCH_3$		
	λ (nm)	$\tilde{\nu}$ (cm^{-1})	$\epsilon \times 10^{-4}$	λ (nm)	$\tilde{\nu}$ (cm^{-1})	$\epsilon \times 10^{-4}$	λ (nm)	$\tilde{\nu}$ (cm^{-1})	$\epsilon \times 10^{-4}$
	299.0	33.450	2.35	332.0	30.100	4.10	319.0	31.300	3.75
	299.0	33.450	2.02	347.0	28.200	3.60	332.0	30.100	3.42
	304.0 318.0	32.850 31.450	2.65 1.78	325.0 —	30.800 —	3.90 —	319.0 334.0	31.350 29.950	3.90 3.48

The fluorescent brightening agents of the group of aryloazolyl-(2) compounds from benzoic acids are obtained by the processes described, preference being given to Process A (Table XXI) for compounds of the (CVIII) type. For the production of arylotriazolyl fluorescent brightening agents of the (CVII) type, the readily available 2-(4-aminophenyl) azolyl compounds, as described, for example, in Table XXVI, are best used as starting materials, using the production methods adopted for the arylotriazolylstilbene compounds.[314] Among these compounds, disperse fluorescent brightening agents for synthetic materials are important.

2. *From Cinnamic Acids*

Among the aryloazolyl-(2) compounds from monocarboxylic acids, those produced from cinnamic acid are particularly important. By introduction of an ethylene bridge between the benzazolyl-(2) and the phenyl radical in compounds of the (CV) type, a shift of the longest-wave UV absorption band by 40 nm is attained (see Table XXIV).

TABLE XXVII



(CX)

X	R	R′	R″	*M.p.* (°C)	*Fluorescence in benzene*	*References*
NH	H	H	*p*-COOH	—	—	315
O	H	CH_3	*p*-CN	196–197	Violet	316, 317
O	H	CH_3	*p*-Cl	154–155	Violet	317
O	CH_3	CH_3	*p*-CN	198–200	Violet	317
O	CH_3	CH_3	*p*-$COOCH_3$	169–170	—	318
O	CH_3	CH_3	*p*-$CON(C_2H_5)_2$	164–165	Blue	319

The 2-styrylaryloazolyl compounds of the (CX) (Table XXVII[315–319]) and (CXI) types (Table XXVIII) are fluorescent brightening agents

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[314] See Section II,A,2.

[315] VGF, *DBP* 1,088,456.

[316] Mitsui Kagaku Kogyo Kabushiki Kasha, *DBP* 1,210,764.

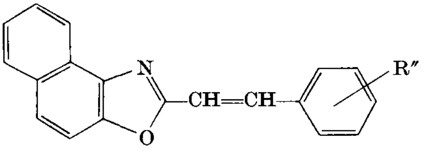
[317] FH, *FP* 1,358,895.

[318] FH, *FP* 1,397,629.

[319] FH, *FP* 1,413,395.

which produce effects with good coloristic properties on polyamides, polyester, polyacrylonitrile, polyolefins, and cellulose acetate.

TABLE XXVIII



(CXI)

R″	*M.p.* (°C)	*Fluorescence in benzene*
m-Cl	114–115	Blue
p-Cl	159–160	Green-blue
p-COOH	300	Blue

Their production from 2-aminophenols and 1-amino-2-hydroxynaphthalene is best carried out by dehydration of the *o*-hydroxyarylides of the cinnamic acids, e.g., (CXII), yields of 80% being obtained.

A simple and smooth reaction for the production of 2-styrylbenzimidazoles and 2-styrylbenzoxazoles is the condensation of 2-methylbenzimidazoles and 2-methylbenzoxazoles with aromatic aldehydes[320] in an inert solvent (xylene) and in presence of an acid catalyst (toluenesulfonic acid, zinc chloride, zinc bromide)[321]; the reaction is facilitated by the addition of dimethylformamide.[322]

Although these reactions proceed smoothly and can also be carried out on an industrial scale, the oxidative cyclization of the Schiff bases (CXIII) with nitrous acid has also been proposed.[323]

For the production of 2-styrylaryloimidazoles an alternative process is available since the 2-formylaryloimidazoles (CXIV)[324] can be readily obtained. These aldehydes condense with 4-nitrotoluenes in the presence

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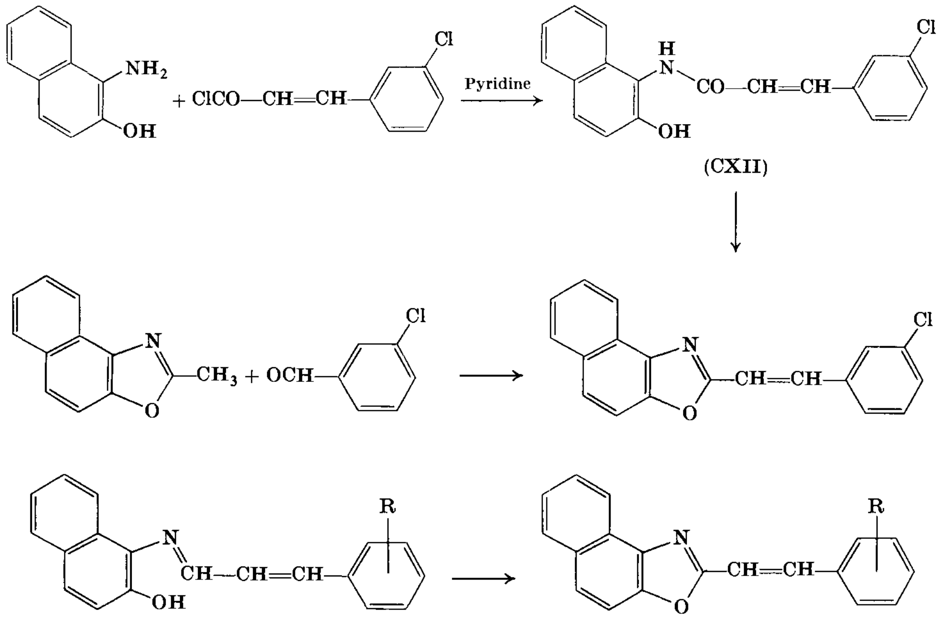
[320] K. Hofmann, "Imidazoles and its Derivatives," p. 278. Wiley (Interscience), New York, 1953.

[321] D. M. Brown and G. A. R. Kon, *J. Chem. Soc.* p. 2147 (1949); Mitsui Kagaku, *FP* 1,336,949; Nisso Chem. Ind., *DBP* 1,210,764; VGF, *USP* 3,137,655.

[322] CCC, *BeP* 659,424.

[323] MCI, *JP* 16,876/66; *CA* **66**, 47330k (1967).

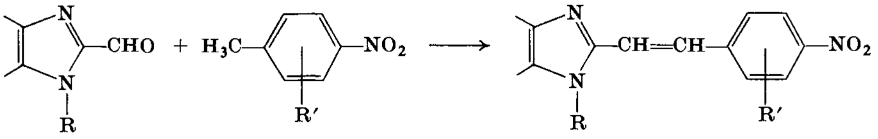
[324] BASF, *DBP* 1,025,415.



(CXII)

(CXIII)

of ammonium salts of aromatic sulfonic acids,[325] forming 4-nitrostyrylaryloimidazoles (CXV), which are important intermediates.[326]



(CXIV) (CXV)

3. *From Stilbene-4-carboxylic Acid*

The 2-[stilbenyl-(4)]benzoxazoles are largely analogous to the 2-styrylbenzoxazoles (Section VI,B,2) in their fluorescence performance. Their UV absorption maximum is only about 8 nm higher, as is also observed in the corresponding symmetrical benzoxazolyl compounds (CI) and (CII) (see Table XXIV). The influence of substituents is only slight. In this connection, an alkyl or phenyl substituent in the 6-position causes a slightly higher bathochromic shift than in the 5-position, up to a maximum of 9 nm. A marked bathochromic shift in 2-[stilbenyl-(4)]-benzoxazole is achieved by fusion of a benzene ring in the 4,5-position

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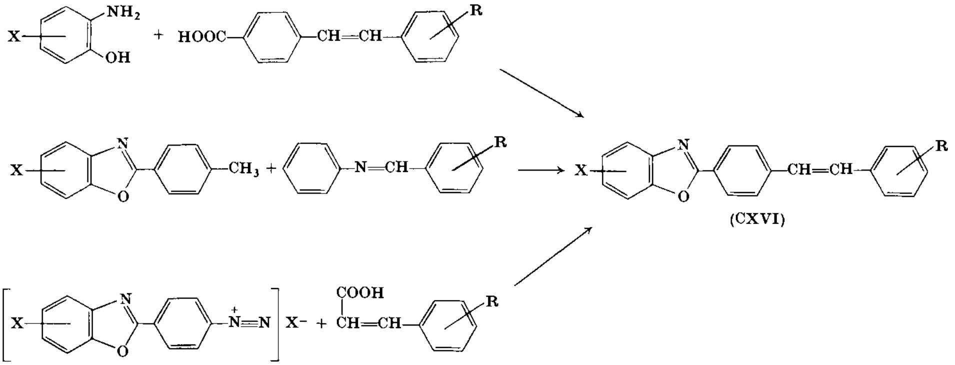
[325] CCC, *Neth. Appl.* 6,710,674.

[326] Gy, *DBP* 1,077,222; HWL, *BP* 996,240.

(by 19 nm) and by an OCH_3 group in the 4′-position of stilbene (by 6–12 nm).[59]

For the production of the 2-[stilbenyl-(4)]benzoxazoles with the general formula (CXVI) several possibilities are available:

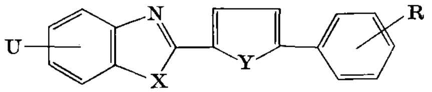
1. The reaction of 2-aminophenols and -naphthols with stilbene-4-carboxylic acid, particularly with the acid chloride[327] or iminoester.[287]
2. The Meerwein arylation of cinnamic acid,[148] using diazonium salts from 2-(4-aminophenyl)aryloazoles.[328]
3. The Siegrist anil synthesis,[59,60] using 2-(*p*-tolylaryl)azoles and Schiff bases from aniline with aromatic aldehydes.



(CXVI)

4. *From Heterocyclic Carboxylic Acids*

Fluorescent brightening agents derived from heterocyclic carboxylic acids can be represented by the general formula (CXVII)[329–331]



(CXVII)

X = O, NR′
Y = O, S
R = Alkyl, COOR″, CN, Cl, Acyl—NH

They are similar in structure to the bis-benzoxazolylthiophene compounds of the type (CIV) (Table XXIV) and to the 2-styryl-(4)-aryloazole compounds described in the previous section.

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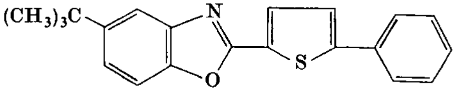
[327] CIBA, *FP* 1,455,329; *BP* 1,126,067.

[328] Nisso Kako Co., *JP* 21,013/67; *CA* **68**, 88208m (1968).

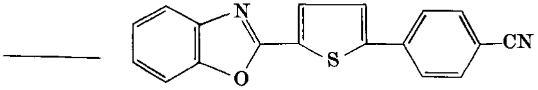
[329] CIBA, *DBP* 1,238,873; 1,278,983.

[330] FH, *FP* 1,488,712.

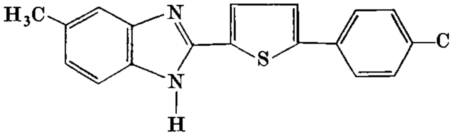
[331] FBy, *FP* 1,464,999.



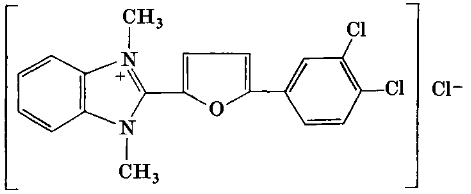
(CXVIIa)



(CXVIIb)



(CXVIIc)

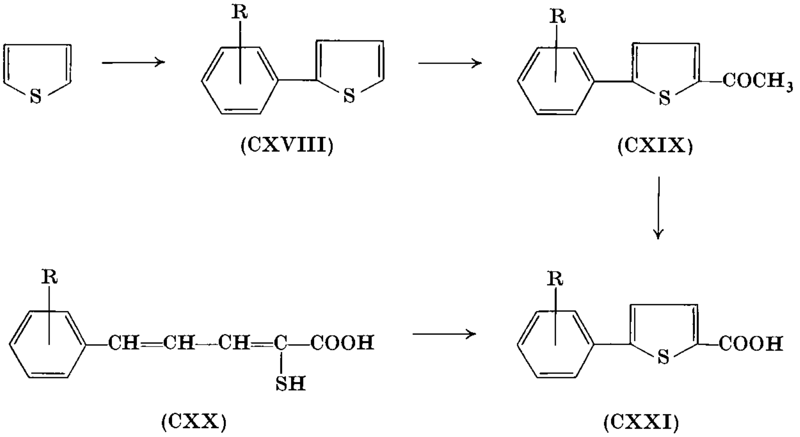


(CXVIId)

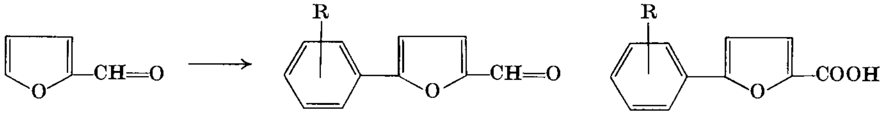
Typical fluorescent brightening agents of this group are the benzazole compounds. Among these, the disperse fluorescent brightening agents (CXVIIa)[329] and (CXVIIb)[330] are suitable for the optical brightening of polyester from aqueous baths (50–90°) in the presence of chemical bleaching agents, and also for the brightening of plastics (polyethylene and polyvinyl chloride) and spinning compositions; (CXVIIb) can be used especially for the fluorescent brightening of polyester textiles at wash temperatures. (CXVIIc)[329] and the water-soluble salt (CXVIId)[331] produces good fluorescent brightening effects on polyacrylonitrile fibers.

For the production of fluorescent brightening agents of the general formula (CXVII), the readily available heterocyclic carboxylic acids (CXXI) and (CXXIII) are used. Their reaction with 2-aminophenols and 1,2-diaminobenzenes is carried out by Process B, or by Processes E and G (Table XXI), in such a manner that acylation and azole cyclization take place in a single operation[329]; use of the acid chlorides permits, particularly in the production of the oxazoles, a definite two-step reaction by way of the *o*-hydroxyarylides.[330] Since the 5-arylfurfural compounds

(CXXII) are easily obtained by arylation reactions of furfural, it is possible to react (CXXII) with primary arylamines which contain an OH or an NHR group in the *o*-position, and subsequently to carry out azole cyclization of the resulting Schiff bases by oxidation.[299–303, 331]



(CXVIII) (CXIX) (CXX) (CXXI)



(CXXII) (CXXIII)

In principle, the aryl heterocycles (CXVIII) and (CXXII) can be obtained by arylation reactions; the arylation of furfural proceeds with good yields.[332] Since the production of (CXXI) by arylation of thiophen,[333] subsequent Friedel-Crafts reaction of (CXVIII), and oxidation (sodium hypochlorite) of the acetyl compound (CXIX) is tedious and involves considerable losses, attention is drawn to the possibility of reacting the disulfide of (CXX) with mild dehydrating agents (iodine, $KMnO_4$).[334]

C. Aryloazolyl-(2) Compounds from Dicarboxylic Acids

As the first disperse fluorescent brightening agent of this group for the optical brightening of polyester fibers by the heat-fixation process[335] and by the exhaustion process, preferably in the presence of nonionics,[336]

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[332] R. Oda, *Mem. Fac. Eng., Kyoto Univ.* **14**, 195 (1952); *CA* **48**, 1935f (1954).

[333] W. E. Bachmann and R. A. Hoffmann, *Org. Reactions* **2**, 224 and 236 (1944).

[334] E. Campaigne and R. E. Line, *J. Org. Chem.* **21**, 39 (1956).

[335] CIBA, *DBP* 1,098,904.

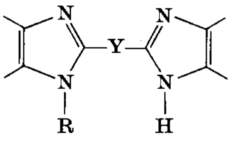
[336] Nisoo Chem. Ind., *JP* 21,509/65; *CA* **64**, 2224d (1966).

bis[5-methylbenzoxazolyl-(2)]ethylene (Uvitex ERN)[337] has gained considerable importance. The replacement of maleic acid, used for condensation with 3-amino-4-hydroxytoluene, by other dicarboxylic acids, such as terephthalic acid, naphthalene-1,4-dicarboxylic acid, 4-carboxycinnamic acid, stilbene-4,4′-dicarboxylic acid, as well as thiophene- and furan-2,5-dicarboxylic acids, produces a range of bisbenzoxazolyl-(2) compounds which differ in the length of continuous conjugation (Table XXIV). The bis-benzoxazolyl-(2) compounds mentioned in Table XXIV meet the requirements for the various fields of application as fluorescent brightening agents, and are suitable for the optical brightening of plastics, spinning compositions for polyester and polyolefin fibers, and also synthetic fibers from aqueous dye liquors.

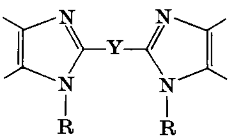
Among the aryloazolyl compounds from dicarboxylic acids, the oxazolyl compounds have achieved more commercial importance. The corresponding imidazolyl compounds, which are obtained by condensation of aromatic 1,2-diamines with the above-mentioned dicarboxylic acids, have not gained the wide interest of the isologous oxazolyl compounds.

The fluorescent brightening agents of the bisbenzimidazolyl type summarized in Table XXIX can be compared directly with the fluorescent brightening agents of the bisbenzoxazolyl type with regard to their UV absorption behavior (see Table XXIV). The bathochromic shift of the absorption demonstrates the same rule: a –CH═CH– group gives a shift of 24 nm and a *p*-phenylene group, of 8 nm.

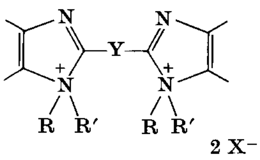
Compounds of type (A), which have at least one free NH group, are soluble in strong alkali; the alkali salts show an affinity for cotton, particularly from wash liquors.[338] The *N*-substituted (B) types possess the characteristics of disperse fluorescent brightening agents and are easily converted into the corresponding imidazolium compounds (C),[339] which are soluble in water and are used as cationic fluorescent brightening agents, for example, in the optical brightening of polyamide and polyacrylonitrile fibers.



(A)



(B)



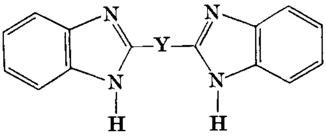
(C)

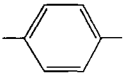
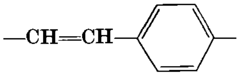
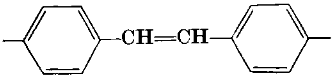
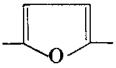
[337] CIBA, *DBP* 1,094,696.

[338] CIBA, *DBP* 841,752; 883,286; 1,090,167; *USP* 2,488,289.

[339] CIBA, *FP* 1,119,854/5.

TABLE XXIX



Y	Absorption maxima[a]		
	λ (nm)	$\tilde{\nu}$ (cm^{-1})	$\epsilon \times 10^{-4}$
—CH=CH—	362	27.620	1.93
	345	28.990	5.39
	370 (389)	27.030 (25.710)	6.19 (4.05)
	377	26.530	7.19
	366	27.320	—

[a] Determined in DMF.

1. *From Fumaric Acid*

Because of the poor yields, particularly of bisarylooxazolyl-(2) compounds (CXXIV), the condensation of fumaric acid with 1,2-diaminobenzene, 2-aminophenols, and naphthols is only little used. Many production methods have been suggested which permit the use of the more easily reacting succinic acid and its substitution products, and which envisage as the decisive reaction the conversion of the bis[benzoxazolyl-(2)]ethane compounds [(CXXV) to (CXXIX)], obtained in good yields. The methods which have been used are summarized in Chart 5.[340–345]

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[340] CIBA, *DBP* 1,134,988.

[341] MDW, *JP* 5180/64; *CA* **61**, 16210c (1964).

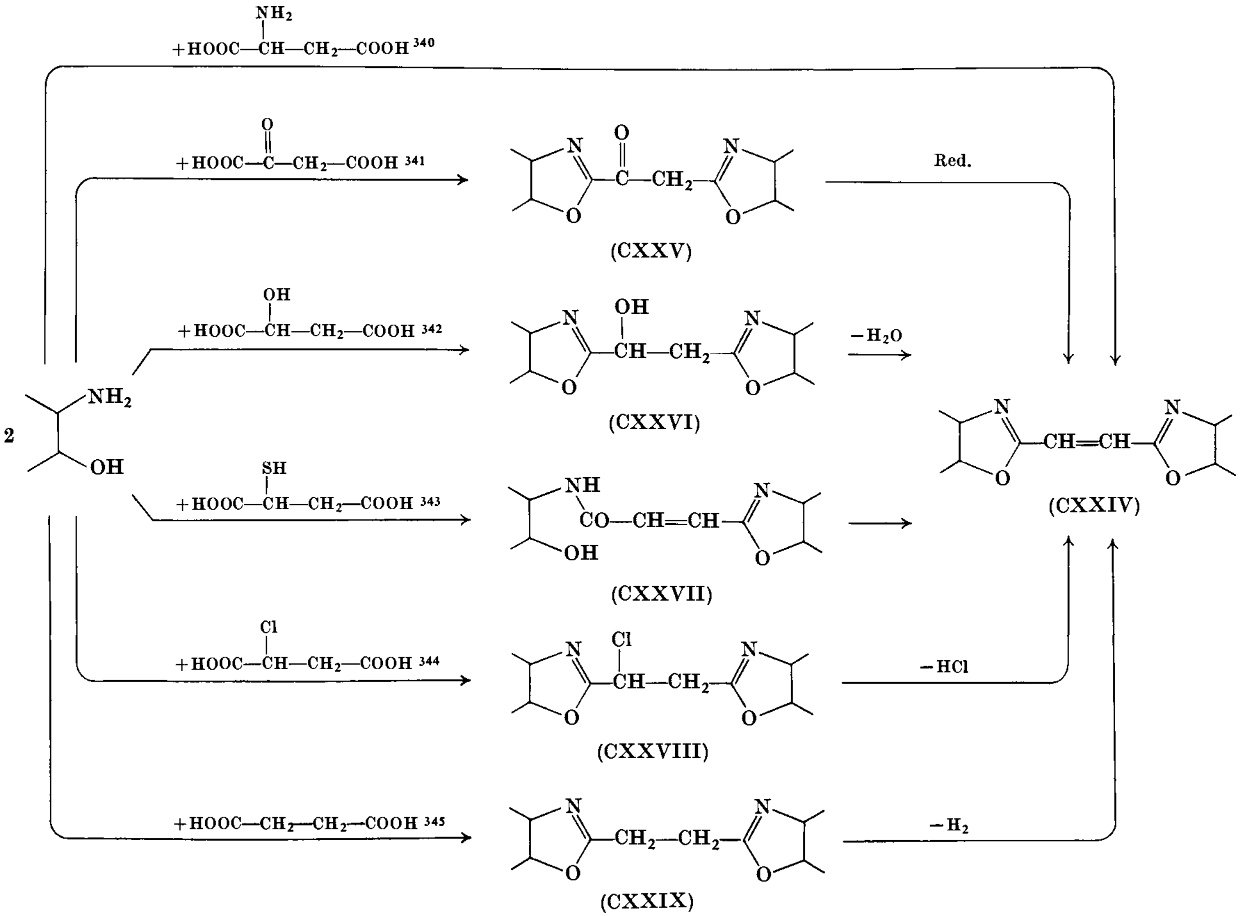
[342] CIBA, *DBP* 1,105,423; 1,090,214; 1,117,125; see also *DBP* 1,039,064.

[343] CIBA, *DBP* 1,052,855; *SP* 345,341; *FP* 1,343,262.

[344] NSK, *JP* 11,992/62; *CA* **60**, 8165h (1964).

[345] CIBA, *DBP* 849,694, 1,040,555; *BP* 623,428; *USP* 2,483,392; *BeP* 607,116.

CHART 5

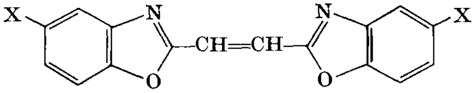

2
NH₂
OH
+HOOC—CH(NH₂)—CH₂—COOH 340
+HOOC—C(=O)—CH₂—COOH 341
+HOOC—CH(OH)—CH₂—COOH 342
+HOOC—CH(SH)—CH₂—COOH 343
+HOOC—CH(Cl)—CH₂—COOH 344
+HOOC—CH₂—CH₂—COOH 345
(CXXV)
(CXXVI)
(CXXVII)
(CXXVIII)
(CXXIX)
(CXXIV)
Red.
−H₂O
−HCl
−H₂

The condensation of 2-aminophenols with α-hydroxysuccinic acid in the presence of dehydrating agents which can split off water from the bridging group gives good results. There have been numerous suggestions for the dehydrogenation[346] of the bis[oxazolyl-(2)]ethane compounds (CXXIX), obtained with succinic acid, by oxidizing agents [air in quinoline, hydrogen peroxide, mercuric acetate[345] (+iodine),[347] ferric chloride, chloranil, nitrobenzene] and halogenating agents (chlorine,[348] bromine, thionyl chloride, sulfuryl chloride), methods by which the aryloimidazolyl compounds can also be produced.[349]

The reaction of 2-aminophenols with maleic anhydride in ethylene dichloride in the presence of zinc chloride and boric acid under azeotropic conditions proceeds with a 96–98% yield.[278]

The UV absorption of the bisbenzazolyl-(2) compounds is influenced by substituents in the 5- and 6-positions of the benzo nuclei. Table XXX illustrates the shift of absorption to longer wavelengths by alkyl and alkoxy groups.

TABLE XXX



X	m.p. (°C)	λ (nm)	$\bar{\nu}$ (cm^{-1})	$\epsilon \times 10^{-4}$
		Absorption maxima		
H	240	355	28.170	4.69
Cl	261	355	28.170	4.38
CH_3	186	363	27.550	4.30
C_2H_5	123	363	27.550	4.23
$C(CH_3)_3$	159	363	27.550	4.20
OCH_3	194	382	26.720	3.69

The formation of water-soluble salts by the reaction of bis-aryloimidazolyl compounds with quaternizing agents (methyl toluenesulfonate, dimethyl sulfate) is unusual in the case of arylooxazolyl compounds. Konishi *et al.*[350] suggested an "external" quaternization in

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[346] DuP, *USP* 2,765,303; NSK, *JP* 19,129/61; *CA* **59**, 10059b (1963).

[347] Daito Chem. Co., *SP* 436,296.

[348] Toyo Rayon, *JP* Publ. No. 11,245/68; Appl. No. 40.566/65; 8.7.65/13.5.68; describes the oxidation with sodium hypochlorite on the fiber.

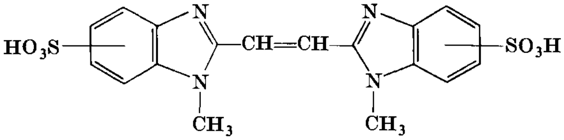
[349] CIBA, *DBP* 841,752; *USP* 2,488,289; *BP* 600,696.

[350] T. Maruyama, N. Juroki, and K. Konishi, *Bull. Univ. Osaka Prefect.* **A13**, 135 (1964); see also *Kogyo Kagaku Zasshi* **67**, 155 and 159 (1964); *CA* **61**, 5820g (1964).

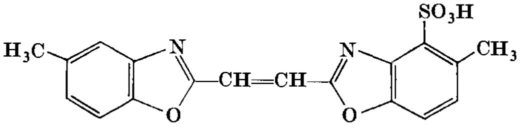
the case of Uvitex ERN which does not change the optical properties as a fluorescent brightening agent, but which converts this product into freely soluble fluorescent brightening agents for PAN.

(CXXX) is converted into the bischloromethyl compound (CXXXI) in a mixture of paraformaldehyde, 98% H_2SO_4, and chlorosulfonic acid. With secondary amines, HNR_2, the amines (CXXXII) are obtained, which yield with dimethyl sulfate the bis-ammonium salts (CXXXIII).[350, 351] In the chlorosulfonation of (CXXX), the sulfonyl chloride (CXXXIV) is formed. The reaction of (CXXXIV) with primary or secondary β-aminoethylamines or the addition of secondary amines to the ethylene imide leads to the aminoamides (CXXXV).[352] With dimethyl sulfate these give the bisammonium salts (CXXXVI).[353] The most important fluorescent brightening agent of this range, the bis-pyridinium salt (CXXXVII), can be obtained from (CXXXI) and pyridine.[354] These reactions are summarized in Chart 6. The absorption and fluorescence performance of the amines and ammonium salts is summarized in Table XXXI.

Bis-benzazolylethylene compounds water-solubilized by the introduction of one or two SO_3H groups are also used as fluorescent brightening agents.



(CXXXVIII)



(CXXXIX)

Of these, (CXXXVIII)[355] is recommended for the fluorescent brightening of cellulosic materials (cotton and paper) and (CXXXIX)[356] for Perlon and nylon.

[351] Daito Chem. Co., *FP* 1,334,584.

[352] Daito Chem. Co., *JP* 21,010/67; *CA* **68**, 88207k (1968); T. Maruyama, I. Araki, N. Kuroki, and K. Konishi, *Kogyo Kagaku Zasshi* **67**, 159 (1964); *CA* **61**, 5820f (1964).

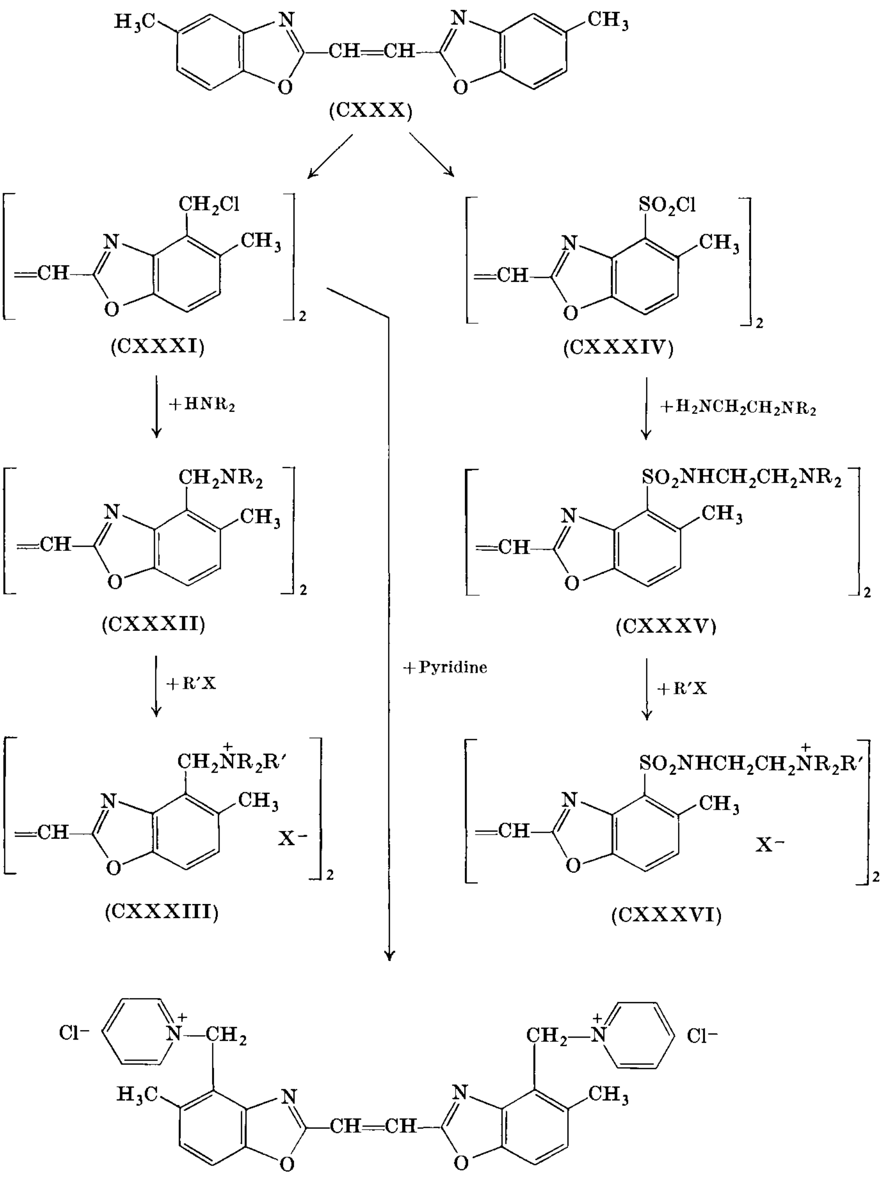
[353] Daito Chem. Co., *JP* Publ. No. 15,571/67; Appl. No. 16.612/63; 30.3.63/28.8.67.

[354] Daito Chem. Co., *USP* 3,178,421; 3,182,059.

[355] CIBA, *DBP* 1,039,064.

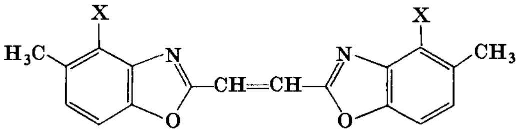
[356] See DuP, *USP* 2,737,516; Diato Chem. Co., *JP* Publ. No. 11,246/68; Appl. No. 51.151; 21.8.65/13.5.68; Nisso Chem. Ind., *JP* 25,834/63; *CA* **60**, 12151f (1964).

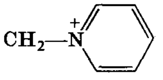
CHART 6



(CXXXVII)

TABLE XXXI



X	*M.p.* (°C)	λ_{max} (nm)	$\epsilon \times 10^{-4}$	Fl_{max} (dil. acet.)	Fl_{max} (PAN)
H	174	363	4.69	—	—
$CH_2\text{—}N(C_2H_5)_2$	175	368	4.46	430	440
$CH_2\text{—}\overset{CH_3}{\underset{+}{N}}(C_2H_5)_2CH_3SO_4^-$	214–218	370	4.59	430	439
 Cl^-	—	370	2.14	—	—
$SO_2NHCH_2CH_2N(C_2H_5)_2$	234–235	373	5.05	435	437
$SO_2NHCH_2CH_2\overset{CH_3}{\underset{+}{N}}(C_2H_5)_2\ CH_3SO_4^-$	271	373	4.97	436	436

2. *From Terephthalic Acid and Analogous Aromatic Dicarboxylic Acids*

The benzoxazole compounds produced from aromatic dicarboxylic acids, terephthalic acid, or naphthalene-1,4-dicarboxylic acid and 2-aminophenol are notable for high melting points (approx. 300° and upwards). The melting point can be reduced considerably by highly branched alkyl groups in the 5-position of the benzoazole nuclei[357]; 1,4-bis[5-*tert*-butylbenzoxazolyl-(2)]naphthalene melts at 167–168°.[358] The fluorescent brightening agents of this group are less suitable for aqueous application to synthetics than for the fluorescent brightening of spinning compositions, for which the 1,4-bis[benzoxazolyl-(2)]-naphthalene compounds of type (CXL) are particularly interesting.[358]

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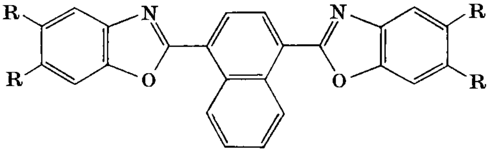
[357] CIBA, *DBP* 1,268,097; Nippon Kayaku, *JP* 11,150/66; *CA* **66**, 19764m (1967).

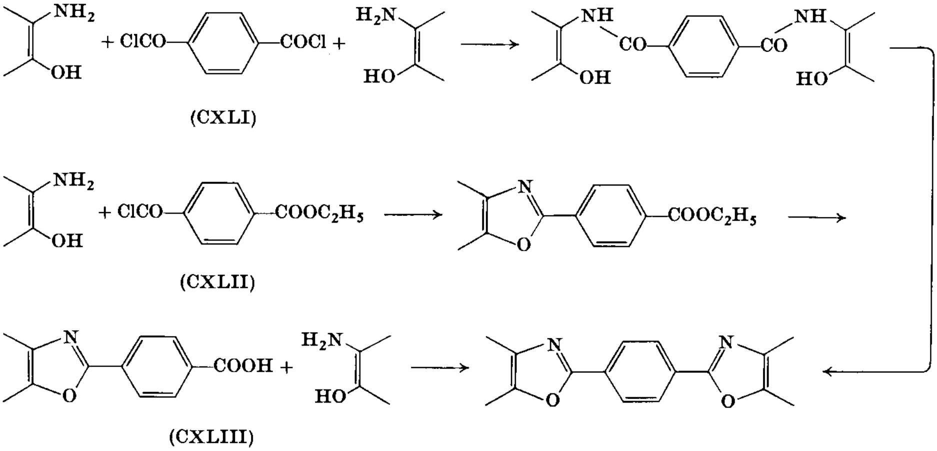
[358] FH, *FP* 1,444,004; 1,508,560.



(CXL)

Owing to the relatively short-wave absorption of 347 nm (see Table XXIV), which may be subjected to a slight bathochromic shift of about 8 nm by alkyl substituents in the 5-position, they produce a pleasing red-violet white.

For the production of fluorescent brightening agents from aromatic dicarboxylic acids, Processes B, J, and S are available; use is made, in particular, of the reaction with dicarbonyl chlorides [e.g., of (CXLI)] and of the subsequent dehydrating cyclization.[358] Use of the semiester acid chloride (CXLII) of terephthalic acid also permits, by the further reaction of 2-(4-carboxyphenyl)aryloazoles (CXLIII),[359] the production of mixed 1,4-bis(aryloazolyl)benzene compounds, e.g., 1-[benzoxazolyl-(2)]-4-[naphthoxazolyl-(2)]benzene.



(CXLI)

(CXLII)

(CXLIII)

The oxidative cyclization of the Schiff bases from terephthaldialdehyde and 2-aminophenols (see Section VI,A,c) has also been proposed for production of the symmetrical 1,4-bis(aryloazolyl)benzene compounds.[360]

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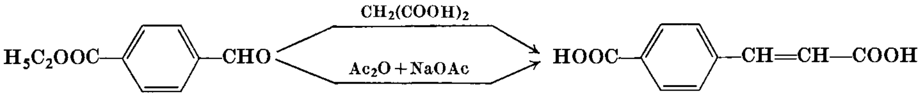
[359] FH, *FP* 1,506,801.

[360] Meisei Chem. Ind., *JP* 18,530/61; *CA* **57**, 9858e (1962).

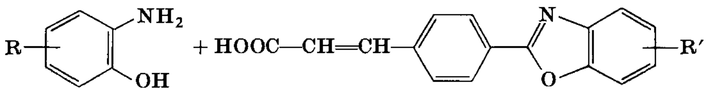
3. *From 4-Carboxycinnamic Acid*

The fluorescent brightening agents of this group of benzoxazolyl compounds are similar in fluorescence behavior to those derived from fumaric acid (Section VI,C,1), in comparison with which their UV absorption is subjected to a bathochromic shift of only 8 nm (see Table XXIV). They are particularly suitable for the fluorescent brightening of polyesters (glycol terephthalates) and polyolefins by incorporation and by application from aqueous dispersions or organic solvents in the presence of carriers or an oxidizing agent. In their performance in the fluorescent brightening of plastics and spinning compositions, the fluorescent brightening agents of this group resemble more closely the bis benzazoles from stilbene-4,4′-dicarboxylic acid (see Section VI,C,4) which because of their physical properties can be used on synthetics only at higher temperatures (see Section VIII) or, alternatively, in spinning melts.

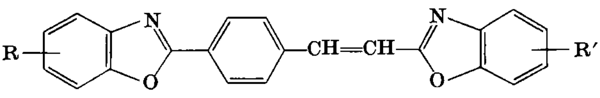
The development of the bis-benzoxazolyl-(2) compounds (CXLVI) from 4-carboxycinnamic acid was carried out mainly by Japanese dyestuff manufacturers.[361, 362] They are produced in the conventional manner by the condensation of 4-carboxycinnamic acid (CXLIV), obtained from terephthalic semialdehyde and malonic acid or acetic anhydride,[362] with aminophenols. Although (CXLIV) is readily available and it is possible to produce mixed bisbenzazolyl compounds by condensation of 4-benzazolylcinnamic acids (CXLV) with aminophenols,[363] syntheses based on the production methods for stilbene compounds



(CXLIV)



(CXLV)



(CXLVI)

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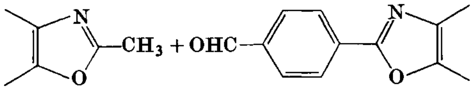
[361] Nippon Chem. Works, *BeP* 631,859.

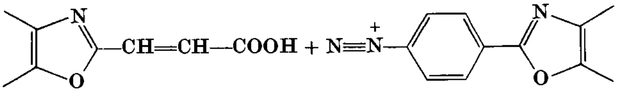
[362] See also CCC, *USP* 3,019,221.

[363] Japan Chem. Works, *JP* 6104/65; *CA* **63**, 18318b (1965).

described in Section II,B have nevertheless been suggested. In this connection, use is made of the condensation of 2-methylbenzazoles with aldehydes,[364]

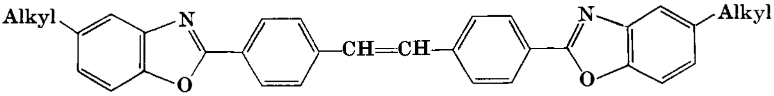


or of the "cinnamic acid coupling" according to Meerwein,[365] e.g.,



4. *From Stilbene-4,4′-dicarboxylic Acids*

In the years 1955 to 1958, Sterling Drug, Inc. described the production of 4,4′-bis[benzimidazolyl-(2)]stilbene by Process Q,[366] Process E,[367] and by sulfur dehydration of 2-(4-methylphenyl)benzimidazole[368] and suggested this compound as a fluorescent brightening agent for natural and synthetic fiber materials from wash liquors. This fluorescent brightening agent corresponds to the Uvitex SIA types of Ciba (see Table XX). Of greater importance are, however, the 4,4′-bis(benzoxazolyl)stilbene compounds (CXLVII) which absorb at 377–379 nm independent of the molecular weight of the alkyl substituents[369] (see also Table XXIV). The importance of fluorescent brightening agents of the formula (CXLVII) is in their application for the optical brightening of polyester fibers as an addition to spinning compositions.[370] For their production from stilbene-4,4′-dicarboxylic acid and 2-aminophenols,



(CXLVII)

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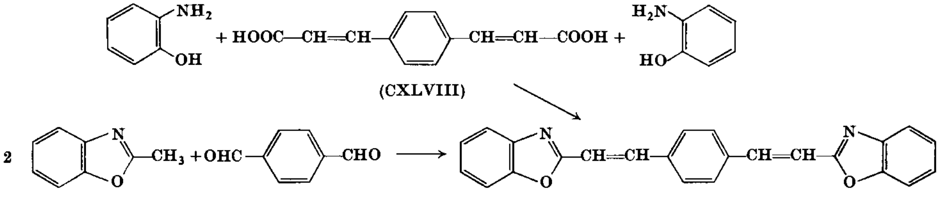
[364] Nippon Kayaku, *JP* 20,226/66; *CA* **66**, 105,897p (1964).
[365] Nippon Kayaku, *JP* 6101/65; *CA* **63**, 18318a-c (1965); *JP* 6105/65.
[366] Sterling Drug Inc., *USP* 2,937,148.
[367] Sterling Drug Inc., *DBP* 1,113,938.
[368] Sterling Drug Inc., *DBP* 1,173,480.
[369] Japan Chem. Works, *JP* 20,225/66; *CA* **67**, 55173x (1967).
[370] Eastman Kodak, *DBP* 1,255,077.

Process A,[371] and particularly Process F,[275] with yields exceeding 50%, are recommended. Because of the very high melting point of stilbene-4,4′-dicarboxylic acid (400°) and of the bis(benzoxazolyl)stilbene compounds, Process R can be used on an industrial scale in addition to the more usual Process E, also with the use of 2-aminophenol ethers.[372] To form the stilbene system the methods described in Section II,B may be used. The *S*-dehydration of 2-(4-methylphenyl)benzoxazoles appears to be a particularly advantageous method for the production of stilbene-4,4′-dicarboxylic acid from 4-methylbenzoic acid.

5. *From* p-*Phenylene-bis(acrylic acid)*

The absorption undergoes a bathochromic shift of about 24 nm when the conjugate system of the bisbenzazolyl compounds from 4-carboxycinnamic acid (Section VI,C,3) is extended by a –CH═CH– group. Nevertheless, the shade of the fluorescence obtained in optical brightening is not so green that compounds of this type (CXLIX) cannot be used as fluorescent brightening agents. They are used mainly for the brightening of polyester and polyolefins in aqueous suspension or in an organic solvent with application of heat.[373] Compounds of type (CXLIX) can be produced by condensation of *p*-phenylene-bis(acrylic acid) (CXLVIII) with 2-aminophenols by Processes A, B, or G[374]. A preferred process is, however, to treat 2-methylbenzoxazole with terephthaldialdehyde with application of heat[375] in the presence of sulfonic acids and DMF in a boiling solvent at 150–200°.[322]



(CXLVIII)

(CXLIX)

6. *From Heterocyclic Dicarboxylic Acids*

Heterocyclic dicarboxylic acids which ensure a continuous conjugate hydrocarbon chain between both aryloazolyl-(2) groups are thiophene-, furan-, and pyrrole-2,5-dicarboxylic acids. The structural features of the fluorescent brightening agents (CLI) of this group are similar to those

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[371] Nippon Chem. Works, *FP* 1,397,799.

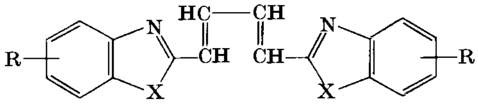
[372] NSK, *FP* 1,411,999.

[373] Nippon Kagaku Kobyosho Co., *JP* Publ. No. 4314/67; 1.6.63/22.2.67; no Appl. No.

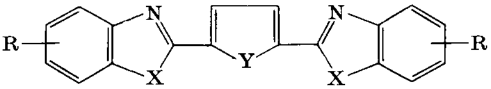
[374] Nippon Kagaku Kogyosho Co., *JP* 3510/66; *CA* **65**, 7328d (1966).

[375] Osaka Seika Chem., *JP* 29,177/65; *CA* **64**, 12857d (1966).

from fumaric acid (Section VI,C,1) in so far as their conjugation of the ethylene bridge is duplicated (CL). Compounds of the (CL) type have also been suggested as fluorescent brightening agents.[376]



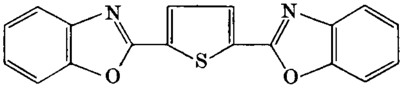
(CL)



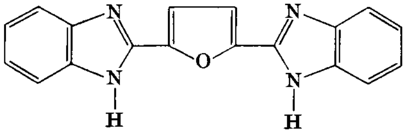
(CLI)

X and Y = O, NR, S

Fluorescent brightening agents of the (CLI) type are valuable because of their suitability for the optical brightening of all synthetic fiber materials and plastics. In addition to substitution, usually only by alkyl substituents, products with optimum properties can be chosen by changes of X and Y in (CLI). Interesting products, e.g., (CLII)[377] and (CLIII),[378] have been found in the thiophene and furan series.



(CLII)



(CLIII)

(1) Compounds of the (CLI) type with X = O and Y = S are easily obtained from thiophene-2,5-dicarboxylic acid by Processes B, D, E, and G,[379] and from the acid chloride or from 2,5-dicyanothiophene[380] by Process M.[286] It is also possible to produce 2,5-bis(benzazolyl)thiophene compounds (CLVI) (a) by use of tetrahydrothiophene-2,5-dicarboxylic acid obtained from dichloroadipic acid and Na_2S and subsequent oxidation of the 2,5-bis(benzazolyl)tetrahydrothiophene compounds

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[376] Nippon Kagaku Kogyosho Co., *JP* Publ. No. 244/68; 9.5.64/8.1.68; no Appl. No.

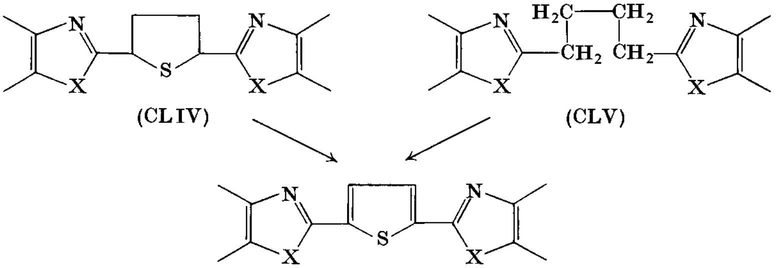
[377] CIBA, *DBP* 1,166,197; *USP* 3,095,421.

[378] CIBA, *DBP* 1,086,237; 1,114,461; 1,147,232.

[379] See also CIBA, *DBP* 1,253,222; Japan Chem. Works.[369]

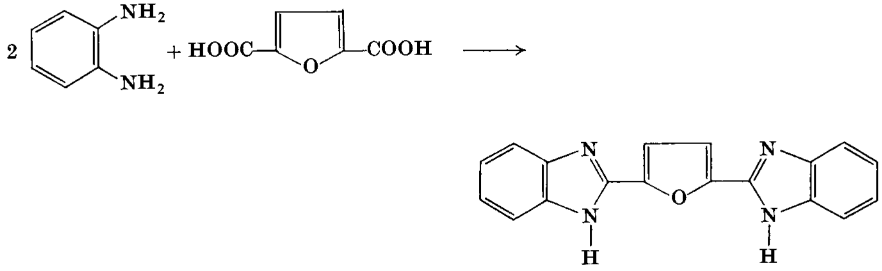
[380] CIBA, *BeP* 658,344.

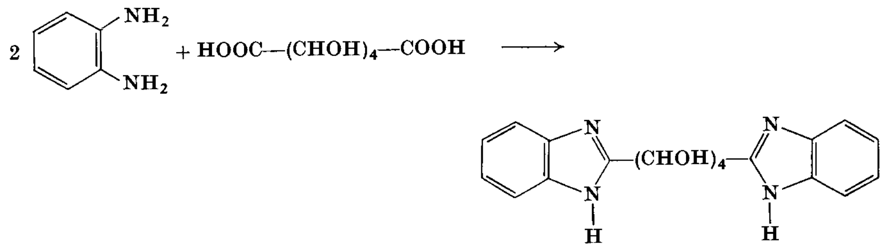
(CLIV),[381] and (b) by the cyclodehydrogenation of 1,4-bis(benzazolyl)-butane compounds (CLV) with sulfur.[382]


(CLIV) (CLV)

(CLVI)

(2) Furan-2,5-dicarboxylic acid (dehydromucic acid) can be condensed with aromatic 1,2-diamines by Processes E, B, and G to 2,5-bis(benzimidazolyl)furan compounds.[383] Since furan-2,5-dicarboxylic acid can be easily obtained from mucic acid or saccharic acid [HOOC—(CHOH)$_4$—COOH] with dehydrating agents, bisbenzimidazolyl compounds [e.g., (CLVII)] can also be produced by this process directly from the tetrahydroxyadipic acids and aromatic 1,2-diamines. In this reaction, the


(CLVII)


(CLVIII)

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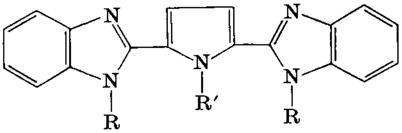
[381] CIBA, *SP* 426,870; *BeP* 607,116.

[382] CIBA, *DBP* 1,226,583.

[383] CIBA, *DBP* 1,086,237; *BeP* 610,558.

primary formation of the tetrahydroxybutane (CLVIII) is probable.[384] This method offers the advantage that the production and a possible decarboxylation of furan-2,5-dicarboxylic acid to pyromucic acid can to a large extent be avoided.

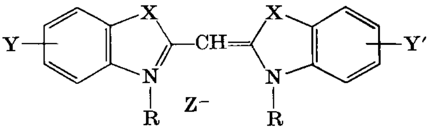
(3) The 2,5-bisbenzazolyl compounds derived from pyrrole-2,5-dicarboxylic acid,[385] e.g.,



are of little technical interest as fluorescent brightening agents. They are produced by reaction of a tetrahydroxybutane of the (CLVIII) type with ammonia or with agents which yield ammonia (R' = H) and, possibly, by subsequent alkylation (R' = alkyl) or acylation.

D. Methine Compounds

Thia- and oxamethinecyanines and their azaisologs[386] absorb in the long-wave UV and near-visible region (see Table XXXII)[388, 397–403] and



(CLIX)

X = O, Se, S

they give on numerous types of substrates fluorescent effects which render them suitable as fluorescent brightening agents.[387–389]

Owing to their favorable UV absorption at 370 or 373 nm, among these methine compounds the oxamethinecyanines (CLXII) and the thia-azacyanines (CLXVI) are suitable for the fluorescent brightening of fibers of cellulose, hydrated ethers, and esters of cellulose and, above all, polyamides and polyacrylonitrile. A bathochromic shift of the absorption

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[384] CIBA, *DBP* 1,147,232.

[385] CIBA, *DBP* 1,101,430.

[386] F. M. Hamer, The Cyanine Dyes and related compounds, *in* "The Chemistry of Heterocyclic Compounds" (A. Weissberger, ed.), pp. 58 and 384. Wiley (Interscience), New York, 1964.

[387] Ilford, *DBP* 898,437.

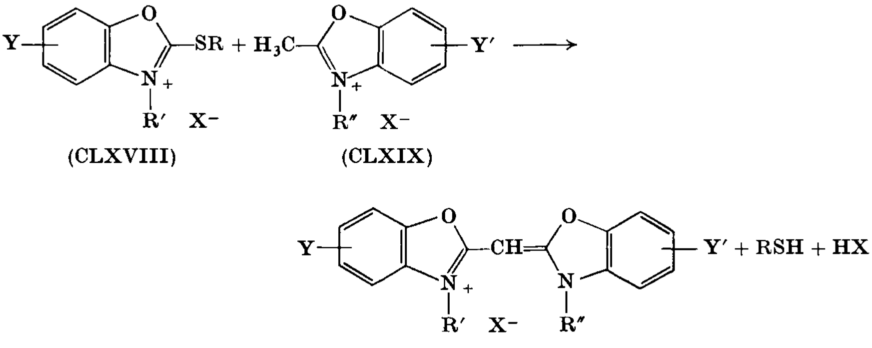
[388] Gy, *DBP* 1,007,726; 1,010,490; *BP* 1,055,671; *USP* 2,620,282; 2,649,385.

[389] BASF, *DBP* 1,089,721.

is effected by substituents in the benzoazole nuclei of the oxamethinecyanines, e.g., by alkyl (CH_3) (CLXIII) and alkoxy (CH_3O) groups, by Cl atoms, particularly when these substituents are introduced in the 5-position,[390] or by fusion of a further benzene nucleus to form naphthoxazolyl compounds [(CLXIV) and (CLXV)].

The replacement of O atoms by Se (CLXI) or S (CLX) is also associated with a bathochromic shift of the absorption by about 50 nm. The aza isologs, corresponding to Kuhn's principle,[391] manifest a hypsochromic shift of the absorption of a similar order (CLXVII). The replacement of both functions in the oxamethinecyanine (CLXII) is compensated in such a manner that the thiaazacyanine (CLXVI) shows the unchanged absorption maximum of the oxamethinecyanine; as in the case of (CLXII) and (CLXIII), (CLXVI) is therefore a suitable fluorescent brightening agent for acrylonitrile-containing polymers, polyamides, cellulose esters, hydrated cellulose ethers, and cotton.[389]

The oxamethinecyanines (CLXX) can be obtained conveniently by the alkylthio method, which consists in the reaction of 2-alkylthio-3-alkylbenzoxazolium salts (CLXVIII) with the 2-methyl-3-alkylbenzoxazolium salts (CLXIX) in the presence of acid-binding agents, e.g.,



(CLXVIII) (CLXIX)

(CLXX)

sodium acetate in alcohol or in pyridine.[392–394] It is possible to produce by this method unsymmetrical oxamethinecyanines substituted by Y and Y′ and also mixed oxathia-methinecyanines. Formation of the

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[390] In this connection, see also the bathochromic shift of the absorption in the bisbenzoxazolyl compounds in Table XXX.

[391] R. Kuhn, *Chimia (Aarau)* **4**, 203 (1950); *Helv. Chim. Acta* **34**, 237 (1951).

[392] Ilford, *BP* 424,559.

[393] J. D. Kendall and H. G. Suggate, *J. Chem. Soc.* p. 1503 (1949).

[394] See also R. A. Geffreys, *J. Chem. Soc.* p. 3396 (1957).

TABLE XXXII
METHINE COMPOUNDS

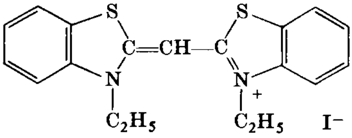
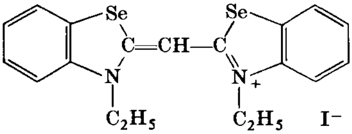
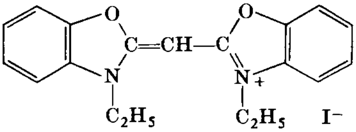
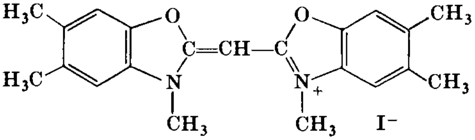
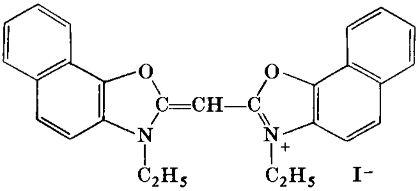
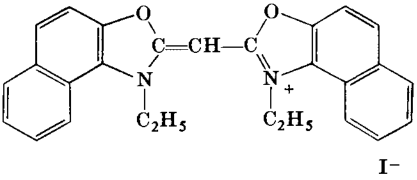
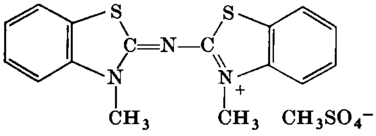
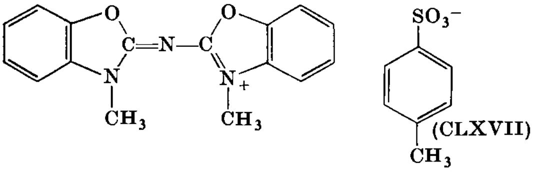
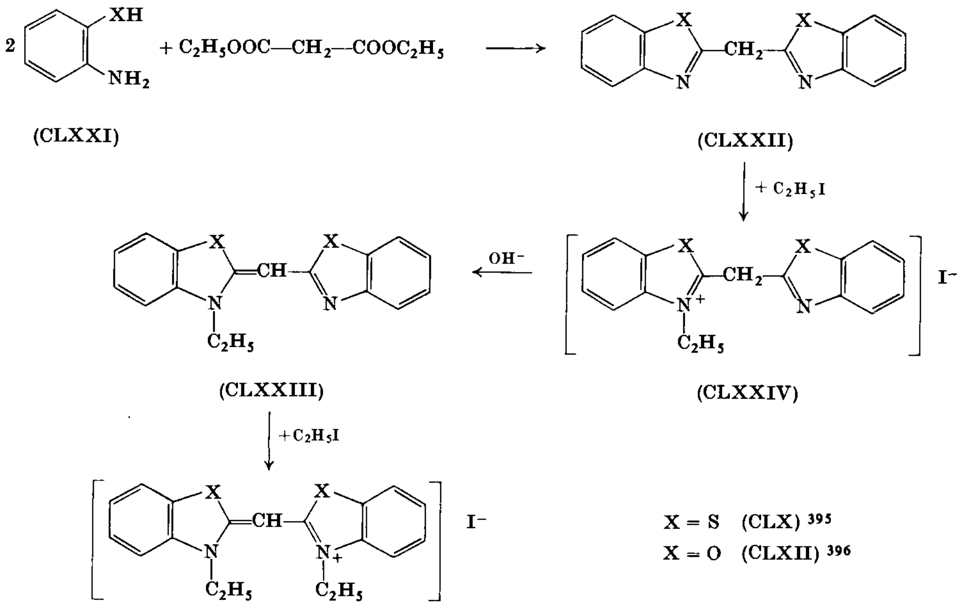
	M.p. (°C)	λ_{max} (nm) in water	*References*
 (CLX)	311	423	400
 (CLXI)	—	420	401, 402
 (CLXII)	301	370	403
 (CLXIII)	320	395	388, 403
 (CLXIV)	315	396	403
 (CLXV)	283	402	403

TABLE XXXII (*continued*)

	M.p. (°C)	λ_{max} (nm) in water	*References*
 (CLXVI)	273	373	397–399
 (CLXVII)	300	323	397

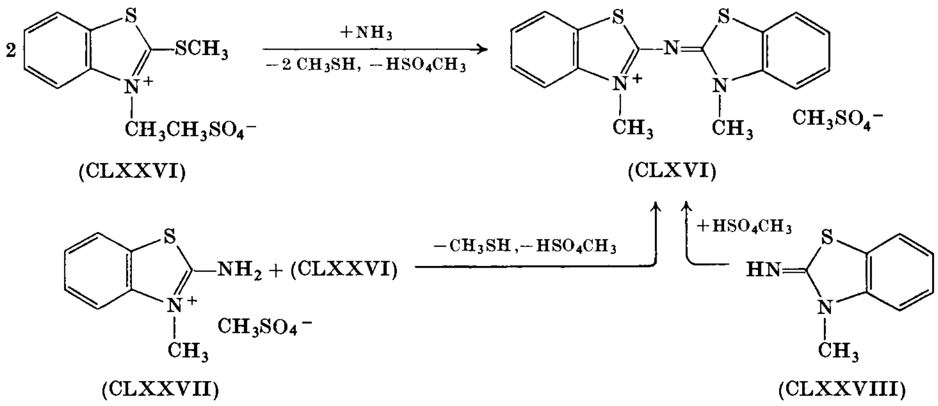
generally unwanted mercaptans can be avoided by carrying out the reaction as follows:



(CLXXI) (CLXXII) (CLXXIII) (CLXXIV) (CLXXV)

X = S (CLX)[395]
X = O (CLXII)[396]

The "anhydro bases" (CLXXII) produced in the reaction of the *o*-amino compounds (CLXXI) with malonic ester yield with ethyl iodide the salts (CLXXIV), which with alkali form the "anhydro bases" (CLXXIII) of the methines (CLXXV). Quaternization of the "anhydro bases" (CLXXIII) then gives the methines (CLXXV) themselves. This synthesis has been described for X = S (CLX) by Mills[395] and for X = O (CLXII) by Geigy.[396] The azacyanine (CLXVI), which is interesting as a fluorescent brightening agent, is obtained by reaction of 2-methylthio-3-methylbenzothiazolium methosulfate (CLXXVI) with NH_3 in the presence of bases,[397] or by condensation of 2-amino-3-methylbenzothiazolium methosulfate (CLXXVII)[398] with (CLXXVI). A method which is often preferred for the production of (CLXVI) consists in the reaction of 3-methylbenzothiazolonimide (CLXXVIII) with methylsulfuric acid in a high-boiling organic solvent[399]



(CLXXVI)

(CLXVI)

(CLXXVII)

(CLXXVIII)

VII. Various Systems

In addition to the fluorescent aromatic, heterocyclic, and mixed condensation systems described in Sections II to VI and investigated thoroughly for the discovery of fluorescent brightening agents, compounds from other fluorescent systems have also been suggested for application as optical brighteners.

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[395] W. H. Mills, *J. Chem. Soc.* pp. 121 and 456 (1922).

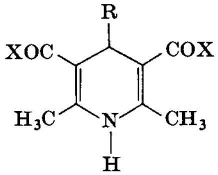
[396] Gy, *BeP* 710,261.

[397] Ilford, *BP* 461,668.

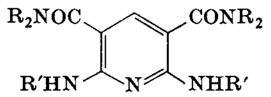
[398] Ilford, *BP* 447,038; 447,109.

[399] BASF, *SP* 419,133; *DBP* 1,144,280; see also method of preparation described by H. Balli, *Ann. Chem.* **647**, 14 and 17 (1961).

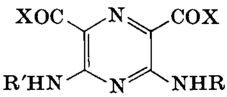
Among the aromatic systems, these include substitution products of anthracene,[404] 9-cyanoanthracene,[405] 2,9,10-trichloroanthracene,[406] and substitution products of pyrene (see Section VII,A), as well as substitution products of hydroquinone dimethyl ether.[407] With the exception of the pyrazolines substituted in the 1-, 3-, and 5-positions by aromatic groups (see Section IV), the wholly or partly unsaturated heterocyclic systems have remained without interest. Among these are the dihydropyridine dicarboxylic acid derivatives (CLXXIX),[408] diaminopyridine dicarboxylic amides (CLXXX),[409] and diaminopyrazine dicarboxylic acid derivatives (CLXXXI),[410] as well as aryl azoles (CLXXXII),[411] 4,5-diarylimidazolones (Section VII,B), diazoles (CLXXXIII),[412] diarylthiophene compounds (CLXXXIV),[413] and diarylfuran compounds



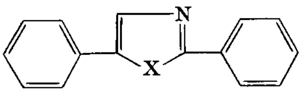
(CLXXIX)



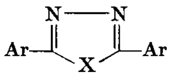
(CLXXX)



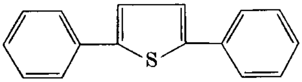
(CLXXXI)



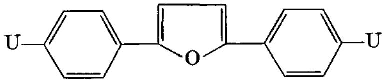
(CLXXXII)



(CLXXXIII)



(CLXXXIV)



(CLXXXV)

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[400] W. H. Mills, *J. Chem. Soc.* pp. 121 and 461 (1922).

[401] R. Kuhn and W. Winterstein, *BP* 328,357.

[402] IG, *BP* 380,702; 423,793.

[403] N. I. Fisher and F. M. Hamer, *J. Chem. Soc.* p. 963 (1934).

[404] The strong fluorescence of the amino- and hydroxy-substituted naphthalinesulfonic acids cannot be utilized for fluorescent brightening (see, however, Lever Brothers, *USP* 2,424,778).

[405] FH, *BeP* 667,090; *FP* 1,441,101.

[406] FH, *FP* 1,162,828.

[407] FH, *SP* 13,047/61.

[408] LBH, *DBP* 849,986; BFy, *FP* 1,113,543.

[409] Gy, *BeP* 609,184.

[410] Gy, *DBP* 1,087,609; 1,102,695.

[411] CFM, *DBP* 869,490, 926,249; *USP* 2,726,246; *BP* 734,981; FH, *DBP* 1,109,690.

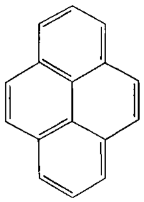
[412] CIBA, *DBP* 932,184.

[413] National Distillers & Chemical Corp., *USP* 3,089,848.

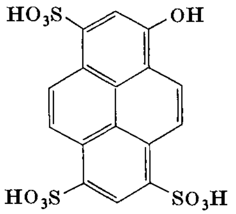
substituted by auxochromes (CLXXXV).[414] Among the aromatic condensed heterocyclic systems, the aryloazoles (Sections II,A,2; II,B,3,*b*; III,A,4; and VI) have considerable importance; and only the pyrazoloquinolines (Section VII,C), dibenzothiophene dioxides substituted in the 2- and 7-position (Section VII,D), and 2-phenylbenzothiophene dioxide[415] possess valuable fluorescence properties for optical brightening effects.

A. PYRENES

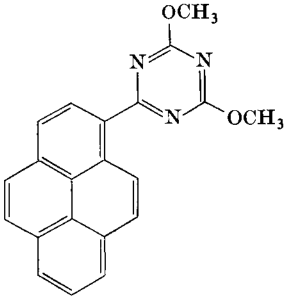
Pyrene (CLXXXVI) is the only hydrocarbon among the polycondensed aromatics from which unusual fluorescent effects can be produced by monosubstitution with auxochromic groups (NH_2, OH). As Tietze and Bayer[416] discovered, 1-hydroxypyrene-3,6,8-trisulfonic acid (pyranine) (CLXXXVII), obtained from pyrene-1,3,6,8-tetrasulfonic acid with alkali, is a greenish luminous substance with a high fluorescence strength.[417]



(CLXXXVI)



(CLXXXVII)



(CLXXXVIII)

The Friedel-Crafts reaction of pyrene with 2,4-dimethoxychlorotriazine, even at room temperature, yields 2-pyrenyl-(1)-4,6-dimethoxy-1,3,5-triazine (CLXXXVIII), which is notable for a strong blue fluorescence. It is an extremely stable pyrene compound which finds application as a fluorescent brightening agent for polyester fibers.[418]

B. *4,5*-DIARYLIMIDAZOLONES

During World War II, IG marketed Blankophor WT as a fluorescent brightening agent for wool and silk. In contrast the triazinylaminostilbenedisulfonic acid fluorescent brightening agents, Blankophor B, and

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[414] CCC, *USP* 2,853,503.

[415] FBy, *DBP* 1,063,571.

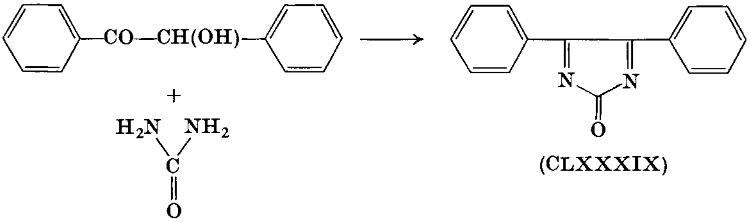
[416] E. Tietze and O. Bayer, *Ann. Chem.* **540**, 189 (1939); see also IG, *DRP* 620,635.

[417] "Ullmann," Vol. 11, p. 690.

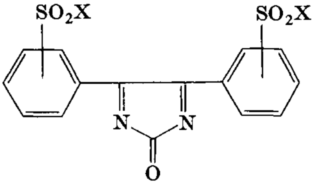
[418] ICI, *BeP* 625,678.

Blankophor R obtained from DAS and phenylisocyanate,[419] Blankophor WT showed a marked affinity for polyamides. IG had thus introduced the first range of fluorescent brightening agents on which the new method of optical brightening was based.

Blankophor WT is the sulfonation product (CXC)[420] of 4,5-diphenylimidazolone (CLXXXIX) which is obtained by condensation of benzoin with urea in boiling glacial acetic acid.[421]



(CLXXXIX)



(CXC) $X = OH$

(CXCI) $X = NR_2$

Since the fluorescent brightening of wool is less important because of the yellow discoloration of wool by photosensitization, while the fluorescent brightening of synthetic polyamides can be carried out with higher white effects and better coloristic properties with products of other groups, from the pyrazoline range (Section IV) for example, Blankophor WT (Ultraphor WT) is now more of historical interest. Moreover, the mono- and dicyclohexylamine salts of the disulfonic acid (CXC)[422] and the amides (CXCI)[423] are without significant practical importance.

C. Pyrazoloquinolines

Among the condensed heterocyclic systems, the pyrazolo[3,4-*b*] quinoline compounds (CXCV)[424] possess interesting coloristic properties as fluorescent brightening agents for textiles made from polyester and

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[419] See *CSD I*, p. 636.

[420] IG, *DRP* 735,468.

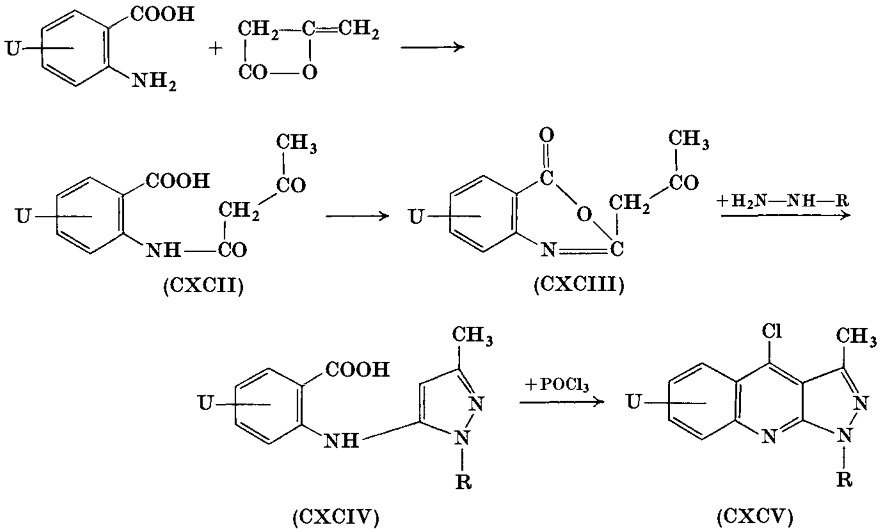
[421] *Org. Syn.* **12**, 34 (1932).

[422] G, *USP* 2,709,702.

[423] G, *USP* 2,691,653.

[424] FBy, *FP* 1,357,445; *DBP* 1,222,885.

from cellulose acetates. They are produced in a simple manner by treatment of the *o*-carboxyphenylaminopyrazoles (CXCIV) with chlorinating and condensing agents ($POCl_3$, $COCl_2$, $SOCl_2$, PCl_5). The pyrazoles (CXCIV) themselves are obtained from the oxazinones (CXCIII), which are produced from the *o*-carboxyarylides of acetoacetic acid (CXCII) with dehydrating agents, e.g., acetic anhydride.[425]



(CXCII) (CXCIII)

(CXCIV) (CXCV)

D. DIBENZOTHIOPHENE DIOXIDES. DERIVATIVES OF BENZIDINE SULFONE

The insufficient hypochlorite resistance of the fluorescent brightening agents from the group of 4,4'-acylaminostilbene-2,2'-disulfonic acids (Sections II,B,2,*a* and *b*) led to the development of *N*,*N'*-bisacyl derivatives of 3,7-diaminodibenzothiophene-dioxide-2,8-disulfonic acid (benzidinesulfone–disulfonic acid BSDS) (CXCVI).[426] In a similar manner to DAS, this diamino disulfonic acid is a long-known azo dyestuff intermediate which is obtained in sulfonation reactions of benzidine[427] or by sulfonation of benzidinesulfonic acid,[428] and is best isolated as the triethylamine salt.[429] Among the acyl derivatives of BSDS, the *N*,*N'*-bis(*p*-methoxybenzoyl) derivative (CXCVII) has aroused technical inter-

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[425] FBy, *BP* 925,566.

[426] "Ullmann," Vol. 16, p. 537.

[427] See also CCC, *DBP* 899,200.

[428] G, *USP* 3,031,460.

[429] CCC, *USP* 2,590,632.

est (Calcofluor White 5B).[430] The salts of *N*,*N'*-bis(*p*-phenylbenzoyl)-BSDS[431] have gained importance as fluorescent brightening agents because of their higher and redder fluorescent effects.

The acyl derivatives are given preference in detergent mixtures as chlorine-resistant fluorescent brightening agents for cotton textiles and for the optical brightening of nylon.[432] The acylation of BSDS with 4-methoxybenzoyl chloride proceeds much less smoothly than the acylation of DAS. The complete acylation can be carried out only in pyridine or by the use of a trialkylammonium salt of BSDS in a nonpolar solvent.[433]

Like the compounds produced from DAS, the *N*,*N'*-triazinyl derivatives of BSDS,[434] e.g., (CXCVIII) (see Section II,B,2,*b*), and the bis-(arylotriazolyl)dibenzothiophene dioxide compounds,[435] e.g., (CIC) (Section II,B,2,*b*), are also fluorescent brightening agents. Because of the more difficult acylation of BSDS, fluorescent brightening agents of the (CXCVIII) type cannot be obtained by reaction with cyanuric chloride. The Ciba method[434] of reacting the bis-triazinylaminodiphenyl compounds (CC) with oleum corresponds to the method of producing BSDS from benzidine[426] and utilizes the smoother acylation of benzidine-disulfonic acid with cyanuric chloride.

These compounds have not, however, attained the commercial importance of the fluorescent brightening agents of the DAS range.

VIII. Application of Fluorescent Brightening Agents

For the application of the usual types of dilute formulations available on the market, determination of the fluorescent brightener concentration is important. Since the titrimetric methods used in chemistry are not always possible,[436] optical methods of determining the concentrations are often given preference.

A simple, though inexact, method which is often used is the visual comparison of the fluorescence strength of the solution of a fluorescent brightening agent under a dark-field UV lamp with a known concentration series of the optical brightener to be measured. The evaluation is

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[430] CCC, *USP* 2,563,492; 2,563,795; 2,702,759; *DBP* 936,386. G, *USP* 2,911,415.

[431] CCC, *USP* 3,226,247.

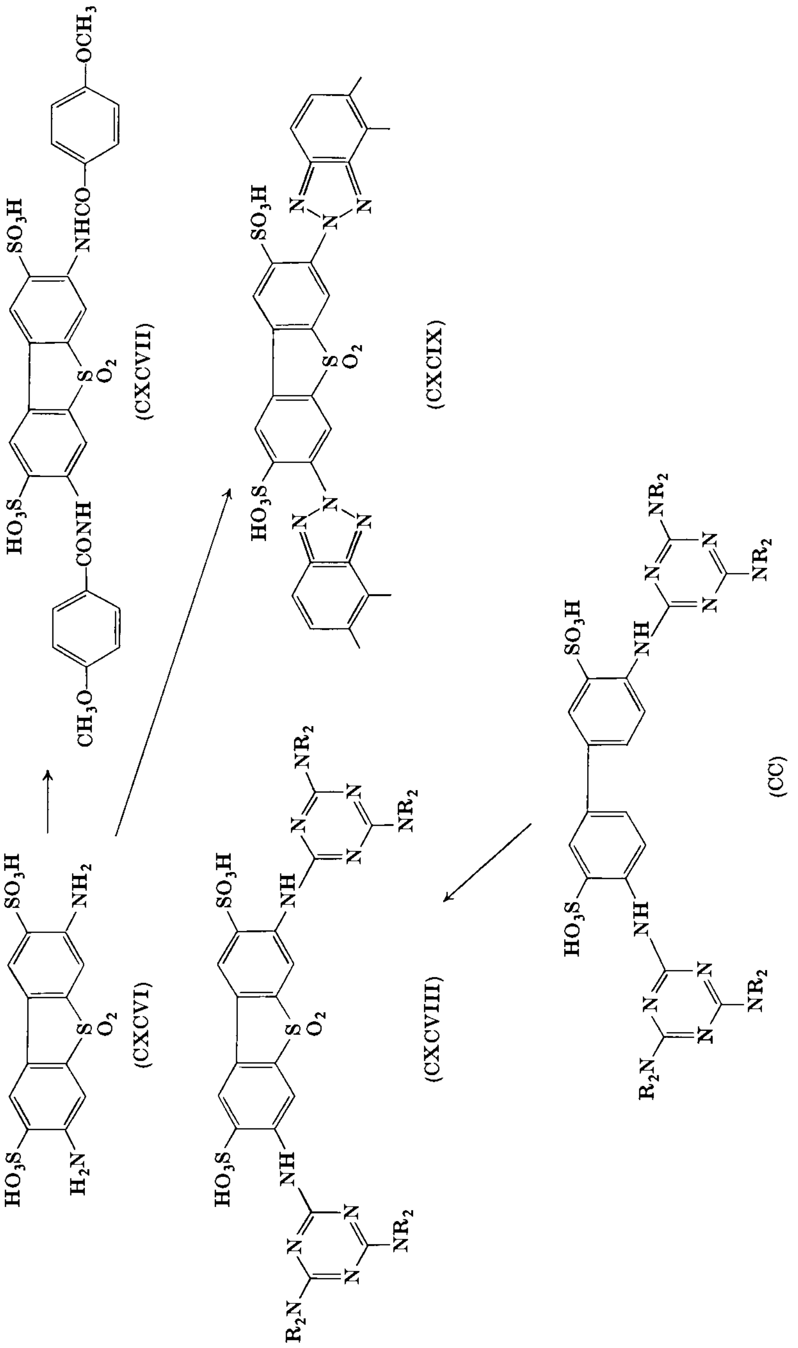
[432] Pro-Nyl Chemicals, *USP* 2,619,470.

[433] CCC, *USP* 2,573,652.

[434] CIBA, *DBP* 949,741; *USP* 2,719,155.

[435] G, *USP* 2,733,165.

[436] See, for example, titration with cetylpyridinium chloride [M. Ernste and J. S. P. Blumberger, *Chem. Weekblad* **63**, 545 (1967)] or with $KMnO_4$ [F. Navratil and M. Matrka, *Chem. Prumysl* **13**, 415 (1967); *CA* **60**, 711g (1964)].



(CXCVI)

(CXCVII)

(CXCVIII)

(CXCIX)

(CC)

facilitated and the accuracy improved by spotting the solutions to be compared onto paper and then assessing their fluorescence strength visually under the lamp. Although the fluorescence strength of solutions of fluorescent brightening agents can also be measured with a spectrophotometer, this method has little practical importance because of the poorer consistency of the measured values.

The highest accuracy in the determination of the brightener concentration of a solution is shown by measurement of the extinction at the UV absorption maximum ($\lambda_{\max}$), using a spectrophotometer. For the dependence of the measured extinction (E) on the concentration of the fluorescent brightening agent, the Lambert-Beer law is applicable in wide limits (0.01–1 g/liter):

$$E = \log I/I_0 = Kcd$$

In a concentration (c) of 1% and a layer thickness (d) of 1 cm, K is the specific extinction constant $E^{1\%}_{1\,\mathrm{cm}}$, which can be calculated from any given measurement. Once $E^{1\%}_{1\,\mathrm{cm}}$ has been measured and established for any given fluorescent brightener, the percent content ($c = \mathrm{g}/100$ ml) of the solution of the fluorescent brightening agent can be ascertained inversely.

To measure the extinction (E), a given quantity (V) of the fluorescent brightener solution is diluted to a volume (V_1) in such a manner that for the layer thickness (d) a measured value of 0.2–0.8 is ascertained. In this case,

$$c = (EV_1)/(E^{1\%}_{1\,\mathrm{cm}}\,Vd)$$

Because of the sensitivity to light of dilute solutions of fluorescent brightening agents, these measurements must be carried out with special care. Instead of an absorption measurement at the UV absorption maximum, measurement at the isosbestic points (see Fig. 13) has also been proposed to determine concentration.[437] This method is less influenced by the sensitivity to light of the solutions to be measured.

In accordance with their effect as "white dyes" (see Section I,A), fluorescent brightening agents are applied by well-known dyeing methods.[438] Substrates to which they are applied include natural fibers (cotton, wool, silk, hair), semisynthetic fibers (from viscose, 2½ acetate, and triacetate), fully synthetic fibers (from polyamides, polyurethanes, polyacrylonitrile, and also copolymers with vinyl chloride and vinyl acetate, polypropylene, and polyester), paper, plastic compositions, and surface coatings.[439]

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[437] V. G. Bocharov and A. F. Penkina, *Zavodsk. Lab.* **28**, 1454 (1962); *CA* **59**, 9470g (1963).

[438] *CSD I*, p. 268.

[439] P. S. Stensby, *Chem. Spec.* **43**, April 41 (1967).

In a similar manner to "colored dyes," fluorescent brightening agents can also be classified according to their dyeing behavior as direct (substantive) cotton brighteners, acid brighteners, basic and cationic brighteners, and dispersed brighteners.[440] Table XXXIII relates a selection of the most important fluorescent brighteners described in Sections II to VII to the substrates and also to the methods of application.

Most of the fluorescent brightening agents applied to cotton are bistriazinyl derivatives of 4,4′-diaminostilbene-2,2′-disulfonic acid (Section II,B,2,*b*). These are all substantive brighteners which are also used for the optical brightening of paper (in the dip process and in the pulp) and of regenerated cellulose (viscose). DAS brighteners, particularly CC/DAS products, can also be used from acid baths for wool and silk. Preference is, however, given to acid brighteners (containing SO_3H groups) which show little or no affinity for cotton, or to basic brighteners (containing amino groups) from the range of coumarin or pyrazoline compounds. Because of the poor fastness to light of the fluorescent brightening effect and the photosensitization of wool by optical brighteners, the fluorescent brightening of wool is less usual than that of cellulosic materials.

For $2\frac{1}{2}$ acetate and triacetate, those dispersed brighteners are generally selected which possess a good solubility in carboxylates. The structures of the typical optical brighteners for synthetic polyamides correspond in principle to those used for the fluorescent brightening of wool. They are mainly the acid, less substantive types from the stilbenesulfonic acid and 1,3-diphenylpyrazoline ranges and basic brighteners from the range of coumarin compounds, as well as optical brighteners with a marked affinity from neutral baths. The optical brightening of fibers made from polyacrylonitrile and copolymers of acrylonitrile with vinyl chloride and vinyl acetate is carried out with dispersed and basic fluorescent brightening agents, particularly with cationic brighteners of all types of constitution free from SO_3H groups. The technically important and interesting optical brightening of fibers made from polyester is carried out with dispersed brightening agents of all fluorescence systems with the exception of 1,3-diphenylpyrazolines. The difficulty of staining polyester fiber is overcome mainly by an improvement of the dispersion and by the use of carriers or high-temperature methods (100–250°).[441]

Plastics and surface-coating materials can be whitened only with fluorescent brightening agents which are sufficiently soluble in these products under the conditions of incorporation.

In addition to the stated application as white dyes, fluorescent

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[440] *CSD I*, p. 268.

[441] H. Hefti, *Textilveredlung* 4, 94 (1969).

brightening agents are also widely used in combination with crease-proofing, washing, and dry-cleaning processes. In the textile industries greater efforts are continually being made to adapt the conditions of application of fluorescent brightening agents to bleaching technology and processing methods in such a manner that a separate operation for optical brightening is no longer required. For this reason, the combination with detergents,[442] aftertreating agents (softeners),[442] dry-cleaning and crease-resist agents[443] is a further application for fluorescent brighteners. Table XXXIV assigns a selection of optical brightening agents described in Sections II to VII to the stated applications.

IX. Evaluation of the Fluorescent Brightening Effects

An evaluation based on a visual comparison is the usual method of assessing materials brightened with fluorescent brightening agents. After several changes of place of the patterns to be compared in a concentration series, the eye of an experienced viewer can detect very slight differences in whiteness and shade (redder, greener). The usual coloristic data regarding the "maximum white" or the "graying limit" can also be determined in this way. It is nevertheless impossible to establish a definite connection between the strength of the brightening effect and the brightener concentration on the substrate, or to guarantee the degree of whiteness and color impression of an optical brightening effect.[444, 444a] To permit reliable information on a definite white, "white scales" have been introduced.[445] These consist of a concentration series of brightened materials (paper, cotton, wool, polyamide 6, polyamide 6,6, polyester fiber) produced by objective methods of determination in which the white graduations are approximately equal. The notes or units allocated to the steps correspond to the relative fluorescence strengths.[444a] Figure 15 represents the white scales A for a CC/DAS fluorescent brightening agent of the bis-carboxyamino stilbene group (Section II,B,1,*b*) on cotton, and B for a benzoazolyl brightener derived from a dicarboxylic acid (Section VI,C) on polyester fiber. The fluorescent

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[442] P. S. Stensby, *Soap Chem. Specialties* **43**, August 98 and September 132 (1967).

[443] See, for example, R. M. Reinhardt, Y. W. Fenner, J. D. Reid, M. S. Furry, and M. Walsh, *Am. Dyestuff Reptr.* **51**, 34 (1961); W. Schifferle and R. Keller, *SVF* (*Schweiz. Ver. Faerbereifachleuten*) *Fachorgan Textilveredlung* **17**, 193 (1962); H. Mantz, "Färbereikalender." Franz Eder Verlag, Stuttgart, 1969.

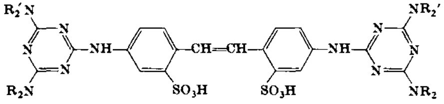
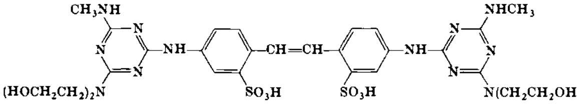
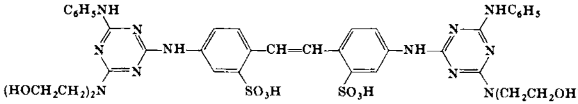
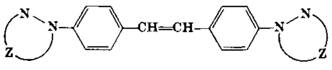
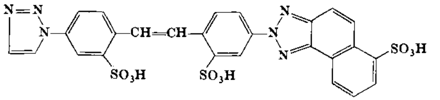
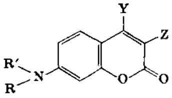
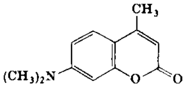
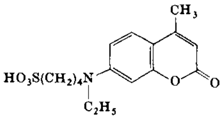
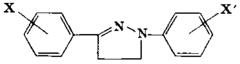
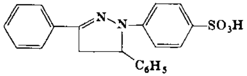
[444] S. V. Vaeck, *Textilveredlung* **2**, 725 (1967).

[444a] S. V. Vaeck and F. van Lierde, *Waeschereitech. Chem.* **17**, 26 (1964).

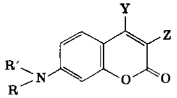
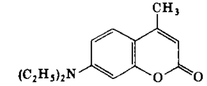
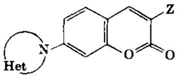
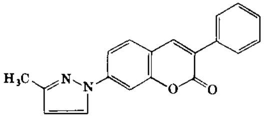
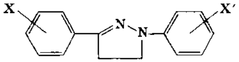
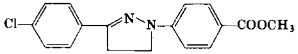
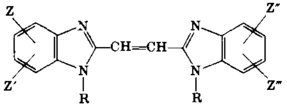
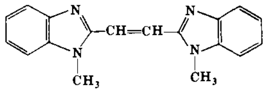
[445] J. Lanter, *Ciba-Rundschau* **13**, 26 (1960); *SVF* (*Schweiz. Ver. Faerbereifachleuten*) *Fachorgan Textilveredlung* **19**, 469 (1964); R. Keller, *ibid.*, p. 480.

TABLE XXXIII

Substrates and Methods of Application of Fluorescent Brighteners

Method of application	*Typical structure*	*Section*	*Example*
	Natural Fiber Materials: (a) Cotton		
0.05–0.60% in the exhaustion process (20–95°) 1–3 g/liter in the padding process		II,B,1,b	
0.05–0.50% in the exhaustion process (70–95°)	—	II,B,1,b	
0.05–0.40% in the exhaustion process in the presence of active chlorine		II,B,2,b	
	Natural Fiber Materials: (b) Wool, Silk, Hair (see also polyamide fibers)		
After H_2O_2 bleach 0.1–1.0% in the presence of 2–4 g/liter dithionite or		III,A,2	 
in combination with the H_2O_2 bleach in the presence of acids		IV	

Semisynthetic Fiber Materials: (a) Viscose (see cotton); (b) Acetate and Triacetate

0.5–1.0% at 60–80° or at the boil from neutral to slightly acidic baths (pH 3–5) in the exhaustion and continuous processes with subsequent treatment in hot air (heat fixation)		III,A,2	
		III,A,4	
		IV	
		VI,C	

Fully Synthetic Fibers: (a) Polyamide Fibers (Nylon 6, Nylon 66, Polyurethane Fibers)

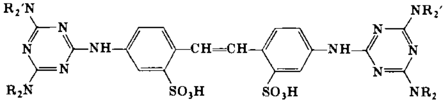
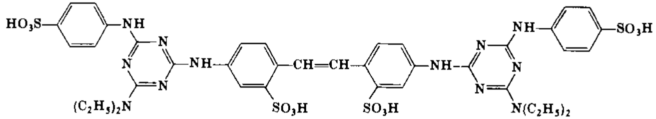
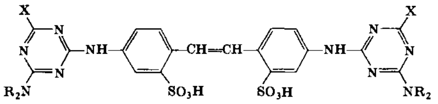
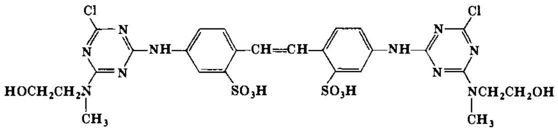
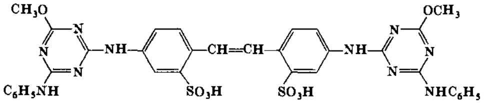
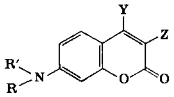
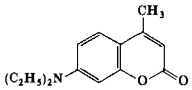
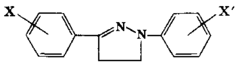
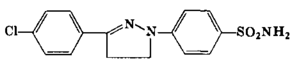
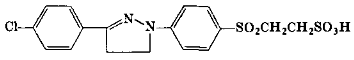
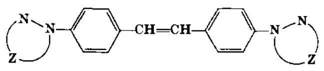
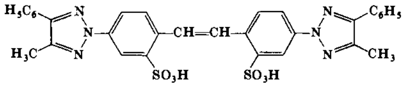
0.5–1.5% at 60–130° in the presence of sodium dithionite or from slightly acidic baths. May be used in HT plants		II,B,2,b	

TABLE XXXIII (*continued*)

Method of application	*Typical structure*	*Section*	*Example*
		II,B,1,b	 
0.1–1.0% from acid and alkaline baths		III,A,2	
		IV	 
In combination with chlorite bleaching		II,B,2,b	

Fully Synthetic Fibers: (b) Polyacrylnitrile (Dralon, Orlon, Exlan, Acrilan)

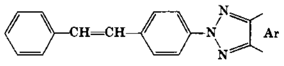
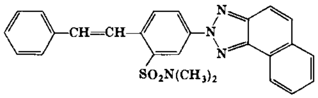
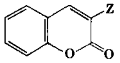
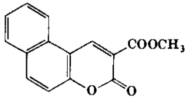
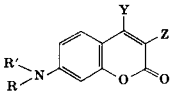
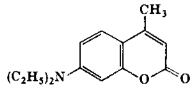
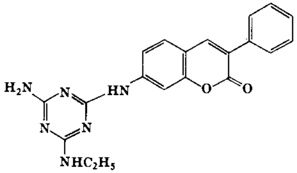
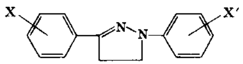
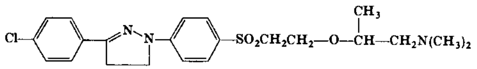
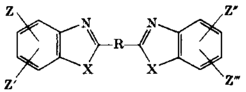
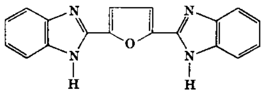
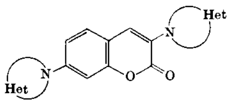
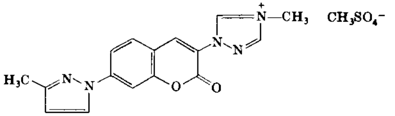
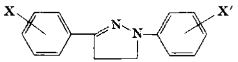
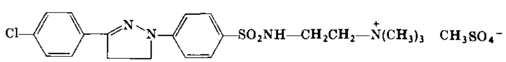
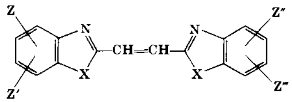
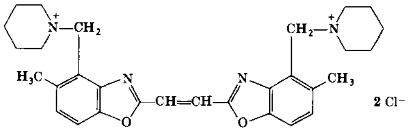
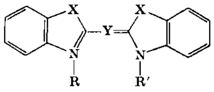
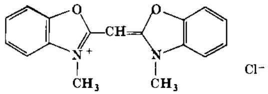
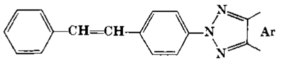
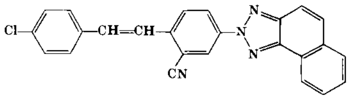
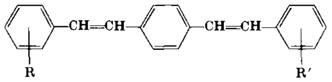
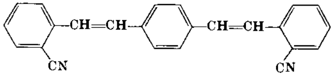
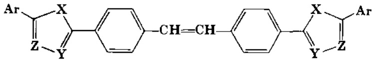
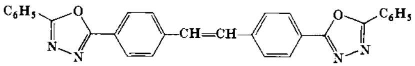
0.05–1% from slightly acidic, boiling baths		II,A,2	
		III,A,1	
		III,A,2	
			
		IV	
		VI,B	

TABLE XXXIII (*continued*)

Method of application	*Typical structure*	*Section*	*Example*
0.05–0.5% from slightly acidic, boiling baths		III,A,4	
		IV	
		VI,C	
		VI,D	
		Fully Synthetic Fibers: (c) Polyester Fibers	
0.2–2.0% from slightly acidic, boiling baths in exhaustion process		II,A,2	
		II,A,3	
		II,B,2,a	

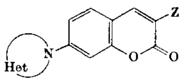
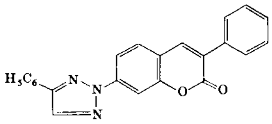
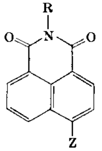
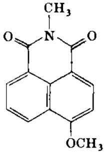
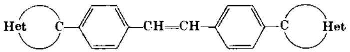
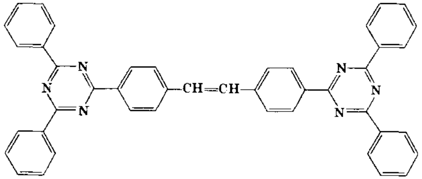
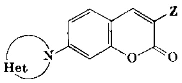
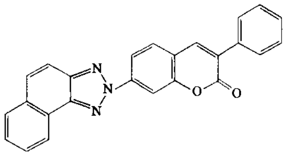
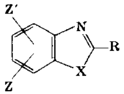
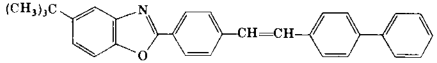
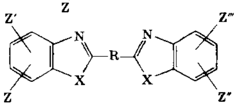
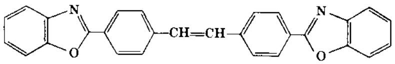
From finely dispersed baths by the HT process, heat fixation method or pad/heat fixation method (120–200°)		III,A,4	
		V	
Incorporation in polyester spinning compositions		II,B,2,a	
		III,A,4	
		VI,A	
		VI,B	

TABLE XXXIII (*continued*)

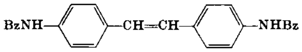
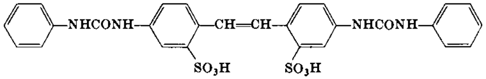
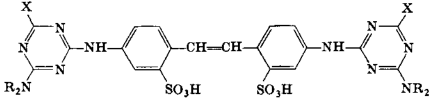
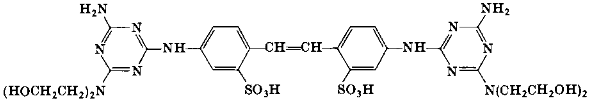
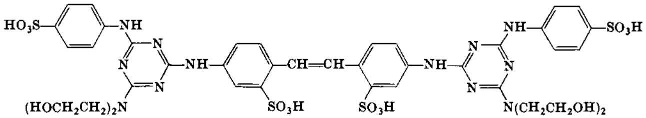
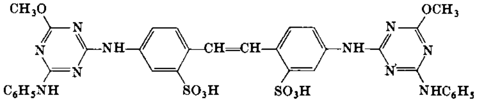
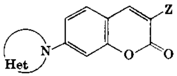
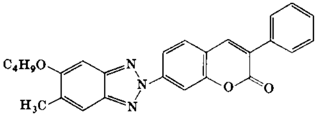
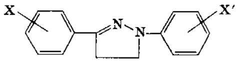
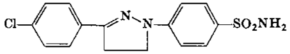
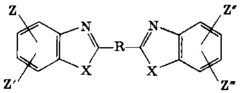
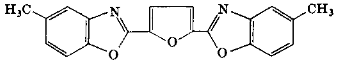
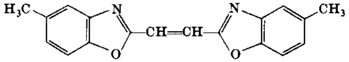
Method of application	*Typical structure*	*Section*	*Example*
Paper		II,B,2,a	
In the dip process, in the pulp, in the surface treatment		II,B,2,b	  
Plastics			
		III,A,4	
		IV	
		VI,C	 

TABLE XXXIV

FLUORESCENT BRIGHTENERS IN COMBINATION PRODUCTS

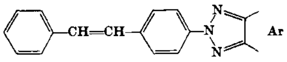
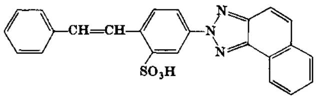
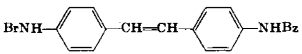
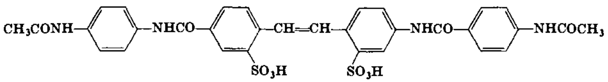
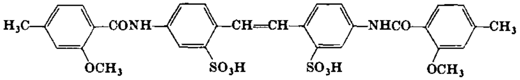
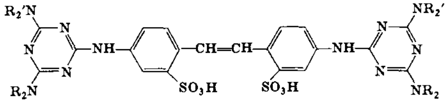
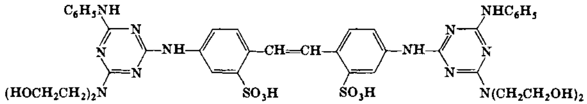
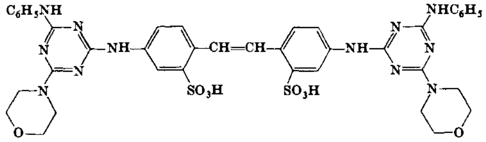
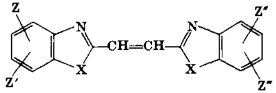
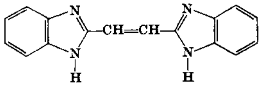
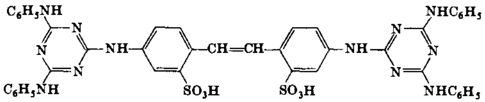
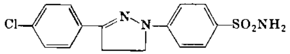
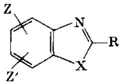
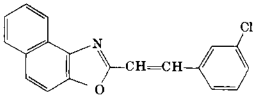
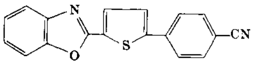
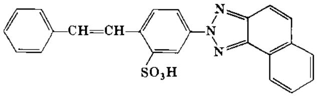
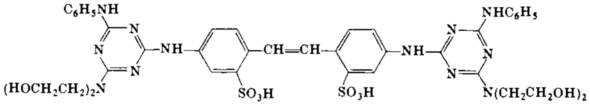
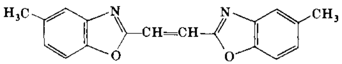
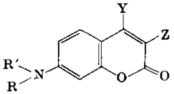
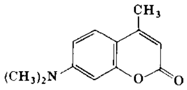
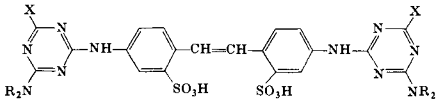
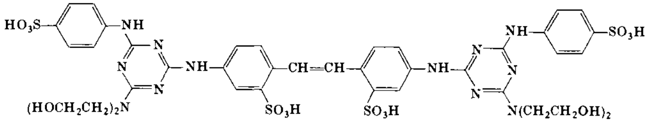
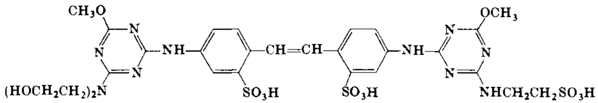
Application		*Section*	*Example*
In detergent mixtures for cotton textiles		II,A,2	
		II,B,1,a	
			
		II,B,1,b	
			
		VI,C,1	
In detergent mixtures for cotton and polyamide textiles	—	II,B,1,b	

TABLE XXXIV (*continued*)

Application		*Section*	*Example*
In detergent mixtures for polyamide textiles	—	IV	
In detergent mixtures for polyester textiles		VI,B	 
For detergents containing active chlorine with polyamide effect	—	II,A,2	
For aftertreating agents (softeners)	—	II,B,1,b	
	—	VI,C,1	
For dry cleaning		III,A,2	
For creaseproofing: Dry condensation and dry cross-linking processes Acid and alkaline wet cross-linking		II,B,1,b	
Moist cross-linking			

brightening effect of an unknown pattern obtained with one of the above-mentioned optical brighteners can be defined by a numerical value, or note, on comparison with the corresponding white scale.

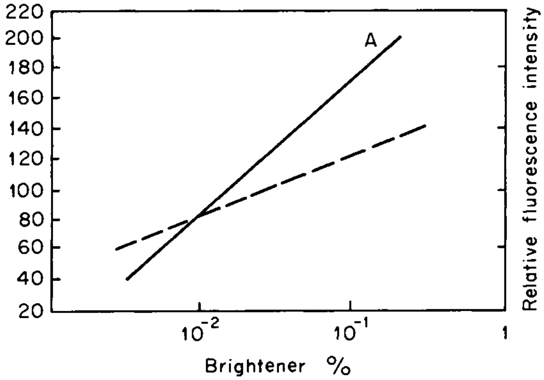


FIG. 15. White scales.

In the lightfast white scale produced from Cibanoid plastic composition,[446] an attempt has been made to simplify the notation of the white graduations. It is divided into 12 steps, which differ by 20 units in each case. The scale is based on the coloration of magnesium oxide, to which a note of 100 is given (see Table XXXV).

TABLE XXXV

CIBA WHITE SCALE

Grade	1	2	3	4	5	6	7	8	9	10	11	12
Note	10	30	50	70	90	110	130	150	170	190	210	230

Steps 1–4 contain diminishing amounts of a yellow pigment, step 5 contains neither dye nor brightener, and steps 6–12 contain a lightfast brightener. This scale has the disadvantage of not containing a peak white, such as that attained on polyamide and polyester, but is nevertheless an evaluation scale of practical importance for industrial practice.

A. DETERMINATION OF THE DEGREE OF WHITENESS

The reflectance curve of an optically brightened substrate measured with a spectrophotometer renders determination of the degree of whiteness independent of comparative tests, white scales, and the evaluation

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[446] G. Anders, *Textilveredlung* **3**, 116 (1968).

of brighteness, shade, and saturation differences. To assign to the degree of whiteness reliable numerical values which take account of the physiological and psychological factors, whiteness formulas have been established by various researchers,[447, 448] that of Berger now being in general use.[448]

The optically brightened test pieces are measured in a tristimulus filter photometer,[449] using an illumination similar to daylight (standard source C = average daylight) or a xenon high-pressure lamp.[450] From the measured values R_x, R_y, and R_z, the degree of whiteness (W) is calculated according to the Berger whiteness formula

$$W = R_y + 3(R_z - R_x)$$

Owing to the simplicity of the calculation, this formula is suitable for the identification of fluorescent brightening agents.

The whiteness of textile test pieces can also be expressed as the "whitening effect" (wf) after measurement with a color difference testing apparatus according to Hunter[451] to determine the L.a.b. value:

$$wf = (\varDelta a^2 + \varDelta b^2)^{1/2}$$

The values correspond to the National Bureau of Standards units.

An evaluation of the fastness properties[452] according to the standards and recommendations of the standards committees (Fastness Convention for the Continent of Europe, ECE) has not yet been possible and various procedures are therefore adopted. The evaluation is based on practical considerations and therefore depends mainly on the concentration of the fluorescent brightening agent applied to the substrate. Instead of the "depth of shade of the standard types" used in dyeing, the highest attainable brightening effect is selected as "white standard type depth" for the evaluation of the fastness properties of applied fluorescent brightening agents.

X. Analysis of Fluorescent Brightening Agents

As in the case of dyestuffs, the presence of fluorescent brightening agents in substance, in combination with other agents, or on a substrate

[447] D. L. McAdam, *Tappi* **38**, 78 (1955); R. Hunter, *J. Opt. Soc. Am.* **48**, 597 (1958); *Am. Dyestuff Reptr.* **50**, 45 (1961); D. B. Judd and G. Wyszecke, "Color in Business, Science and Industry." Wiley, New York, 1965; S. V. Vaeck and F. van Lierde, *Ann. Sci. Textiles Belges* p. 7 (1964); *Waeschereitech. Chem.* **18**, 155 (1965).

[448] A. Berger, "Die Farbe," Vol. 8, 195 1959.

[449] Electric reflectance photometer (Elrepho) of Messrs. Zeiss.

[450] *CSD I*, p. 306.

[451] R. S. Hunter, *USP* 2,574,264; P. S. Stensby, *Soap Chem. Specialties* **43**, May 84 (1967).

[452] H. Heuberger, *Textilveredlung* **4**, 101 (1969).

can be recognized from the external appearance. Under a UV dark-field lamp, it is manifested clearly by a blue-green or blue fluorescent light. For the analytical determination of fluorescent brightening agents several dependable tests are available, based on coloristic, physical, and chemical methods.

The fluorescent brightening agents to be expected in the analysis of about 1200 commercial products have been described in Sections II to VII with the aid of constitutional features, in Section VIII from coloristic standpoints in technical application, and in Section IX from the standpoint of their optical behavior. Coloristic tests carried out on a fluorescent brightening agent of unknown constitution may provide valuable information regarding its structure. The optical behavior described in Section IX is, however, of such a general nature in fluorescent brightening agents that it is of lesser importance for analytical purposes. On the other hand, IR, NMR, and mass spectra, generally combined with the results of chemical and chromatographic methods, provide unequivocal evidence for the assignment of a constitution.

Selection of the analytical methods depends upon the availability of a sufficiently large sample in substance, which after freeing from diluents and purifying can be subjected to chemical or spectroscopic methods, or upon whether only a sample of material treated with a fluorescent brightening agent, or a detergent containing a brightener is available. In a commercial fluorescent brightening agent (powder, dispersion, solution), the test for solubility in water or in organic solvents gives the first indication whether the active substance contains sulfonic acid groups or quaternary ammonium groups. After isolation of the active substances, the melting point, elementary analysis [C, H, N, O, S(Cl)], the resulting atomic ratio and the molecular weight, and also the evaluation of IR, NMR, and mass spectra are the main indications of the chemical constitution.

In 35–40% of the fluorescent brightening agents on the market, compounds of the CC/DAS type of brightener (Section II,B,1,*b*) may be expected. The analysis of the DAS fluorescent brightening agents by chemical methods is therefore particularly important, the more so because spectroscopic examination furnishes less evidence than can be obtained by simple chemical methods.

Where the fluorescent brightening agent is to be determined on a substrate brightened with it, chromatography should then be preferred to any other analytical method since in this way exact information can be obtained by simple means. The very small amounts of substance (2–5 micrograms) required for this purpose can be extracted with pyridine–water (1:1) or with glycol monomethyl ether–ammonia (7:3) from only 0.5 g of a textile or paper test piece, or with cold methanol from a detergent.

In all analyses, control substances must be available for an exact determination of constitution. Among the fluorescent brightening agents used in industry, 160–180 active substances defined by their constitution may be expected and are distributed among the groups of compounds discussed in the preceding sections of this chapter as follows:

II,A,2	7	III,A	28
II,A,3	3	II,B	2
II,B,1,*a*	6	IV	16
II,B,1,*b*	58	V	3
II,B,2,*a*	6	VI	22
II,B,2,*b*	3	VII	10

In the case of new, unknown fluorescent brightening agents, comparable substances should be synthesized on the basis of indications obtained in various tests. The constitution of such optical brighteners may be considered certain when matching results are achieved in coloristic, chemical (e.g., mixed melting point), spectroscopic, and chromotographic tests.

A. Coloristic Methods

Determination of the substrates which are suitable for the fluorescent brightening agent to be analyzed (Section VIII) and answers to questions about the dyeing properties, such as *affinity* for various fiber types[453] (cotton, polyamide, cellulose acetate, polyester, polyolefins, polyacrylonitrile) depending on pH value, temperature, and salt content of the dyebath, and *fastness properties*, particularly the fastness to bleaching, limit the constitution possibilities considerably.

In the case of optically brightened textiles, the spot reactions proposed by Schlachter[454] with sulfuric acid, hydrochloric acid, caustic soda, sodium hypochlorite, and nitrous acid may give additional information on the type of compound.[455]

B. Chromatographic Method

During the last ten years, chromatography has gained in importance as a widely used and time-saving method in the analytical determination of fluorescent brightening agents. The methods and techniques have

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[453] K. Kindner, "Textilhilfsmittel und Waschrohstoffe," p. 641. Wiss. Verlagsges., Stuttgart, 1965.

[454] F. Schlachter, *Fette, Seifen, Anstrichmittel* **56**, 9 (1954).

[455] P. S. Stensby, *Soap Chem. Spec.* **43**, August 97 (1967).

been developed, in particular, by Sayato,[456] Meckel,[457] Thiedel,[458] Latinak,[459] and Gasparic.[460] Comparative chromatography with known control products leads to unequivocal and dependable determinations when carried out by the most diverse systems (carrier + flow-promoting agent).[458] Well-tried and established systems are summarized in Table XXXVI.[462]

TABLE XXXVI

CHROMATOGRAPHY SYSTEMS FOR FLUORESCENT BRIGHTENERS

Carriers	*Flow-promoting agents* (vol. parts)
Paper 2045 a S & S[a] (partly siliconized)	DMF, *n*-butanol, methanol, ammonia, water (35:50:10:5:20)
Paper 2043 b S & S	Butyl acetate, pyridine, water (30:40:30)
	Tetrahydrofuran, water (25:75)
Kieselgel G[b]	*n*-Hexanol, pyridine, acetic ester, methanol, ammonia (5:5:5:3:5)
	Benzene, chloroform (4:6)
	Methylene chloride
	Isoamyl acetate, methanol, acetone, ammonia (50:20:20:10)
Polyamide	Methanol, ammonia, water (10:4:1)
	Methanol, 6*N* HCl (10:2)

[a] Schleicher and Schüll, paper-mill, Düreu, Germany.

[b] Reference 462.

When in three systems using flow-promoting agents with various pH adjustments no differences in R_f value of the unknown fluorescent brightening agent can be ascertained in comparison with the control substance, there is no doubt that the substances are identical. Even slight differences in the structure of the amine, alcohol, or phenol components in CC/DAS fluorescent brightening agents and differences in the position of substituents are easily recognized when this method is used. The recognition of slight structural differences is also facilitated considerably by the clearly perceptible difference in the rate of migration of the cis and trans isomers of stilbene compounds and substances of similar structure.[458]

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[456] Y. Sayato, *J. Food Hyg. Soc. Japan* **2**, 56 (1961); *CA* **56**, 878d (1962).

[457] R. Meckel, *Textil-Praxis* **16**, 737 and 1032 (1961).

[458] H. Theidel, *Melliand Textilber.* **45**, 514 (1964); *J. Chromatog*, **27**, 413 (1967).

[459] J. Latinak, *J. Chromatog.* **14**, 482 (1964).

[460] J. Gasparic, *J. Chromatog.* **14**, 484 (1964).

[461] J. Kurz and M. Schuierer, *Fette, Seifen, Anstrichmittel* **69**, 24 (1967).

[462] E. Stahl, *Angew. Chem.* **73**, 646 (1961).

AUTHOR INDEX

Numbers in parentheses are reference numbers and indicate that an author's work is referred to, although his name is not cited in the text.

SUBJECT INDEX

Numbers in italics refer to *Colour Index* numbers and those following refer to pages in this volume.