CONTRIBUTORS

N. R. AYYANGAR
DONALD R. BAER
J. BAILEY
G. E. FICKEN
OSKAR GLENZ
HANS MEIER
KARL NEUFANG
B. D. TILAK
L. A. WILLIAMS

The Chemistry of
SYNTHETIC DYES

VOLUME IV

Edited by
K. VENKATARAMAN
National Chemical Laboratory
Poona, India

1971
ACADEMIC PRESS New York and London

ACADEMIC PRESS, INC.
111 Fifth Avenue, New York, New York 10003

United Kingdom Edition published by
ACADEMIC PRESS, INC. (LONDON) LTD.
Berkeley Square House, London W1X 6BA

LIBRARY OF CONGRESS CATALOG CARD NUMBER: 52-5201

PRINTED IN THE UNITED STATES OF AMERICA

LIST OF CONTRIBUTORS

Numbers in parentheses indicate the pages on which the authors' contributions begin.

N. R. Ayyangar (103), National Chemical Laboratory, Poona, India

Donald R. Baer (161), Jackson Laboratory, Organic Chemicals Department, E. I. DuPont de Nemours and Company, Wilmington, Delaware

J. Bailey (341), Research Laboratories, Kodak Limited, Wealdstone, Harrow, Middlesex, England

G. E. Ficken (211), Research Laboratories, Ilford Limited, Ilford, Essex, England

Oskar Glenz (1), Farbenfabriken Bayer AG, Anwendungstechnische Abteilung, D-509 Leverkusen, West Germany

Hans Meier (389), Staatliches Forschungsinstitut für Geochemie, Bamberg, West Germany

Karl Neufang (75), Farbenfabriken Bayer AG, Anwendungstechnische Abteilung, D-509 Leverkusen, West Germany

B. D. Tilak (103), National Chemical Laboratory, Poona, India

L. A. Williams (341), Research Laboratories, Kodak Limited, Wealdstone, Harrow, Middlesex, England

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 Mr. J. V. Rajan who has assisted me in all 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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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
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., AG., Biebrich a. Rhein, Germany
Kewanee	Keewanee 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, now 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
SP	Swiss Patent
USP	United States Patent

Chapter I

APPLICATION OF DYES BY DYEING

Oskar Glenz

FARBENFABRIKEN BAYER AG, ANWENDUNGSTECHNISCHE ABTEILUNG,
D-509 LEVERKUSEN, WEST GERMANY

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I. Textile Fibers

A. CELLULOSIC FIBERS

1. *Cotton*

Despite the enormous increase in the production of manmade fibers, cotton has remained the most used fiber for clothing textiles. With a world production of about 11,500,000 tons in 1969, cotton easily takes the lead over wool with a production of about 1,600,000 tons, and over regenerated cellulose fibers and manmade fibers with a production of about 8,070,000 tons.[1]

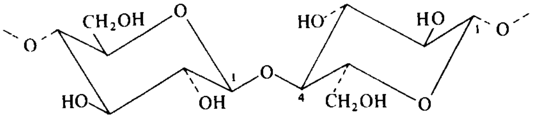
In addition to its use in 100% form, cotton is now being used on an increasing scale in blends with synthetic fibers. At present, the most usual blends are as follows: 30–80% cotton/70–20% polyester fiber; 50% cotton/50% polyacrylonitrile fiber; 80–90% cotton/20–10% polyamide. To a lesser extent, three-fiber mixtures consisting of cotton, polyester, and polyacrylonitrile fibers are also on the market. In all cases,

---

[1] *Kunststoffberater* **15**, 252 (1970).

cotton is esteemed in woven and knitted fabrics for clothing because of its high water absorption and moisture transfer.

Cotton consists of practically pure cellulose. The structure and configuration of the cellulose molecule is shown in formula (I). The formula



(I)

shows the constantly recurring cellobiose unit in the cellulose molecule, consisting of two glucose units each with six carbon atoms. In natural cellulose fibers there are 3000–5000 C_6 or glucose units joined together. This corresponds to a molecular weight of the order of 300,000–500,000.

The supramolecular structure of cellulose is at least as important as the molecular structure for the chemical and physicochemical behavior of cotton. Radiographs of cellulose have shown a remarkable agreement between the length of a unit cell along the fiber axis and the value 10.4 Å calculated for the cellobiose unit. The chains must therefore lie in an almost straight arrangement along the fiber axis.[2,3] From bundles of parallel oriented chains (micellae) supramolecular crystallites are constructed. About 80% of the cellulose chains are arranged in crystalline form, the remaining 20% being amorphous. Micellae and noncrystalline components together form micellar structures which are held together in microfibrils by secondary valencies. Inside of these microfibrils a microcapillary system is developed. A macrocapillary system is also produced by the arrangement of microfibrils in the cotton fiber. These two capillary systems are responsible for all the swelling and absorption processes which are so important for the dyeing and finishing of cotton.[4]

One of the most important properties of cotton is its water-absorbing capacity. The swelling of cotton in water proceeds anisotropically and amounts in the transverse direction to 40% of the diameter and along the fiber axis to 1%. Contrary to regenerated cellulose, the tensile strength of cotton when wet is 10–20% higher than in the dry condition.

In low concentrations mineral acids merely cause swelling, but in higher concentrations a hydrolytic degradation occurs which results in

---

[2] N. Normann, *Textile Res. J.* **33,** 711 (1963).

[3] A. Frey-Wyssling, *Science* **119,** 80 (1954).

[4] H. Ruck, *Faserforsch. Textiltech.* **14,** 146; 171; 233 (1963).

a decrease of the degree of average polymerization and in a reduction of the mechanical strength.[5]

The sum of all the resulting hydrolytic degradation products between glucose and the unchanged cellulose fiber molecule is known as hydrocellulose. Because of the presence of aldehyde groups, hydrocelluloses have a reducing action and are more freely soluble in alkali.[6] Cellulose reacts with caustic soda, mainly at a lower temperature, forming sodium cellulose. This treatment opens up the previously mentioned supramolecular structure of cellulose, thereby increasing the water absorption (mercerization).[7]

Oxidizing agents also lead to a degradation of cellulose with formation of oxycellulose.[8] On the other hand, cellulose is stable to reducing agents.

Although the water absorption and moisture-transfer capacity of cotton are very desirable properties for comfort in wearing, the associated loss of shape in moist or wet condition is a great disadvantage. Consequently, in recent years innumerable chemical products and processes have been developed to increase the wet-swelling resistance of cellulose and therefore to ensure, in a similar manner to synthetic fibers, the retention of shape during washing and other wet processes. From the well-established crease-resist processes with synthetic resins in the range of urea or melamine/formaldehyde addition compounds, it is recognized that the wet stability of cellulose can be increased, in particular, by cross-linking compounds. These include, above all, DMEU, DMPU, DMEU$(OH)_2$, and TMEDU (see Table I).

Moreover, a cross-linking of cellulose can also be achieved with polyoxymethylene[9] and epichlorohydrin. The conditions under which these cross-linkings proceed are generally at temperatures of 140–150° and under the catalytic action of potential acids, e.g., ammonium or magnesium salts of strong acids. In the case of epichlorhydrin and certain other compounds, cross-linking takes place in an alkaline medium.[10,11]

The aim of all these cross-linking processes is to achieve dimensional stability. To set textile materials to the shape conferred on them during makeup the so-called Permanent Press process has been developed.[12] The precure process is distinguished from the postcure process. In the precure process, the fabric is treated with cross-linking agents

[5] A. Parisot, *Bull. Inst. Textile France* **93,** 7 (1961).

[6] R. Colbran and G. Davidson, *J. Textile Inst., Transe* **52,** T73–T78 (1961).

[7] U. Rössner, *Deut. Textiltech.* **16,** 304 (1966).

[8] B. Porter and W. Goynes, *Textile Res. J.* **34,** 467 (1964).

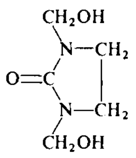
[9] D. Jones, *Textile Res. J.* **34,** 257 (1964).

[10] B. Dorset, *Textile Mfr.* **92,** 189; 1097 (1966).

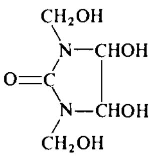
[11] J. Frick, *Am. Dyestuff Reptr.* **56,** 684 (1967).

[12] S. Vail, *Melliand Textilber.* **47,** 402 (1966).

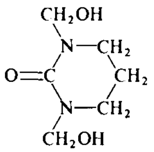
TABLE I
CROSS-LINKING AGENTS FOR CREASE-RESIST FINISHES



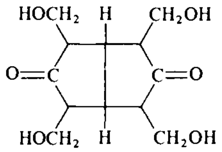
Dimethylolethyleneurea
(DMEU)



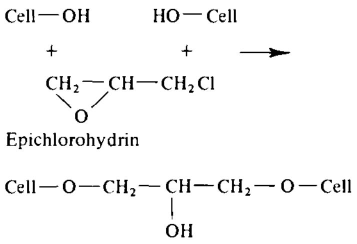
Dimethyloldihydroxyethyleneurea
(DMEU(OH)$_2$)

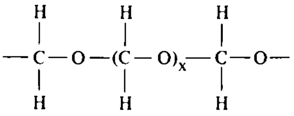


Dimethylolpropyleneurea
(DMPU)



Tetramethylolethylenediurea
(TMEDU)





$$-\overset{H}{\underset{H}{C}}-O-(\overset{H}{\underset{H}{C}}-O)_x-\overset{H}{\underset{H}{C}}-O-$$

Polyoxymethylene (POM)

and catalyst, and then subjected to a heat treatment which starts, but does not complete the cross-linking and polycondensation reactions. Curing of the cross-linking products, with a simultaneous setting to shape of the fabric, is carried out at 220–240° for 15–20 seconds on the heating presses of makeup enterprises.

In the postcure process, after impregnation of the fabric with cross-linking products and catalysts, the material is gently dried, but not cured. The reaction of the cross-linking compounds is carried out only after makeup, i.e., when setting to shape in special curing ovens at 170–175° for 15–20 seconds.

a. Regenerated Cellulose Fibers. In contrast to cotton, the degree of average polymerization of regenerated cellulose is 300–600, i.e., much lower. There are also differences in the supramolecular structure compared with cotton and, as a result, the swelling power is considerably higher than that of cotton. The tensile strength of swelled regenerated cellulose falls to about 50% of the original value. As a result of strong water absorption, the wet processing of regenerated cellulose causes a so-called wet-stiffness, which sometimes produces an objectionable effect. The level of this effect depends, however, on temperature. Dehydration and an increasing flexibility occur as the temperature rises. Moreover, suitable textile softening agents are available which partly counteract wet-stiffness.

The most remarkable development in the field of regenerated fibers led to the so-called HWM fibers (High Wet Modulus), whose swelling value and stretch were considerably reduced.[13] Only those fibers with an elongation below 15% under a load of 2.5 g/den in the wet condition may be called HWM fibers.

The lower swelling and extension properties in comparison with normal regenerated cellulose are due to higher degrees of average polymerization, which attain 900 in HWM types. Moreover, the covering layer is thicker in these fibers and sometimes extends homogeneously over the entire cross section. These characteristics are achieved by a special precipitation process of the spinning solution after leaving the spinneret.[14]

b. 2½ Acetate Fiber. Acetate fibers are produced from linters or refined wood pulp, which are acetylated at temperatures up to 50° with acetic anhydride in the presence of glacial acetic acid and concentrated sulfuric acid. A marked decrease occurs in the degree of polymerization, which permits the production of a spinnable solution even in higher concentrations.

Esterification leads first to triacetylcellulose with an acetyl content of 62.5%, which is used in the production of triacetate fiber (see Section I,A,1*c*). By contrast, a partial resaponification is carried out in the case of 2½ acetate fiber. The resulting secondary acetate has an acetyl content of 53–55% and is precipitated in warm, dilute acetic acid.

To spin it into fibers, acetylcellulose is dissolved in acetone. The dry spinning process is mainly used, since this method ensures on the one hand a high rate of production, while on the other hand the resulting fiber requires no further aftertreatment.

Because of its acetyl groups, the acetylcellulose molecule has a very bulky structure, which complicates the close packing together of the

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[13] G. Centola, *Melliand Textilber.* **44,** **551** **(1963)**.

[14] W. Bandel, *Melliand Textilber.* **42,** **185** **(1961)**.

molecules or crystallites. The formation of hydrogen-bridges is also restricted and the tensile strength of acetate fiber is therefore limited. Since the hydroxyl groups of the cellulose component are partly blocked, acetate fiber undergoes considerably less swelling in water than other cellulosic fibers (see Table II, at the end of Section I). Because of their ester formation, acetate fibers are soluble in most polar solvents and insoluble in most nonpolar solvents, in some of which, however, swelling occurs. Under the action of alkalies, and also in water at temperatures exceeding 80°, saponification involving a dulling effect is produced at the surface. Acetate fiber is much more resistant to acids and oxidizing agents than other cellulosic fibers. The softening of acetate fiber starts below 100° (m.p. 240°). This must be remembered during further processing.

c. Triacetate Fiber. Triacetate obtained as an intermediate in the production of 2½ acetate is used as a 20% spinning solution in methylene chloride, and the fiber is produced by the dry spinning process. With regard to dyeing behavior, because of its stronger hydrophobic behavior, triacetate must be placed among the manmade fibers. In general, triacetate fibers are more resistant than 2½ acetate fibers. In boiling water triacetate is neither hydrolyzed nor dulled. Its melting point is about 300° and its moisture absorption 3–4% under normal conditions. Unlike 2½ acetate, triacetate is insoluble in acetone, tetrahydrofuran, and other strong polar solvents, but is soluble in chloroform. Bleaching is usually carried out with sodium chlorite.

To creaseproof and set triacetate fabrics, they are subjected to a treatment in hot air, superheated steam, or hot water, which results in an increase of the crystalline zones.

B. Protein Fibers—Wool

Wool fiber consists mainly of keratin, a protein which contains sulfur. The building blocks of keratin are 19 different amino acids which are linked together to polypeptides, as chain molecules in spiral form. A polypeptide chain consists of about 350–400 amino acid molecules. The chief amino acids found in wool keratin are glutamic acid (15.3%), cystine (12.7%), leucine (11.3%) arginine (10.4%), and serine (9.4%). It is assumed that the peptide chain is wound in spiral form round an imaginary axis (helical structure),[15] so that 3.7 amino acid residues go to a turn. The helical structure explains the extremely high stretch of wool (particularly in the wet condition).

The following chemical structures inside the wool keratin molecule

---

[15] E. Bendit and M. Feughelman, *Encycl. Poly. Sci. Technol.* 8, 1 (1968).

contribute to the chemical behavior and are capable of chemical interactions: cystine and cysteine groups; saltlike bonds between glutamic acid or aspartic acid residues and free amino groups; and finally hydrogen bridges at close range. Wool keratin is thus revealed chemically as a polyelectrolyte. The histological structure of wool fiber comprises essentially three layers: (1) the scaly covering layer (cuticle); (2) the fibrous or fibrillar layer (cortex); (3) the medullary layer (medulla). The separate layers (and the intermediate layers not mentioned here) differ in the composition of the polypeptide chains.

The peptide chains of wool are relatively stable to acids. Nevertheless, in weak acids or at a higher temperature also in water, a breakdown of the salt bonds and hydrogen-bridge bonds takes place. This breakdown is, however, reversible and can be utilized for permanent changes of shape. Under the action of alkali the cystine bridges are also broken. In strong alkali wool is decomposed by hydrolysis of the peptide chain. Oxidizing and reducing agents attack the cystine bridge. Several methods of permanent setting to shape are based on a temporary reduction of the cystine bridge (e.g., with ammonium thioglycolate).[16,17,18]

As an amphoteric substance, wool possesses an isoelectric range. This occurs at about pH 4.5 to 5. At this pH value wool is electrically neutral and therefore shows a maximum chemical resistance. Dyeing and other treatments should therefore be carried out as close to this pH value as possible where a maximum protection of the material is required.

The chemical processes to change the surface structure of the wool fiber aim at a reduction of the felting tendency of wool. Owing to the scaly structure of the cuticle, friction between the wool fibers is dependent on the longitudinal direction, i.e., is greater in one direction than in the other. Shrinking therefore occurs when wool is subjected to mechanical stresses, particularly in the wet swelled state.

A reduction of the felting tendency of wool is a long-standing need. In the age of easy-care notions and their virtual realization in textiles made from synthetic fibers, this has become an urgent necessity for the wool industry. The following methods are mainly used to confer a nonshrink finish on wool[18-21]: (1) Scale removal by oxidation: (a) chlorine; (b) chlorine-forming substances; (c) peroxide oxidizing agents. (2)

---

[16] J. Caldwell, S. Leach, A. Meschers, and B. Milligan, *Textile Res. J.* **34,** 627 (1964).

[17] A. Farnworth, *Am. Dyestuff Reptr.* **49,** 996 (1960).

[18] B. Dorset, *Textile Mfr.* **91,** 249 (1965).

[19] H. Rouette, *Textil-Praxis* **23,** 254 (1968).

[20] M. Andrews, A. Inglis, and V. Williams, *Textile Res. J.* **36,** 407 (1966).

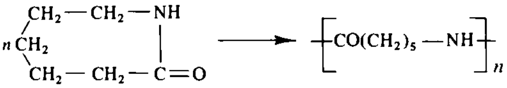
[21] M. Bahra, *Z. Ges. Textil-Ind.* **66,** 519 (1964).

Covering of the fiber surface with polymeric or polycondensation products. (3) Interfacial polymerization within the wool fiber, e.g., polyamide formation.

C. Synthetic Fibers

1. *Polyamide Fibers*

From the standpoint of production figures, polyamide fibers are still the most important of the synthetic fibers. The main types are nylon 6 and nylon 6,6.[22] Nylon 6 (II) is the polymerization product made from ε-caprolactam (III).[23]



(III) (II)

Nylon 6,6 (VI) is produced by polycondensation from adipic acid (IV) and hexamethylenediamine (V) by way of the salt of these two compounds.[24]

$$n\,\mathrm{HOOC(CH_2)_4{-}COOH} + n\,\mathrm{H_2N{-}(CH_2)_6{-}NH_2} \longrightarrow \left[\mathrm{CO(CH_2)_4{-}CO{-}NH(CH_2)_6NH}\right]_n \quad (1)$$

(IV) (V) (VI)

It can be recognized from the formulas that the two nylon types differ somewhat in the sequence of functional groups and in the number of methylene linkages. These differences also cause slight variations in the dyeing and physicochemical behavior. Responsible for the dyestuff-binding power are terminal amino and acid groups which will be formed during polymerization and polycondensation, respectively.

Further removed from the properties of the nylon types is polyamide (VIII) made from caster oil by way of ω-aminoundecanoic acid (VII).

$$n\,\mathrm{H_2N{-}(CH_2)_{10}{-}COOH} \longrightarrow \left[\mathrm{NH(CH_2)_{10}{-}CO{-}NH(CH_2)_{10}{-}CO}\right]_n \quad (2)$$

(VII) ω-Aminoundecanoic acid

(VIII) Polyamide 11

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[22] P. Schlack, *Z. Ges. Textil-Ind.* **56**, 823 (1954).

[23] P. Schlack and IG, *DRP* 748253.

[24] W. Carothers and DuP, *USP* 2,130,948.

This fiber has, however, remained far behind the two first-mentioned nylon types in importance.[25]

a. Modified Polyamide Fibers. As a result of chemical and, in certain cases, physical modifications of the hexamethylenediamine adipate or caprolactam, various deep-dyeing and light-dyeing polyamide types have recently been developed. Moreover, polyamide fibers have been produced which are no longer dyed with acid dyestuffs, but with basic dyestuffs. Fibers made from these starting materials are used, above all, in the carpet industry. On mixtures of different fiber types, dyeings in different depths of shade, as well as multicolor effects, can be produced in one bath with a suitable selection of dyestuffs (see Section II,C,1,*d*).

All polyamide fibers are subjected to a drawing process in which they are stretched to 3.5–5 times their original length. This drawing treatment considerably reduces the elongation of the filament and markedly increases its tensile strength. In this process the filament obtains properties which permit of its further processing. It is assumed that the changes which occur in the filament during drawing are caused by an alignment of the molecular chains, with the development of secondary valency forces between the carbamide groups of adjacent chains.

Slight differences in the degree of drawing, particularly in the range of 300%, cause variations of the dyestuff absorption. Less-stretched filament sections pick up the dyestuff more quickly, and in a given time therefore dye a darker shade. Moreover, as a result of their larger filament diameter, such sections appear optically darker after dyeing, so that the two effects act in the same direction. Differences in the degree of drawing of the fibers may therefore be responsible for difficulties in obtaining level shades on nylon.[26] In the subsequent rinsing, setting, and knitting processes, however, factors may also occur which impair the level dyeing of polyamide filaments or textiles.

The chemical properties of polyamide fibers are notable for a relatively high resistance to alkali even at higher temperatures. Polyamide fibers are less resistant to acids. A degradation is caused even by dilute mineral acids after a prolonged exposure. Organic solvents do not attack the fiber, but certain polyamide types are soluble in phenols even in the cold (see Table II). A notable feature of polyamide fibers is their moisture absorption. At 65% relative humidity and 20–22° this amounts in equilibrium, for nylon 6, to 4.0–4.5%, and for nylon 6,6, to 3.8–4.2%. In comparison with other conventional manmade fibers, polyamide has a relatively high moisture absorption (see Table II).

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[25] P. Schlack, *Melliand Textilber.* 47, 1175 (1966).

[26] F. Fourné, "Synthetische Fasern," p. 101. Wissenschaftliche Verlags-Gesellschaft, Stuttgart, 1964.

TABLE II[1]

Fiber type	*Density* (g/cm^3)	*Moisture absorp. at 65% rel. humidity* (%)	*Water retention, swelling power* (%)	*Breaking length* (km)	*Weather resistance* +++ *Very good* ++ *Moderate-good* + *Poor-moderate*
Cotton	1.5–1.54	7	45	27–44	+
Viscose fibers	1.5–1.52	13	90–125	18–27	+
HWM fibers	1.5–1.52	11–13	60–90	32–45	+
Polynosic fibers	1.5–1.52	11–13	55–70	32–54	+
2½ acetate	1.29–1.33	6.5	20–25	11–14	+
Triacetate	1.30	3.2	12–18	10–14	+
Wool	1.32	13–15	42	9–18	+
Nylon 6	1.14	3.5–5	9–12	36–63–81	+++[2]
Nylon 6,6	1.14	3–4.5	9–12	36–63–81	+++[2]
Nylon 11	1.04	1.2	—	48–63	+++[2]
Polyester	1.38	0.3–0.4	3–5	34–60–86	+++–++
Polyacrylonitrile	1.0–1.5	1–1.5	4.5–6	22–29	+++
Polyurethane elastomer	1.0–1.2	0.3–3	—	4.5–13	As nylon, turns yellow
Polypropylene	0.90–0.91	0.01–0.1	—	22.5–54	++
Poly(vinyl alcohol)	1.30	3.4	25	36–54	+
PVC	1.38	0.1	0–6	22–26	+++

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[1] Based on the fiber table of the Deutsche Forschungsinstitute fur Textilindustrie Reutlingen-Institut fur Textiltechnologie.

[2] Worse behavior where material is insufficiently protected against light.

PHYSICAL PROPERTIES OF FIBERS

Resistance to acids + *Resistant* — *Not resistant*	*Resistance to alkalies* + *Resistant* — *Not resistant*	*Resistance to bleaching agents*	*Elongation at break, dry*	*Elongation at break, wet*
— Hot dilute, cold, conc. acids + Cold weak acids	+ No destruction, but swelling (mercerization)	Bleaching with NaOCl, $NaClO_2$ and H_2O_2	6–10	7–11
As cotton	— 10% NaOH swelling and, possibly, destruction of the fiber structure: solubility in alkali 8–10% NaOH at 20° 50–60%	Resistant to NaOCl and $NaClO_2$ in usual concentrations; susceptible to high H_2O_2 concentrations at higher temperature	18–25	20–30
	As viscose, solubility in alkali 8–10% NaOH at 20° 40–50%		10–20	12–25
	As viscose, solubility in alkali 8–10% NaOH at 20° app. + 10% in 5% NaOH solution		5–15	7–18
— Conc. solution of strong acids	— Strong alkalies, saponification	— Strong oxidizing agents + Hypochlorite and peroxide bleaching solutions	25–45	35–50
— Conc. solution of strong acids (similar to 2½ acetate)	— High alkali conc., saponification + pH 9.5/95°	As 2½ acetate	22–45	30–50
— Conc. H_2SO_4 + Other acids	— In alkalies, in weak alkalies increased felting	With peroxides or SO_2	25–45	30–60
— Strong mineral acids, benzoic and oxalic acid, loss of elasticity and strength + Weak acids	+ Good alkali resistance	Bleaching with $NaClO_2$	25–46	30–50
As nylon 6	+ As nylon 6	Bleaching with $NaClO_2$	25–46	30–50
— Conc. acid and boiling picric and formic acid + Dilute and weak acids	— Conc. alkalies from 60° + Dilute or weak alkalies	Depending on the bleaching agent used, resistance moderate to good	15–38	20–40
— Partial decomposition in conc. H_2SO_4	— Strong alkalies, higher temperature	+ Bleaching agents and other oxidizing substances	16–38	16–38
+ Very resistant to most mineral acids	+ Weak alkalies	+ Bleaching agents and other oxidizing substances	25–35	25–35
— Conc. H_2SO_4 and conc. HNO_3 + very good resistance to dilute acid	+ Weak alkalies	— Hypochlorite discolors + Bleaching agents liberating oxygen in usual conc. as 60°	450–490	450–490
+ Good resistance to most dilute and cold acids, yellow discoloration in dilute HCl and H_2SO_4	+ Resistant to most alkalies	+ In general good resistance	20–90	20–90
— Chlorosulfonic acid and oxidizing agents + In most acids	+ Except oxidizing agents	+ Bleaching agents, good bleaching effect with $NaClO_2$	20–25	20–25
— Conc. acids + Dilute acids, hot and cold	+ Hot and cold in strong alkalies	+ In general good resistance	23	23

In close connection with moisture absorption is the swelling which occurs in an aqueous medium. This is shown in the following table.

Nylon 6,6	13%
Nylon 6	13%
Polyacrylonitrile	2%
Polyester	0.5%
Wool	42%
Cotton	45%
Viscose	95%

In comparison with vegetable fibers, the lower moisture absorption results in rapid drying, i.e., about 5–6 times quicker than cotton and wool.

The photochemical behavior of polyamide fiber is less favorable. A prolonged exposure to sunlight results in a very considerable loss of strength, although this can be prevented by incorporation of manganese salts,[27] e.g., manganese pyrophosphate, or titanium salts, such as titanium(III) chloride hexahydrate.[28]

An important part of the total quantity of polyamide fiber used in the textile sector is for textured polyamide filaments. These may be highly elastic (nylon-stretch) or reduced in their elasticity by setting (see also Section 1,C,2).

To attain the highest dimensional stability, woven and knitted fabrics made from polyamide fibers must be set in heat.[29] The fabrics are usually heat-set in open width. For the setting of nylon 6,6 temperatures of 200–225°, and for nylon 6 temperatures of 190–195° are used. The time required for setting depends largely on the weight of the material per square meter and on the heat-transfer properties of the setting unit.[30] On normal frames heat setting usually requires 30 seconds.

2. *Polyester Fibers*

In the last few years, polyester fibers[31] have attained an extraordinary importance. Their application ranges from 100% pure material in the form of plain or textured filaments to mixtures with practically all other vegetable or synthetic fibers. Particularly important applications are in blends with cotton and viscose staple fiber for outer wear and rainwear, and in blends with wool for worsted fabrics. Polyester fibers are, how-

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[27] B. Marek and E. Lerch, *J. Soc. Dyers Colourists* **81**, 481 (1965).

[28] G. Illing and BASF, *DAS* 1,147,381.

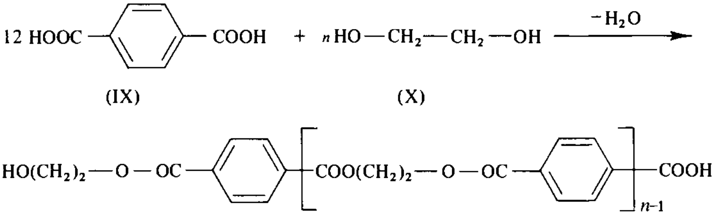
[29] F. Fourné, "Synthetische Fasern," p. 664ff. Wissenschaftliche Verlags-Gesellschaft, Stuttgart, 1964.

[30] F. Fourné "Synthetische Fasern," p. 652. Wissenschaftliche Verlags-Gesellschaft, Stuttgart, 1964.

[31] P. Koch, *Textilveredlung* **3**, 22 (1968).

ever, also blended with polyacrylonitrile fibers and used with these in three fiber blends with cotton. Blends with polyamide are not common.

Conventional polyester fiber (XI) is produced by polycondensation from terephthalic acid (IX) and ethylene glycol (X).[32] Both starting products must be extremely pure.



(IX) (X)

(XI)

(3)

Polyester fiber is the chief manmade fiber which contains aromatic structures in the chain. This fact is responsible for a particularly high crystallinity as a result of strong intermolecular forces after alignment of the molecules. It also brings about the very high resilience and the outstanding crease resistance of this fiber. On the other hand, the dyeing behavior is adversely affected.

With regard to the chemical properties, the high resistance of this fiber to acids, and also to alkalies, is remarkable. A treatment of the fiber with concentrated acetic or formic acid at 80° causes a loss of strength of less than 6% after 72 hours. Mineral acids in cencentrated form (over 30%) cause a stronger degradation. Under mild conditions, soda ash and caustic soda only slightly attack the fiber, therefore in mixtures with cotton the material can be mercerized. At higher temperatures, caustic soda solutions hydrolyze the fiber surface, which slowly flakes off. For this reason, polyester fiber is not resistant to kier-boiling. Polyester fiber is resistant to oxidizing and reducing agents. It also possesses very good resistance to light and weather.

To remain stable in the required width, woven and knitted fabrics made from polyester fibers must be heat-set. Heat setting[33] improves the elasticity and wrinkle recovery properties to an optimum. Materials made from polyester fibers or polyester/cotton blends are stretched to full width and set at 195–220°. Mixtures containing wool should not be set at temperatures exceeding 185°.

A very large part of the present polyester fiber production is used in the ladies' dress goods sector in the form of materials—mostly knitted

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[32] W. Carothers and J. W. Hill, *J. Amer. Chem. Soc.* **54,** 1579; 1959 (1932).

[33] F. Fourné, "Synthetische Fasern," p. 638ff. Wissenschaftliche Verlags-Gesellschaft, Stuttgart, 1964.

fabrics—made from textured filaments. In texturization,[34] the filament is given a permanent crimp which results in a wool-like, bulky structure on the finished goods.[35] In this connection, a distinction is made between filaments with a high elasticity and those whose elasticity has been reduced by a further setting process. The most widely known process is the false twist method, where in a continuous sequence of processes the filament is first given a high degree of twist. Then the material is set and detwisted again beyond the zero point. After a further setting, although the bulk effect is obtained, the elasticity is reduced to the normal requirements for knitwear and hosiery.

For the dyeing of textured synthetic filaments it is important to carry out the separate crimping and setting operations with utmost precision as regards tension, speed of goods, and temperature, otherwise uneven shades may be obtained as a result of the varying dyestuff absorption.

a. Modified Polyester Fibers. To open up the compact structure of polyester fiber and to facilitate the penetration of dyestuff molecules into the fiber, terephthalic acid is partly replaced by isophthalic acid in the production of polyester by polycondensation with glycol. If a sulfonic acid group is introduced additionally into the isophthalic acid, the fiber produced from such a polymer can be dyed with basic dyestuffs (differential dyeing).[36]

3. *Polyacrylonitrile Fibers*

Polyacrylonitrile fibers have gained a firm footing primarily in the knitwear and hosiery industry, but also in the field of furnishing fabrics. In addition, they are used in mixtures with wool for light worsted materials and also in blends with polyester fibers with or without cotton. Continuous filaments made from polyacrylonitrile are used in the weaving of ties. Moreover, carpets and floor coverings are produced from polyacrylonitrile plush materials.

The polymer (XIII) of acrylonitrile (XII) can be dyed only with

$$\underset{\text{(XII)}}{n\mathrm{CH_2{=}CH{-}CN}} \longrightarrow \underset{\text{(XIII)}}{\left[\mathrm{CH_2{-}CHCN}\right]_n}$$

difficulty and is used in filament and staple form mainly for technical applications. The polymer types used in the textile industry contain something in the order of 10% of additives incorporated in the polymer

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[34] M. Baumgartner, *Textilveredllng* **2,** 831 (1967).

[35] F. Fourné, "Synthetische Fasern," p. 854ff. Wissenschaftliche Verlags-Gesellschaft, Stuttgart, 1964.

[36] P. Barrett, *Am. Dyestuff Reptr.* **54,** 147 (1965).

to open up the molecular structure of the fiber. For this methacrylate is generally used. These polymers incorporating additives are to be understood whenever polyacrylonitrile fibers are mentioned in the following discussion. In contrast to these types are copolymers with a higher proportion of associated polymers, whose properties then differ considerably from those of polyacrylonitrile fibers.

Since polyacrylonitrile cannot be subjected to melt-spinning without decomposition, it must be spun from solvents.[37] The most usual solvent is dimethylformamide; 15% solutions emerge from the spinneret in long tunnels at 400°. This is known as a "dry spinning process." In the "wet spinning process," 10–25% solutions of polyacrylonitrile in dimethylformamide are spun into aqueous solutions of salts or alcohols, where they coagulate. Between wet- and dry-spun fibers there are certain differences in the fiber surface which have an influence, in particular, on the kinetic behavior during the dyeing process.[38] As also in the case of other manmade fibers, spinning is followed by a process of stretching to 8–12 times the original length.

The absorption and fixation of cationic dyestuffs by polyacrylonitrile fibers can be explained by formation of saltlike linkages between the dyestuff cations and the acid groups situated at the chain ends of polyacrylonitrile.[39]

In addition to basic dyestuffs, disperse dyes are also used for the dyeing of pale shades on polyacrylonitrile.

Polyacrylonitrile fiber is a very lightweight fiber (see Table II). As a bulked staple fiber it has a very high volume and a wool-like handle. Its bulk elasticity surpasses that of all other synthetic fibers.

The chemical properties of polyacrylonitrile fiber are notable for a very high acid resistance (acid-proof suits made from polyacrylonitrile) and also for resistance to the oxidizing and reducing agents used in the textile industry. The fiber is not completely resistant to alkali, although in this respect it meets the requirements of textile finishing. The good weather resistance of polyacrylonitrile, and also its fastness to light and to UV radiation, enable this fiber to be used for awning fabrics and other materials which are exposed to the weather. Under normal conditions, the moisture absorption of polyacrylonitrile amounts to 1–1.5%. The water retention, and therefore the swelling power, amounts to about 4.5–6%.

Textiles made from polyacrylonitrile fibers shrink in heat and must therefore be set. Dimensional stability is attained by a heat treatment

[37] H. Rein, *Angew. Chem.* **A60,** 159 (1948).

[38] W. Beckmann and W. Langmann, *Deutsche Textil-Techn.* **18,** 243 (1968).

[39] O. Glenz and W. Beckmann, *Melliand Textilber.* **38,** 296; 783; 1152 (1957).

either in saturated steam for 10 minutes (or for yarns in hank form in a slightly acidic hot water bath) or on a stenter for 30 seconds at 180°.

The shrinkage of the fiber is utilized in the production of high-bulk yarns. For this application, 60% of preset fiber and 40% of nonset fiber are spun into a yarn. The fiber which has not been set contracts during the shrinking process and in this way brings about a natural crimp, the effect of so-called "high-bulk yarns."

The polymer has also been modified with basic compounds to allow dyeing with acid dyestuffs. The following products are used: vinyl compounds of nitrogen-containing heterocyclic substances or alkyl esters of the same.[40]

The term "modacrylic fiber" is applied to copolymers with vinyl chloride or vinylidene chloride in which the polyacrylonitrile content is below 85%.[41] They are dyed with basic dyestuffs in the presence of carriers. Modacrylic fibers are being used on an increasing scale for seat coverings, particularly in the automotive trade, for blends with other fibers in outer clothing, and for pile fabrics, particularly long-stapled types, and also for wigs.

4. *Polyurethane Elastomeric Fibers*

In the textile sector, polyurethane fibers are mostly used in the form of elastomeric filaments for foundation garments, swim suits and sportswear, hose, half-hose, etc. Polyurethane elastomeric filaments consist of at least 85% polyurethane segments. The chain molecules are made up of hard segments—crystalline, high-melting polyurethane—and of soft segments—low-melting, amorphous polyesters or polyethers. Hydrogen bonds are mainly formed between the hard segments.[42,43]

Because of their chemical structure, which is similar to that of the polyamides, polyurethane fibers show an affinity for most dyestuff groups, although in certain cases with poor fastness to light and wet-fastness properties. Most suitable are the metal-complex dyestuffs.

Polyurethane fibers have a density of 1.0–1.2 g/cm^3; under normal conditions the moisture absorption is 0.3–3%, while the elongation at break amounts to 450–900%. Elastomeric fibers are resistant to dilute and cold acids, and also to alkalies. Polyurethane is soluble in boiling

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[40] F. Fourné, "Synthetische Fasern," p. 144ff. Wissenschaftliche Verlags-Gesellschaft, Stuttgart, 1964.

[41] F. Fourné, "Synthetische Fasern," p. 158ff. Wissenschaftliche Verlags-Gesellschaft, Stuttgart, 1964.

[42] H. Oertel, *Melliand Textilber.* **46,** 51 (1965).

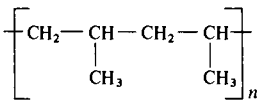
[43] H. Rinke, *Chimia (Aarau)* **16,** 93 (1962).

dimethylformamide, but insoluble in acetone, white spirits, concentrated hydrochloric acid and concentrated formic acid. At temperatures exceeding 150° a yellow discoloration and loss of strength occur.

In comparison with elastic rubber threads, polyurethane elastomeric filaments offer the following advantages: They are resistant to oxidation, faster to light and lighter in weight. They possess twice the amount of stretch, two to four times the tensile strength, better intermittent and permanent abrasion resistance, and their elasticity is more durable.

5. *Polypropylene Fibers*

Polypropylene fibers were at first mainly used for technical articles (e.g., polyolefin bands for packing material), but have recently been gaining in importance—particularly in the U.S.A. and Japan—for the production of carpets and similar furnishing materials. In this case, isotactic polypropylene is used, the CH_3 groups all being located on one side (XIV). The filaments are produced by the melt spinning process in a similar manner to polyester, i.e., the chips are melted, the melt is forced through a spinneret at 290°, cooled in air, and then wound at high speed (600–900 meters/minute). A subsequent drawing process stretches the fibers to 3–8 times their original length.



$$\left[-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-\right]_n$$

(XIV)

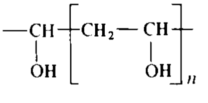
Since polypropylene fiber contains no dyestuff-binding groups, dyeing in the melt was formerly the only possible coloring method. A modification of the chain molecules has, however, recently permitted the production of polypropylene fibers which can be dyed with acid or disperse dyestuffs. Moreover, fibers have been modified with nickel complexes and are readily dyed with disperse dyestuffs, which form complexes with nickel.

Polypropylene fibers are notable for high tensile strength and good resistance to acids and alkalies. At room temperature they are insoluble in all solvents, but swell in hydrocarbons and chlorinated hydrocarbons. Despite their relatively low fastness to light and to oxidizing agents, they are not attacked by sodium chlorite solution (5 g/liter $NaClO_2$, pH 4, 80°). With a specific gravity of about 0.9, polypropylene fiber are lighter than water, and are the lightest fiber group (see Table II).

6. *Polyvinylalcohol Fibers*

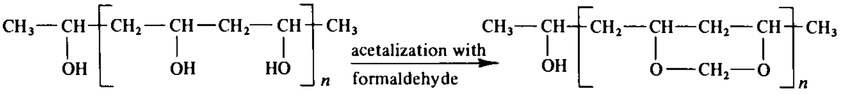
Polyvinylalcohol fibers are the group of manmade fibers with properties most resembling those of natural and regenerated fibers. They are of considerable importance, mainly in Japan, where they are used in blends with cellulosic fibers for cloths. A further application is in the technical sector, for fishing tackle, etc.

The starting material, polyvinylalcohol (XV), is obtained by saponification of polyvinylacetate, produced from acetylene and acetic acid with subsequent polymerization. Spinning of the aqueous solution in carried out in the usual way by the wet spinning process into an aqueous precipitating bath with electrolyte additions. To prevent shrinkage, the coagulated filaments are dried and then given a heat treatment, either briefly in dry heat at 210–230° or in an ammonium sulfate solution at 140° under pressure. This is usually followed by acetalization with formaldehyde to reduce the hydrophilic property and water solubility (XVI).



$$-\underset{OH}{\underset{|}{CH}}-\left[CH_2-\underset{OH}{\underset{|}{CH}}\right]_n-$$

(XV)



$$CH_3-\underset{OH}{\underset{|}{CH}}-\left[CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{HO}{\underset{|}{CH}}\right]_n-CH_3 \xrightarrow[\text{formaldehyde}]{\text{acetalization with}} CH_3-\underset{OH}{\underset{|}{CH}}-\left[\underbrace{CH_2-CH-CH_2-CH}_{O—CH_2—O}\right]_n-CH_3$$

(XVI)

Polyvinylalcohol fibers are easily dyed with most conventional dyestuffs, such as direct, vat, disperse, metal complex, basic, and sulfur dyes. The elasticity is higher than that of viscose and natural silk, but lower than that of nylon, polyester, and polyacrylonitrile. The water absorption at 65% relative humidity amounts to 3.4%, and the water retention (swelling value) to 25%. Polyvinylalcohol fibers possess very good resistance to alkalies and good resistance to acids and to most organic solvents, except formalin, phenol, cresol, and formic acid above 60° (see Table II).

7. *Identification of Fibers*

The field of fiber identification has become very extensive and complex as a result of the large number of manmade fibers at present on the market. The natural fibers can always be recognized by a microscopic examination of the longitudinal section and cross section, by burning tests, and by staining in specially developed dyestuff solutions.

Difficulties are experienced with synthetic fibers, which generally have a more or less smooth surface or, depending on the spinneret used, profiled surfaces for specific applications, their cross sections thus being uniformly circular, oval, or of any other shape. In the identification of synthetic fibers, solvent tests must always be made in addition to microscopic, burning, and staining tests. Even solvent tests may be misleading, however, when it is uncertain whether a test specimen consists of a single component or of a fiber mixture. Table III shows the behavior of the most important fibers in the most usual solvents. Table IV shows the melting points, results in the burning test and a few typical reactions which generally take place only in the case of a single fiber type, without being specific to any other type.[44]

II. Dyeing Methods and Dyestuffs

A. Dyeing of Cotton and Other Cellulosic Fibers

Cellulosic fibers are dyed mainly with direct dyestuffs where the fastness properties attained are sufficient for the required goods. This also applies to those dyestuff groups whose fastness properties are improved by an aftertreatment with copper or by reaction with a diazonium salt, or else by diazotization on the fiber and coupling with a suitable component. Where a higher level of fastness properties is required, particularly with regard to the wet- and weather-fastness properties, vat dyes or naphthol dyes are used.

Although dyeings produced with sulfur dyestuffs possess very high wet-fastness properties and are generally economical, they are nevertheless somewhat inferior to vat dyes in their fastness to chlorine and to light.

Among the dyes which form a pigment on the fiber are Phthalogen dyestuffs, in which phthalocyanine is built up from a precursor. These dyestuffs also meet the highest fastness requirements. The numerous possibilities to obtain fast colors on cellulosic fibers are augmented by the reactive dyestuff range. Reactive dyestuffs form a covalent bond with cellulose fiber and therefore ensure very high wet-fastness properties with a very simple method of application. The possibility of reaction between the fiber and low molecular weight dyestuffs with little affinity

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[44] M. Strattmann, *Z. Ges. Textil-Ind.* 64, 746; 850; 948 (1962).

TABLE III
Behavior of Synthetic Fibers in Solvents[1,2]

Fibers	2½ Acetate	Triacetate	Polyester	Polyamide 6,6	Polyamide 6	Polyamide 11	Polyurethane elastomer fibers	Polyvinylidene chloride Polyvinyl chloride	Polyvinyl chloride Polyacrylonitrile	Polyacrylonitrile Polyvinylidene chloride	Polyacrylonitrile	Polyvinyl alcohol	Polypropylene
Hydrochloric acid 37%	□	□	■	□	□	●	■	■	■	■	■	□	■
Sulfuric acid 97–98%	□	□	□	□	□	□	□	○	○[3]	□	□	□	●[4]
Nitric acid 65%	□	□	+	□	□	○	○	■	○	△	□	□	■
Potassium hydroxide sln. 40%	■	■	△	■	■	■	■[6]	■	●[4]	■[4]	■[4]	■[4]	●
Acetone	□	+[5,7]	■	■	■	■	■	■	□	○	■	■	■
Cyclohexanone	○	○	■[4]	■	■	○	○	○	○	○	■	■	○
Formic acid 96–100%	□	□	■	□	□	○	○	■	●	△	■[8]	□	■
Glacial acetic acid	□	□[9]	■	○	○	○	■	■	●	■	■	■	■
Ethyl acetate	△	■[10]	■	■	■	■	■	■	■	■	■	■	■
Toluene	■	■	■	■	■	■	■	○	■	■	■	■	○
Phenol 90%	□	□	○	□	□	□	○	○	○	△	●[4]	△	○
Dimethylformamide	□	○	○	■	○	○	○	○	□	□	○	●	●
Dioxane	□	□	■	■	■	■	■	○	●	■	■	■	■
Methylene chloride	△	□	■	■	■	■	■	■	■	■	■	■	■
Chloroform	△	□	■	■	■	■	■	■	■	■	■	■	■
Monochlorobenzene	■	■	■	■	■	■	■	○	●	■	■	■	○
o-Dichlorobenzene	●	■[11]	○	■	■	○	△	○	○[4]	■	■	■	○
Ethylenediamine hydrate	□	○	△	■	■	■	■	■[3,4]	●	○[3,12]	■	△	■
Nitrobenzene	○	○	○	■[6,11]	△	○	○	○	○	○	■[4]	■	○

[1] According to M. Bumiller, *Chemiefasern* **13,** 488 (1963).

[2] Legend: ■, insoluble; □, soluble at room temperature; ○, soluble at boiling temperature; ●, insoluble, but fibers show an alteration at boiling temperature (i.e., forming lumps, swelling or shrinkage); △, destruction of the material at boiling temperature to coarse fiber fractions or to fine particles; +, soluble to some extent at boiling temperature, obviously diminished quantity of fibers, the undissolved fibers usually disintegrate.

[3] Fiber shows a discoloration at room temperature (i.e., from yellow to orange or brown), sometimes even before dissolution.

[4] Fiber discolors at boiling temperature (yellow, brown, or black).

[5] The reaction (disintegration, partial solubility, or forming of lumps) begins at room temperature and there is no change at boiling temperature.

[6] Possibly, a little decomposition of the material is observed.

[7] There are many different types of triacetate fibers, some are partly soluble, some are completely soluble, but there are insoluble types as well.

[8] Some polyacrylonitrile types of various origin and different times of manufacture are already soluble at room temperature.

[9] Sometimes only soluble at boiling temperature.

[10] Some polyacrylonitrile types of various origin and different times of manufacture form lumps at boiling temperature.

[11] Sometimes a small part of the fiber material seems to be soluble, because there is some precipitation after a while, when the solvent has cooled.

[12] A few insoluble parts of the fiber are left.

TABLE IV
BEHAVIOR OF MANMADE FIBERS

Fibers	*Start of production*	*Thermic behavior*		*"Type" reactions*	
		Softening point (°C)	*Melting point (°C)*		
Polyamide 6	1939	170°	215°	Soluble in cold phenol (80%); insoluble in cold glacial acetic acid	Soluble in boiling dimethylformamide
Polyamide 6,6	1938	235°	250°		Insoluble in boiling dimethylformamide
Polyamide 11	1950	160°	189°		Insoluble in cold hydrochloric acid
Polyester	1947	230–249°	256°	Soluble in cold concentrated sulfuric acid; soluble in boiling *o*-dichlorobenzene, insoluble in cold phenol (80%)	
Polyurethane elastomer fibers	1960	175°	250°	Insoluble in cold phenol (80%), insoluble in cold dimethylformamide, soluble in boiling cyclohexanone	
Polyacrylonitrile	1942	235–330°	Decomposition before melting	Soluble in concentrated nitric acid, soluble in boiling dimethylformamide, insoluble in concentrated formic acid, insoluble in boiling cyclohexanone	
Polyvinyl alcohol	1939	200°	230–238°	Soluble in concentrated formic acid, insoluble in glacial acetic acid, cold and boiling	
Polypropylene	1959	150–155°	163–175°	Soluble in monochlorobenzene, insoluble in cyclohexanone at 100°	
60% Polyvinyl chloride +40% Polyacrylonitrile	1949	125–135°	190–200°	Soluble in boiling acetone, insoluble in boiling dioxane, soluble in cold cyclohexanone	
80% Polyacrylonitrile +20% Other Vinyl compounds	1956	150–230°	Carbonizes before melting		Insoluble in cold cyclohexanone

has led to the production of fast dyeings on cellulosic fibers in very brilliant shades.

1. *Discontinuous Dyeing Processes*

In the dyeing processes described here, the goods are dyed in a solution of the required dyestuff in such a manner that the proportion by weight of dyestuff solution (liquor) to the goods to be dyed, the so-called liquor ratio, is between 5:1 and 40:1. The dyestuffs must therefore always possess an affinity for cellulose so that they are taken up by the fiber from the solution. Depending on the stage of processing in which dyeing is carried out, the following apparatus and machinery equipment is used:

Package dyeing machine: Liquor ratio 10:1–15:1. For dyeing loose stock, i.e., cotton or rayon staple fiber. The textile material is packed into a dye vessel and the dye liquor is circulated from center to outside and vice versa.

Cheese dyeing machine: Liquor ratio 10:1–15:1. Yarn which is wound in cheese form on perforated cones, springs, etc., is placed on perforated spindles. The dye liquor is circulated through the cheeses from center to outside and vice versa.

Beam dyeing machine: Liquor ratio 10:1. For dyeing warps and woven or knitted piece goods. The textile material is wound round a horizontal perforated beam. The dye liquor can be pressed through the material from the center or from the outside.

A feature of the above-mentioned dyeing machines is that the dye goods are stationary with an alternating liquor circulation. They can be operated at normal pressure, i.e., at 100°, and also at an increased pressure, i.e., at 120–130°, in the form of autoclaves. In the following dyeing machines, the textile material is moved in the liquor:

Hank dyeing machine: Liquor ratio 15:1–20:1. For dyeing yarn in hanks, where the goods must be subjected to virtually no tension. The hanks, which are arranged on sticks, are dipped into the liquor at regular intervals.

Winch beck: Liquor ratio 20:1–30:1. For dyeing piece goods with a minimum of tension. The piece, sewn into an endless band and running on a winch, is drawn through the dye liquor into a trough.

Jig: Liquor ratio 3:1–5:1. For dyeing longer lengths of piece goods. The material is wound alternately from one roll on to another while passing through the dyebath. The jig is the dyeing unit which permits to use the shortest liquor ratio by the exhaustion dyeing method.

The last-mentioned dyeing units can also be constructed as open or closed machines, and are therefore suitable for high temperature dyeing. This is more common in the case of the winch beck, less often with jigs and hank dyeing machines.

a. Dyeing with Direct Dyestuffs. The following method is used for dyeing direct dyestuffs on loose stock, slivers, yarns, and piece goods on one of the described dyeing machines: The dyestuff is dissolved in hot water and the solution is made up to the required volume with water at 50–60°. Depending on the type and amount of dyestuff used, 5–20% sodium sulfate and 0.5–2% soda ash are added to the solution. The goods are entered into the liquor, or the liquor is pumped into the dyeing unit. The temperature is then increased in 30 minutes to 85–90° and dyeing is continued at that temperature for about 1 hour. After the dyeing process, the liquor is drained and the goods are well rinsed.

This standard procedure may be modified according to the dyestuffs used. The main characteristics of direct dyestuffs are the leveling properties and the so-called *temperature optimum.* In the case of direct dyestuffs, a distinction is made accordingly between cold-dyeing types, which produce an optimum shade on the fiber when dyed at 40–60°, and hot-dyeing types with an optimum at about 100°. Most direct dyestuffs are warm-dyeing types with a temperature optimum at about 80°. Particularly where cold-dyeing types are used, the temperature stipulated in the standard procedure must be altered accordingly. Only dyestuffs of the same category should be used in mixtures.

It must be understood that the temperature optimum of direct dyestuffs is not an exactly definable physical concept. It comprises a thermodynamic factor, i.e., the distribution equilibrium of the dyestuff between fiber and liquor, and also a kinetic factor, i.e., the rate of diffusion. If the dyeing time could be prolonged indefinitely, cold-dyeing would be possible in all cases, since the equilibrium of the dyestuff between fiber and liquor shifts with rising temperature in favor of the liquor.[45] This phenomenon is utilized in the so-called cold pad-batch process (see Section II,A,2,*d*) with direct dyestuffs, where almost a real equilibrium is attained after the very concentrated dyestuff liquor has been in contact with the textile material for 24 hours.

Regardless of the dyeing equilibrium, the optimum dyeing temperature is all the higher the lower the rate of diffusion of the dyestuff.[46] Diffusion of the dyestuffs is increased by raising the temperature. On the other

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[45] T. Vickerstaff, "The Physical Chemistry of Dyeing," p. 87ff. Oliver and Boyd, London, 1954.

[46] T. Vickerstaff, "The Physical Chemistry of Dyeing," p. 191ff. Oliver and Boyd, London, 1954.

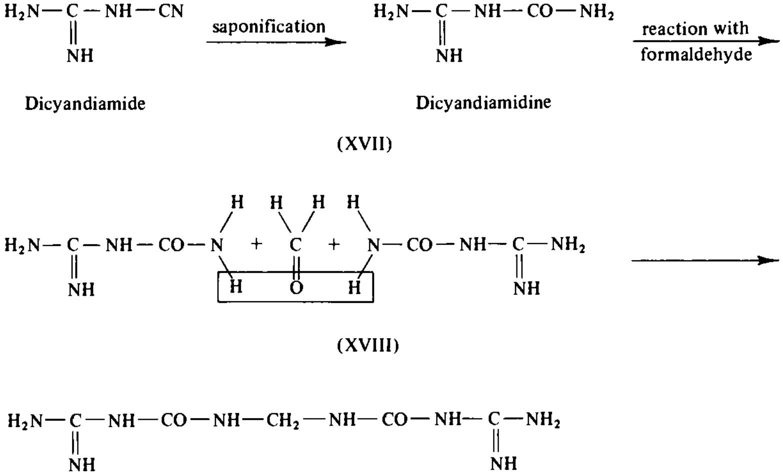
hand, those dyestuffs with a lower rate of diffusion (hot-dyeing types) possess better wet-fastness properties, since the rate of diffusion also is a component of the desorption process.

When dyeing is carried out on the jig, particularly suitable dyestuffs are those whose affinities vary only slightly in the normal dyeing time in the temperature range of 40–80°. If this is neglected, differences of shade will occur between the edges and the middle of the piece, since the edges of the batched-up goods cool more rapidly than the middle and are therefore, on an average, always somewhat colder.

Since dyestuff mixtures are generally used in practice, the different components of a mixture must also be carefully adapted to each other with regard to their leveling power. An addition of nonionic or anionic auxiliaries increases the leveling capacity of the dyestuffs.

In principle, viscose staple fiber is dyed in the same way as cotton. The leveling capacity of the dyestuffs is particularly important, since the dyeing processes take place more quickly as a result of the different molecular structure and much higher absorption capacity of viscose staple. To prevent the wet-stiffness of regenerated cellulose, the goods are entered at the highest possible temperature, and 0.5–1 g/liter of an anionic softening agent is added to the dyebath, which also avoids boiling and running creases.

To improve the wet-fastness properties of direct dyestuffs, an aftertreatment may be given with cationc auxiliaries. As an example, a polycondensation product of dicyandiamidine (XVII) and formaldehyde may be taken, molecular weight, 1000–3000. The effect of these products is based on an ionic bond with the sulfo-group-containing dyestuff molecule attached to the fiber. The decreased solubility results in an improve-



$$H_2N-\underset{\underset{NH}{\|}}{C}-NH-CN \xrightarrow{\text{saponification}} H_2N-\underset{\underset{NH}{\|}}{C}-NH-CO-NH_2 \xrightarrow[\text{formaldehyde}]{\text{reaction with}}$$

Dicyandiamide

Dicyandiamidine

(XVII)

$$H_2N-\underset{\underset{NH}{\|}}{C}-NH-CO-\overset{H}{N}H + \underset{\underset{O}{\|}}{\overset{H\ \ H}{C}} + H\overset{H}{N}-CO-NH-\underset{\underset{NH}{\|}}{C}-NH_2 \longrightarrow$$

(XVIII)

$$H_2N-\underset{\underset{NH}{\|}}{C}-NH-CO-NH-CH_2-NH-CO-NH-\underset{\underset{NH}{\|}}{C}-NH_2$$

ment of the wet-fastness properties. The dyeings are rinsed and these products are then applied in a weak acid solution at temperatures between 20° and 60° for 30 minutes. Depending on the depth of shade, 1% to 4% of the aftertreating agent is used, related to the weight of the goods.

Those dyestuffs which are able to form copper complexes can be treated on the fiber with solutions of copper salts and brought into complex form. This results in a considerable improvement of the fastness to light and wet-fastness properties. Simultaneously, a bathochromic change of shade takes place, mostly to duller shades. It should be noted that dyeings obtained with copper-developed dyestuffs may have the copper removed by histidine, as contained in perspiration. This results in a change of shade and in a reduction of the fastness properties.

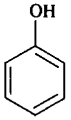
The copper aftertreatment is carried out as follows: The dyeing, produced by the method generally used for direct dyestuffs, is rinsed thoroughly and aftertreated in a fresh bath containing 1–3% copper sulfate and 2–3% acetic acid 30% for about 30 minutes at 80–90°.

i. Diazo dyestuffs. When direct dyestuffs contain one or more diazotizable amino groups, an increased molecular weight and reduction of solubility can be achieved by diazotization of the dyestuff applied to the fiber and development with suitable coupling components, giving dyeings which are faster to water and to washing. No improvement generally takes place in the fastness to light. The procedure is as follows: The goods are dyed in the usual way, then rinsed and diazotized for 20 minutes in a fresh bath set with 1.5–2.5% sodium nitrite, 5–7.5% hydrochloric acid 30%, or 3–5% sulfuric acid 96%, and thoroughly rinsed again.

The diazo compounds are destroyed by direct sunlight, and even diffuse daylight reduces the depth of shade and leads to the production of spotty dyeings. The diazotized dyeing must therefore be kept away from light and developed as soon as possible. Diazotized dyeings must be protected against alkali, since noncoupling *anti*diazotates are formed in a basic medium. To prevent a destruction of the diazo compound higher temperatures should also be avoided.

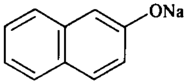
Development requires 15–20 minutes. In most cases the following coupling compounds are being applied: (1) 1-phenyl-3-methylpyrazolone (XXII) for yellow and orange shades, (2) sodium β-naphtholate (XX) for red shades, and (3) *m*-tolylenediamine hydrochloride (XXIII) for brown shades. When the dyeing is finally completed it is rinsed and soaped.

ii. Coupling dyestuffs. Direct dyestuffs containing free amino and hydroxyl groups in a position suitable for coupling can be considerably



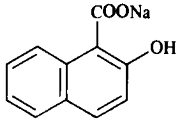
(XIX)

Phenol



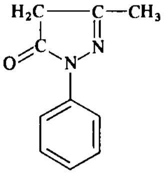
(XX)

Sodium β-naphtholate



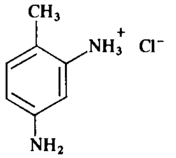
(XXI)

Sodium β-naphtholcarboxylate



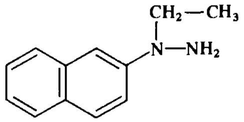
(XXII)

1-Phenyl-3-methylpyrazolone



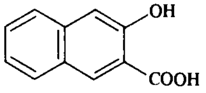
(XXIII)

m-Tolylenediamine hydrochloride



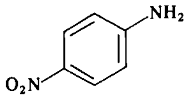
(XXIV)

2-Hydroxy-3-nepthoic acid



(XXV)

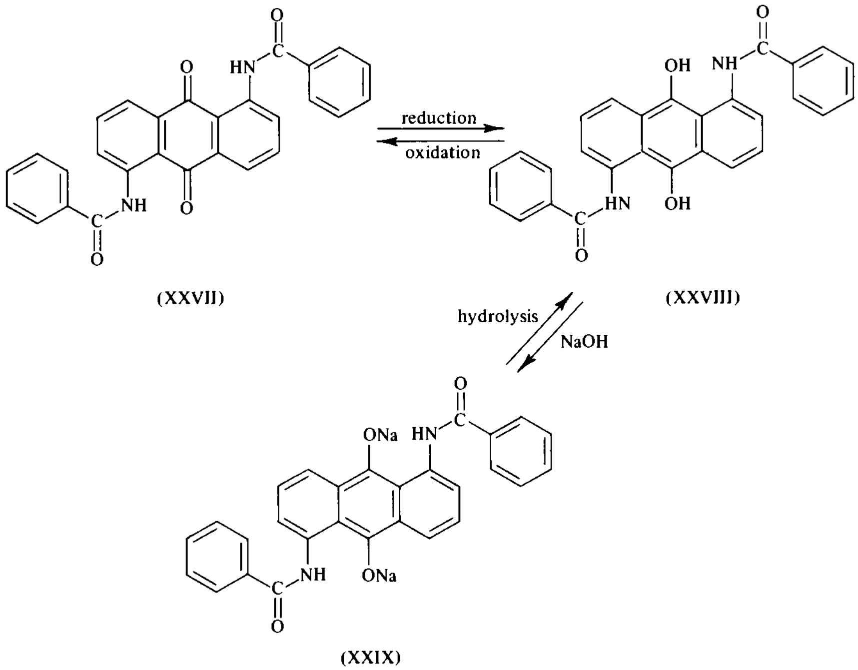
improved in their wet-fastness properties and depth of shade by coupling on the fiber with diazonium salts. This process has less importance. In practice it can be carried out only with diazotized *p*-nitroaniline (XXVI), which is marketed as a stabilized diazonium salt. Coupling is carried out with 1.5–3% of the diazonium salt in a cold, neutral bath.



(XXVI)

b. Vat Dyestuffs. To achieve higher to maximum fastness properties on cotton and regenerated cellulose fibers vat dyestuffs are used. Vat dyes are water-insoluble pigments (XXVII) which in an alkaline, reducing solution (vat) are converted into soluble leuco compounds. The sodium salts of these leuco compounds show a certain affinity for cellulose fiber and are therefore taken up by the fiber from a long liquor. The original pigment is re-formed on the fiber by subsequent oxidation with atmospheric oxygen or other oxidizing agents. Dyeings produced with these dyestuffs possess maximum wet-fastness properties. Selected members of the vat dyestuff ranges also meet the highest requirements with regard to fastness to light.

Sodium dithionite is generally used as a reducing agent. Reduction is carried out in the presence of caustic soda solution, which develops the full redox potential of the dithionite and also converts the leuco compound (XXVIII) to the sodium salt (XXIX). The amount of dithionite required for reduction and also the stability of the vat depend on the electrochemical redox potential of the various vat dyestuffs. The redox potentials can be determined by means of a platinum–calomel measuring device.[47] For conventional vat dyestuffs they range between —0.5 and —1.2 volts.



In some cases, sodium dithionite is now being replaced completely or in part by alkali borohydrides in alkaline solution and an initiator, such as sodium tetracyano nickelate-$Na_2[Ni(CN)_4]$.

The reduction takes place as follows (XXIXa), (XXIXb):

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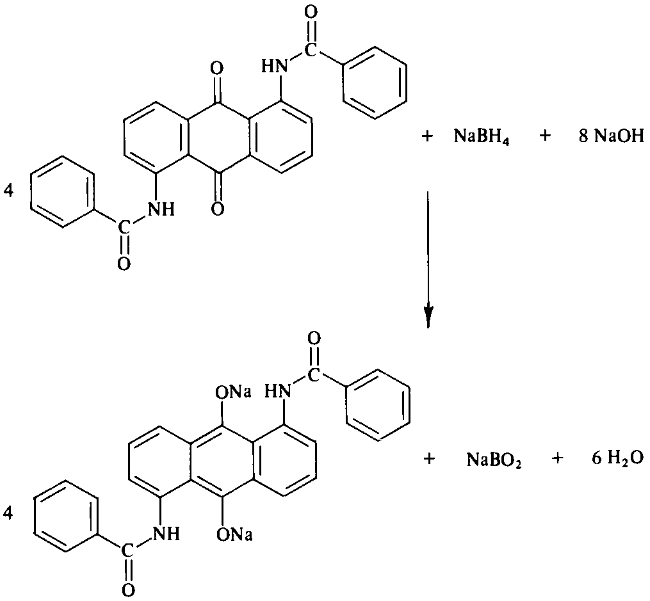
[47] T. Vickerstaff, "The Physical Chemistry of Dyeing," p. 282ff. Oliver and Boyd, London, 1954.

$$NaBH_4 + 2\,H_2O \longrightarrow NaBO_2 + 4\,H_2$$

(XXIXa)



(XXIXb)

The advantage of this reducing system over sodium dithionite is that it is chemically far more stable to both atmospheric oxygen and dyestuffs, so that its rate of decomposition is much lower than that of sodium dithionite in a cold chemical pad and there is no danger of prereduction. At high temperatures, e.g., steamer conditions, the metal borohydrides are about as reactive as sodium dithionite.

Vat dyestuffs can be applied from a long liquor in all processing stages of cotton or viscose staple fiber. The exhaustion process is usually carried out on the jig, winch beck, or on cheese dyeing machines.

Depending on the vat dyestuff type, three different application processes are distinguished according to the temperature and the amounts of caustic soda and dithionite required for vatting. In a similar manner to direct dyestuffs, a distinction is made between cold, warm, and normally dyed products. The "normal" dyeing temperature is 50–60°, warm-dyeing types are dyed at 45–50° and cold-dyeing types at 20–25°. The required amounts of caustic soda and dithionite increase from the cold-dyeing types to the normally dyed products. In principle, these dyestuffs are distinguished by their vatting property. While cold-dyeing types are easy to vat, normal-dyeing types are vatted with difficulty. Associated with this to a certain extent is the affinity for cellulose fiber, which although very high in the case of hot-dyeing types must be increased in that of cold-dyeing types by an addition of salt. Contrary to the affinity, the leveling capacity of these dyestuffs is very good for cold-dyeing types, moderate for normal-dyeing types. Table V contains a summary of the properties of the three types.

The dyestuffs are applied in such a manner that vatting first takes place with the required amounts of caustic soda and sodium dithionite at a temperature of about 50° in an interval of 5–20 minutes. After this has been done, the dyestuff is brought into contact with the goods and applied uniformly by a vigorous movement of goods or liquor. With cold-dyeing types the dyeing process is started at 40–50° and the affinity is increased by reducing the temperature. For warm- and normal-dyeing

TABLE V
PROPERTIES OF THE THREE GROUPS OF VAT DYES

Dyeing process	*Vat dyestuff, cold*	*Vat dyestuff, warm*	*Vat dyestuff, normal*
Caustic soda 38°Bé (ml/liter)	6	8	15 (−22)[1]
Sodium dithionite conc. (g/liter)	2.5	3	3.5
Glauber salt (sodium sulfate) (g/liter)	25	15	—
Dyeing temperature	20–25°	45–50°	50–60°
Time of dyeing	30–60 minutes	30–60 minutes	20–45 minutes
Dyeing behavior	Cold-dyeing type	Warm-dyeing type	Hot-dyeing type
Vatting properties	Easy	Medium	Difficult
Degree of absorption	Low, high addition of salt	Medium, medium addition of salt	Very high
Leveling properties	Very good	Good	Poor, needs special preventive measures
Rate of diffusion in the fiber	High	Medium	Low
Condition of the solution	Molecular dispersion	Partly associated	Considerably associated
Reoxidation	Difficult	Medium	Easy
Possibility of saponification and dehalogenization	Little	Medium	Much

[1] Special vat-normal dyes.

types the starting temperature is 20–30° and the affinity is increased by slowly raising the temperature. The dyeing process is generally completed after 20–60 minutes.

Care must be taken to ensure that during the entire vat dyeing process the amounts of alkali and reducing agents do not fall below a minimum value; otherwise reoxidation to the insoluble pigment will take place, resulting in precipitation and spotty dyeings or in poor fastness to crocking. Particular attention must be paid to this point where the dye liquor is in close contact with air, as is especially the case on the winch beck.

If the amount of caustic soda falls below a certain level, the free vat acid is precipitated and this no longer shows any affinity for the material to be dyed. It is therefore recommended to check the vat constantly for alkalinity and redox potential.

When dyeing is completed, the goods are rinsed and then oxidized. In addition to atmospheric oxygen, sodium perborate, hydrogen peroxide, and sodium chlorite may also be used as oxidizing agents.

i. Dyestuffs promoting tendering of the fiber by action of light. In the case of certain vat dyestuffs, the redox processes during a prolonged dyeing time result in a tendering of the cellulose fiber. This can be prevented by addition of tannin or pyrocatechin to the dyebath. The exposure to sunlight of dyeings obtained with certain vat dyes also causes a marked tendering of the fiber. In this case, the fiber is presumably decomposed by oxidation, forming oxycellulose. It is assumed that the dyestuff is first reduced by the action of light and is then transformed into a peroxide compound, which oxidizes the fiber as the pigment is re-formed.[48,49]

c. Naphthol Dyestuffs. Naphthol dyestuffs are azoic dyes which are formed on the fiber. Since they contain no solubilizing sulfo groups, dyeings produced with this dyestuff group possess high wet-fastness properties and, in certain cases, very bright shades. The naphtholating or coupling component shows a certain affinity for cellulose fiber and is therefore taken up by the fiber from a long liquor. The fiber, pretreated in this way, is introduced into an aqueous solution of the diazonium component, then the coupling reaction takes place on the fiber.

The naphtholating or coupling component is dissolved as the naphtholate with caustic soda and the material is naphtholated with this solution. Dissolving can be carried out by two methods.

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[48] A. Landolt, *J. Soc. Dyers Colourists* **65**, 659 (1949).

[49] F. Doerr, "Optische Anregung," p. 732ff. Verlag Chemie, Weinheim, Germany (1966).

(a) *Hot dissolving method*

1 kg	Naphthol is pasted up with a wetting oil or protective colloid and with
1.5 liter	caustic soda solution 38°Bé. This paste is dissolved to a clear solution with
15 liter	hot water;
15 liter	cold water is added, and generally
1 liter	formaldehyde 33% is also added, the required volume being made up after about 5 minutes with cold water.

(b) *Cold dissolving method*

1 kg	Naphthol is pasted up with
1 liter	alcohol and to this paste
0.5 liter	caustic soda 38°Bé is added. Solution is obtained by dilution with
1.5 liter	cold water, while stirring, generally,
0.5 liter	formaldehyde 33% is added and after 10 minutes the solution is stirred into the naphtholating bath, which contains 10 ml/liter of caustic soda 38°Bé in addition to a wetting oil or protective colloid.

The dissolving instructions may be varied more or less according to the naphthol type used.

To improve the affinity, 10–50 g/liter of Glauber salt or common salt may be added to the naphtholate; it falls very markedly with increasing temperature, and naphtholating is therefore generally carried out at 30° in the discontinuous dyeing processes. To ensure well-penetrated and level dyeings, particularly where dyeing is carried out on machines, the temperature is raised to 40–45°. The material must subsequently be freed from superfluous naphtholating solution, since this leads to the formation of insoluble azoic dyestuff in the diazotizing liquor. Some of the dyestuff precipitated in the liquor is fixed mechanically on the fiber and results in a poor fastness to crocking of the dyeing. Hydroextraction is carried out by squeezing, suctioning off, or centrifuging. The naphtholated material is susceptible to hydrolysis and must therefore be protected against water spots, acid fumes, and an uneven drying to ensure the production of level shades.

To form the dyestuff, the naphtholated material is *developed* with a suitable diazonium compound with regard to shade and fastness properties. An excess of diazonium salt is used to couple all the naphtholate applied to the fiber. Bases which are soluble in hydrochloric acid are diazotized by running into their solution a sodium nitrite solution. Bases which are insoluble in hydrochloric acid are pasted up with sodium nitrite solution and the paste is introduced into dilute hydrochloric acid. The temperature is kept below 10–15°. Since the reaction is exothermic, provision must be made for cooling to prevent decomposition. Gas bubbles and foam formation are signs of decomposition. This is promoted by light, heat, and also by metals acting as catalysts. Therefore copper, tin, and iron containers are unsuitable for diazonium salts.

The diazo solutions, prepared as described, are added to the amount of liquor (cold water) required for development. To prevent the naphtholate previously applied to the goods from dissolving, 20–50 g/l of salt is also added to the liquor. Development generally takes place at room temperature for 20–30 minutes. To simplify the procedure, stabilized diazonium salts have been marketed which readily give the required diazonium solutions when dissolved in water.

To ensure good wet-fastness properties and fastness to crocking, the developed dyeing must be thoroughly rinsed and soaped at the boil with 2–3 g/liter soda or corresponding dilutions with dispersing agents. By this operation the dyeing fixed on the fiber is generally brighter and deeper in shade and often shows an increased fastness to light and to chlorine.

d. Phthalocyanine Developing Dyestuffs (*Phthalogens*). Phthalogen dyes are developed on the fiber from monomeric aminoiminoisoindolenines or from polymeric metal complexes of aminoiminoisoindolenines.[50] With these compounds extremely brilliant blue, turquoise, and green shades are obtained, whose fastness to light is equal to that of vat dyeings and whose wet-fastness properties and fastness to crocking are also very good.

The respective products are insoluble in water and must be dissolved by addition of certain reducing solvents. A suitable copper complex compound, e.g., the copper complex of ethylene-bis-imino-diacetic acid is added to the solution of aminoiminoisoindolenines, and the material is padded with this liquor on a padding mangle after adjustment of the pH to 7 to 8. The padded material is then dried at 70–80° and the dyestuff is developed by heating to 140° for a few minutes. To remove byproducts and excess pigment, an acid passage is first given, followed, after rinsing, by a soaping process at boiling temperature.

e. Reactive Dyestuffs. Since 1956 a new group of dyestuffs has been available for the dyeing of cellulosic fibers. These dyestuffs react chemically with the cellulose fiber, by forming covalent bonds. With reactive dyestuffs, dyeings with maximum wet-fastness properties can be produced in a simple manner. With modern reactive dyestuff ranges the fastness to washing achieved is equal to that obtained with Indanthrene dyes. In addition to the high wet-fastness properties which result from the fiber–dyestuff bond, another feature which has contributed to the success of reactive dyestuffs is the production of extremely brilliant shades on cotton. Dyestuffs of high brilliance in general have only one chromophoric center and therefore are of relatively low molecular weight. For this reason, direct dyestuffs, which must be of a certain molecular size to show sufficient affinity for cellulosic fibers, generally do not exceed

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[50] J. Eibl, *Melliand Textilber.* **39,** **522**; **660**; **772** **(1958)**.

a medium brilliance. As will be discussed in greater detail below, although the affinity also plays a part in the case of reactive dyestuffs, it is not a major role as in that of direct dyes. The molecules of reactive dyestuffs can therefore be built up irrespective of this consideration.

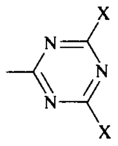
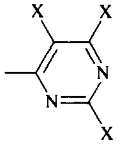
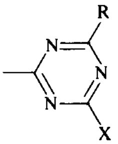
The chemical structure of reactive dyestuffs can be represented as F—R—X, where F is the dyestuff molecule; R, the reactive group; and X, the so-called leaving group. The reaction with cellulose fiber proceeds as follows:

$$\text{F—R—X} + \text{HO—Cell.} \rightarrow \text{F—R—O—Cell.} + \text{XH}$$

As can be seen, the leaving group is split off and is afterwards generally present as an acid anion. The nature of the bond formed with cellulose depends on the type of reactive group. Certain reactive groups form esterlike and others etherlike bonds. Whether the resistance of the dyeing to acid or alkaline hydrolysis is good or bad depends on the type of bond formed. Etherlike bonds are, of course, more resistant to hydrolysis than esterlike bonds. The usual reactive groups are summarized in Table VI.

The rate at which the leaving groups in each case are exchanged by the cellulose anion depends on the reactive group, on the structure of the dyestuff molecule, and on the dyeing conditions. The most important dyeing conditions are the temperature and alkalinity at which the reaction occurs. There are, for example, dyestuffs which react with cellulose

TABLE VI
THE MOST USUAL REACTIVE GROUPS OF REACTIVE DYES

Reactive groups which form ester linkages	Reactive groups which form ether linkages
$-CO-X$	
$-SO_2-X$	
  	$-O-CH_2-CH_2-X$ $-SO_2-CH_2-CH_2-X$ $-CO-NH-CH_2-X$ $-SO_2-NH-CH_2-CH_2-X$ $-NH-CO-CH_2-CH_2-X$ $-CH_2-CHOH-CH_2-X$

in soda-alkaline solution at 20° (reactive group: dichlorotriazine) and those which in soda-alkaline solution react only at 70–80° (reactive group: monochlorotriazine). In all reactive dyestuffs the reaction with the fiber competes with a reaction with water which produces a hydrolysate no longer showing any reactivity with the fiber. The competing reaction with water, i.e., the susceptibility to hydrolysis of the dyestuffs, is all the stronger the higher the reactivity of the respective dyestuff. Care must be taken to reduce the amount of hydrolysate to a minimum by a suitable selection of the reaction conditions, i.e., by suitable methods of application.

A certain affinity of the dyestuffs for the cellulose fiber is required where reactive dyestuffs are applied from a long liquor, since otherwise the bath may not be exhausted. Even in a short liquor ratio, i.e., in continuous and semicontinuous processes, a certain affinity offers an advantage, since a reaction with the fiber does not take place until the dyestuff is bound by absorption to the cellulose fiber.

This absorptive bond is less sensitive to water and atmospheric moisture the higher the affinity of the dyestuff. Dyestuffs with a relatively high affinity can therefore be fixed even in a moist atmosphere, whereas those with a relatively low affinity can be fixed only in an absolutely dry atmosphere (thermofixation).

Reactive dyestuffs can be applied from a long liquor to cotton and viscose staple fiber in all processing stages. Cheeses, warp beams, and piece goods are best dyed with these products on the winch beck or on the jig. As previously mentioned, dyeing in a long liquor ratio must be carried out with selected dyestuffs which possess a certain affinity for cellulose fiber. The fiber is first allowed to take up a certain percentage of the dyestuff from a neutral bath. The dyestuff is absorbed on the surface of the fiber, but no reaction takes place. After dyeing for about 20–30 minutes in a neutral bath, the amount of alkali of the type prescribed for the respective dyestuff group is added. This addition starts the reaction with the fiber. As the reaction with the dyestuff absorbed by the fiber proceeds, further dyestuff is taken up from the liquor by absorption and, finally, is chemically bound.

The curve shown in Fig. 1 illustrates the course of the dyeing process. The curve shows that before the alkali addition a certain saturation of the fiber is brought about by absorptively bound dyestuff and that after the addition further dyestuff is taken up by the fiber. The difference between the broken and the full line represents the amount of dyestuff absorbed, but not bound, by the fiber. The height of the broken line shows the so-called fixation yield of the respective dyestuff. Where reactive dyestuffs are used in mixtures, care must be taken to ensure that the

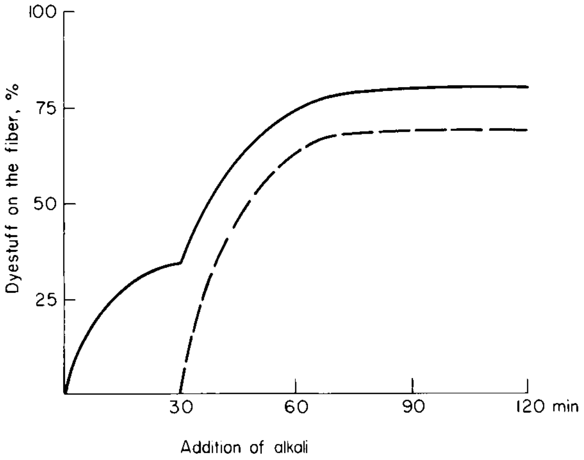


FIG. 1. Absorption curves for reactive dyes applied from long liquor. (——: total quantity of absorbed dyestuff; — —: chemically fixed dyestuff.)

fixation curves follow approximately the same course to avoid differences of shade between ends.

A typical dyeing method for reactive dyestuffs in the exhaustion process is as follows: The dyestuff is added to the bath at 20–25°, 30 g/liter of sodium sulfate is added after 10 minutes and 5 g/liter of soda, previously dissolved in water, after a further 20 minutes, dyeing then being continued for 1 hour at 20–60° (according to dyestuff group). The dyeings are then rinsed thoroughly and soaped at the boil for 20–30 minutes.

The selection of the dyeing temperature depends on the respective dyestuff group. Cold-dyeing types, i.e., quick-reacting dyestuffs such as derivatives of dichlorotriazine, can be dyed at 20–25°. Warm-dyeing types, e.g., derivatives of monochlorotriazine, must be dyed at 50–60°. A part is also played in the selection of the dyeing temperature by the size of the molecule, i.e., the rate of diffusion. Dyestuffs with large molecules, such as those always present in the turquoise brands, must therefore generally be dyed at a high temperature (70–80°), since at lower temperatures insufficient diffusion takes place and the fixation yield is therefore reduced.

Selection of the temperature also depends on the goods to be dyed. Viscose staple piece goods, for example, are best dyed at 70°, since at this temperature the so-called wet-stiffness resulting from the absorption of water of hydration is reduced to a minimum. In this case, alkali is added in portions to control the reactivity of the dyestuffs in such a manner that the reaction of the dyestuff with water does not predominate. The alkalinity is thus increased gradually to the final pH value.

The higher affinity of regenerated cellulose fibers for dyestuffs applies equally to reactive dyestuffs and is counteracted by using only small quantities of sodium sulfate.

2. *Continuous and Semicontinuous Dyeing Processes*

Continuous processes are particularly important for cotton and regenerated cellulose fibers because textiles produced from these fibers are often dyed in larger quantities in one and the same shade.

To produce continuous dyeings on piece goods, the dyestuff is applied on the padding mangle, of which there are various constructions. In principle, the goods are always passed once or several times through the dye liquor and are then squeezed evenly in full width between two rollers, once or several times. It is most important that the textiles should retain a definite amount of dye liquor and, therefore, also an exactly calculated amount of dyestuff. In this way the dyestuff is applied evenly to the goods, although fixation is not yet obtained. The fixation process depends on the nature of the textile material and on the dyestuff type.

In all padding processes it is important that little or no dyestuff should be taken up substantively during the passage of the goods through the liquor in the trough, since in course of time the strength of the dye liquor would otherwise be reduced. This leads to differences between ends, i.e., differences of shade between the beginning and end of a run. To avoid differences between ends, the immersion time for the goods must be reduced to a minimum (small trough), or else the affinity must be reduced by raising or lowering the temperature.

a. Direct Dyestuffs. Since the solubility of direct dyes required for pad liquors is generally attained only at higher temperatures, a selection must be made of those dyestuffs which at a higher temperature do not show a particularly high affinity for cotton. The dyestuff solution is applied as previously described. The fixation of direct dyestuffs is best obtained on cellulosic fibers in a steam medium. A steamer is used, in which the fabric is subjected in open width for 1–3 minutes to saturated steam at about 100°. Dry heat or superheated steam are not suitable to obtain complete fixation of direct dyes. It has been found that the presence of *moisture* is indispensable for fixation of the dyestuffs. Depending on the rate of fixation speed, direct dyestuffs are divided into groups requiring a more or less prolonged steaming time.

A continuous dyeing plant for direct dyestuffs consists, accordingly, of padder and steamer with adjacent washing units, known as a *pad-steam plant.* The first baths of the washer may, of course, be used for aftertreatments with cationic products to improve the wet-fastness properties, or with copper sulfate/acetic acid to improve the wet-fastness properties and the fastness to light of copper-developed dyestuffs.

Semicontinuous dyeing may be carried out on a *pad-roll plant*. Padding is carried out with direct dyestuffs and fixation of the batched-up material is then obtained discontinuously in interchangeable steam boxes. This is a quasicontinuous process, since padding is continuous and fixation is obtained in several steam boxes, where the material rotates in a saturated steam atmosphere at 70–95°, according to dyestuff type. Before the material runs into the steam box, it passes through an infrared heating zone to bring it up to the required temperature. Depending on the required depth of shade, the batched-up material remains in the steam box for 3 to 6 hours. The material is then unrolled and passes through a washer. Any aftertreatments can be given, also in this case, on the washing unit.

The *pad-jig process* is also a semicontinuous method which is used, in particular, in the dyeing of linings made from viscose filament. The material is padded, as described above, fixation of the dyestuff then being obtained on the jig. Over a pure jig-dyeing this method offers the advantage of an even dyestuff application during longer runs.

b. Vat Dyestuffs. The above-mentioned pad-steam process is widely used for vat dyestuffs. The general procedure is to pad the vat dye in pigment form and to impregnate the material with alkaline sodium dithionite solution shortly before entry into the steamer. Reduction to the leuco compound and its fixation on the goods then take place in the steamer. Oxidation and soaping at the boil are carried out in the following washbaths after the steamer passage.

In this process, differences of shade between ends caused by affinity will not occur, since the dyestuff is applied in pigment form, which possesses no affinity. The steamer must be free from air, since a premature reoxidation of the dyestuff may otherwise take place. This process is also often used for polyester/cotton and polyester/viscose staple blends when the cellulosic component is to be dyed with vat dyestuffs (see also Section II,C,2).

In the so-called *Standfast process*, the fixation of the reduced dyestuff takes place in molten metal at 95–105°. This method, however, is used only very seldom.

The fixation of Indanthrene dyestuffs on the above-mentioned principle of the pad-jig process is often used for smaller batches. The dyestuff in pigment form is padded, vatting and fixation subsequently being carried out on the jig.

c. Naphthol Dyestuffs. Because of the rapidity of dyeing, naphthols are particularly suitable for continuous processes. The material is padded on the padding mangle at the highest possible temperature (90–100°) with the dissolved naphtholate, which possesses a minimum affinity. Squeezing is then carried out uniformly, followed by intermediate continuous drying on a hotflue (hot air, without tension), cylinder drying machine (contact heat), or stenter frame (hot air, with tension). A formaldehyde addition is not required, since the naphtholate is sensitive to air only in moist condition, while at higher temperatures insoluble compounds may be formed from naphtholate and formaldehyde.

After intermediate drying, the material is led through the developing liquor, previously adjusted to a definite pH value and buffered. The short passage is insufficient to achieve full coupling and a subsequent air passage is therefore arranged next to the padder. In the continuous method, it is particularly important to maintain a definite pH value during the entire developing process, since the coupling activity changes with a varying pH value and differences of shade between ends may therefore be obtained.

d. Reactive Dyestuffs

i. Cold pad-batch process. A process which has gained particular importance for reactive dyestuffs is the cold pad-batch process on cotton and viscose staple fiber. In this process, the material is padded with the alkali-containing dyestuff solution, squeezed to a certain increase in wet weight and then batched up. With the roll slowly rotating, the reaction with the cellulose fiber is allowed to proceed until complete. Depending on the reactivity of the reactive dyestuffs and on the type of alkali used, the time required to obtain an optimum fixation amounts to between 2 and 24 hours. For most reactive dyestuffs, such as those of the dichlorotriazine type, the following procedure is used: The fabric is padded on the padding mangle with a dyestuff solution containing an equal quantity of soda dissolved in water, and is then immediately rolled up and protected from drying by a plastic foil covering. After about 2–4 hours (depending on the depth of shade), the fabric is rinsed and soaped at the boil. Because of the high reactivity of this dyestuff group, the alkali-containing dyestuff solution remains stable for a maximum of 15 minutes. To dye longer runs, an automatic metering device is required for alkali and dyestuff. In this process, alkali and dyestuff solution are stored separately and enter the padder trough only just before application to the fabric. Feed and metering are controlled by a pump. Dyestuffs of medium reactivity remain stable for several hours and no metering device is therefore required. The reaction time then amounts, however, to 8–22 hours. Dyestuffs with a low reactivity, e.g., derivatives of monochlorotriazine, must be fixed with caustic soda or other strong alkalies and need at least 24 hours to obtain an optimum degree of fixation. Because of the strong alkali, a metering device is also recommended in this case to prevent hydrolysis in the padding mangle.

ii. Pad-cure and pad-steam processes. For application in continuous processes those reactive dyestuffs which have little affinity for cellulose fiber are most suitable. The dyestuffs are applied on the padding mangle, as described for the cold pad-batch process, the alkali being added beforehand or with a metering pump according to reactivity. Fixation of the padded material is obtained continuously (a) by steaming, or (b) by a treatment in dry heat. The duration of the steam treatment depends largely on the reactivity of the dyestuffs and on the alkali used. Highly reactive dyestuffs can be fixed with soda in 30–60 seconds. Slowly reacting dyestuffs require about 3–10 minutes.

Fixation in dry heat is carried out at about 140–150° in 30–60 seconds. An addition of about 100 g/liter of urea to the dye liquor is recommended when fixation is to be obtained in dry heat. The urea addition considerably increases the yield of fixed dyestuff. In any case, rinsing in hot water is carried out continuously after dyeing. The lower the affinity of the dyestuff groups used, the more easily any hydrolyzed dyestuff remaining on the fiber can be washed away. Thorough washing is in any case indispensable, since hydrolyzed dyestuff residues on the fiber simulate poor wet-fastness properties.

The fixation of reactive dyestuffs in dry heat plays a particularly important part in the dyeing of polyester cotton blended fabrics, since in this way the polyester and cotton components can be dyed simultaneously in a single step. The procedure adopted is to dissolve or disperse the reactive and disperse dyestuffs together and to apply them to the blended fabric on the padder. The dyeing is then dried and the disperse dyestuff is fixed on the polyester fiber by the thermosol process. During this time, the reactive dyestuff undergoes no reaction with the fiber because no alkali is present. After fixation in heat, the fabric is treated with the alkali solution on a second padder, then dried again and steamed or subjected to a heat treatment to fix the reactive dyestuff. Provided that suitable dyestuffs are selected, the process can be simplified still further by padding a liquor which contains alkali, disperse and reactive dyestuffs together, as well as thickening agent. This, of course, is only possible with a selected range of both dyestuff groups, which are stable to alkali. Padding and drying are followed by thermosol fixation. The disperse and reactive dyestuffs are both fixed by the hot air treatment. Rinsing and soaping are then carried out in the usual way.

e. Pigment Dyestuffs. Dyeing with pigment dyestuffs is different from the traditional dyeing processes in certain important respects. The insoluble color pigments used are applied to the fiber in this form. They possess no affinity for the material and are not bound by intermolecular forces, but are fixed with the aid of a binding agent. While the conventional, soluble dyestuffs (or those which pass through a soluble intermediate stage, such as vat dyes) are taken up in molecular form, or slightly associated, pigment dyestuffs are always present in larger molecular agglomerates and, because of their lack of affinity, are not taken up by the fabric. For this reason only padding processes can be used. On the other hand, the pigment process can be used on *all* fiber types which are resistant to the temperatures employed during the dyeing process. For this reason, solid shades can also be obtained on blended fabrics in one operation. Since the final shade can be recognized immediately, matching to pattern is simpler than in the classic processes. Most pigments possess a very good fastness to light. The other fastness properties, such as crocking, washing, and solvent, are governed mainly by the type and stability of the binding agent.

The binding agents form on the fiber an invisible film which envelops the pigment particles, fixation on the fiber thereby being obtained. The binder film must be elastic, i.e., neither brittle nor tacky, and its properties must undergo the least possible change during subsequent use of the textiles (washing, ironing). The film must be resistant to aging and must not become brittle or yellow under the action of light and heat. It must not impair the handle of the goods.

Polyacrylates, in particular, are used as binding agents. To obtain films and dyeings which are sufficiently resistant to washing and to solvents, the substances used for film formation must be capable of cross-linking either with themselves or with another component. In general, an aqueous dispersion is nowadays considered the most favorable medium for binders.

Pigment dyestuffs are applied only to piece goods, i.e., woven, knitted, and, possibly, to nonwoven fabrics, in which case the pigment binder is also used as a fiber-bonding agent. The procedure comprises padding, drying, and fixation. Precise instructions cannot be given, since binders of widely varying types may be used in the pigment processes.

The material to be dyed, carefully freed from size and chemicals and evenly dried, is padded at room temperature on a padding mangle equipped with uniform squeeze-rolls. The liquor pickup must be reduced to a minimum (60–80%) to prevent, as far as possible, any migration of the pigment during drying. The material should be dried at temperatures between 80° and 120° immediately after padding. Suitable drying equipment consists of hotflue, stenter, or cylinder drying machine where the material is led over the cylinders on alternate sides. It is particularly important that the material is heated evenly over its full width, since differences of shade may otherwise occur at the edges. After drying, cross-linking of the binder is obtained in a heat treatment. The dyeings now attain their optimum fastness properties. Fixation is generally obtained in 5 minutes at 140°. The time of treatment can be reduced by increasing the temperature.

After fixation, the pigment dyeing process is completed. In contrast to the classic processes, where dyeing is always based on an equilibrium between dyestuff in the liquor and dyestuff on the fiber, all the dyestuff used in this case is fixed completely. In the pigment process no after-treatment is required to remove any unfixed or superficially attached dyestuff which would reduce the fastness to crocking.

3. *Dyeing of 2½ Acetate*

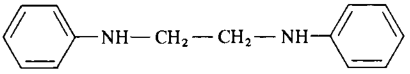
Certain general rules must be observed in the dyeing of 2½ acetate. Temperatures exceeding 70–80° and alkalies must be avoided, since 2½ acetate is extremely susceptible to hydrolysis and under these conditions loses the luster which is typical of this fiber. In the manufacture of acetate, most of the alcoholic hydroxyl groups of cellulose are esterified, so that direct dyestuffs generally have little or no affinity for acetate fibers.

a. Disperse Dyestuffs. The most frequently used dyestuff group for acetate is that of disperse dyestuffs, which are taken up in the form of a dispersion by acetate fiber. The dyeings obtained possess really good all-around fastness properties.

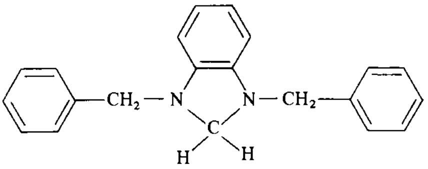
Dyeing method: The disperse dyestuffs, which already contain dispersing agents, are pasted up with water at 40–50° and added to the dyebath, which also contains dispersing agents or alkali-free soap. The material is dyed for ½–1 hour at 60–75° and is then thoroughly rinsed and dried.

b. Basic Dyestuffs. Basic dyestuffs are used where very bright shades are required, particularly in the presence of additions with a swelling effect, such as zinc salts, pyridine, sodium phenolate, etc. The dyestuff yield increases with rising temperature and rising pH value (pH 3–7). The material is dyed for about ¾ to 1 hour at 70°.

Since acetate fibers absorb nitrous gases, the dyeings—particularly those based on anthraquinone—are considerably sensitive to the oxidizing action of these gases. To counteract this effect, inhibitors are added either to the acetate spinning solution or to the dyebath, or else they are applied in a further process after dyeing. These inhibitors capture the nitrous gases by means of basic nitrogen-containing groups. Very good inhibitor effects are shown, *inter alia*, by *N,N'*-diphenyl ethylene diamines (XXX) and benzimidazolidines, e.g., *N,N'*-dibenzylbenzimidazolidine (XXXI). Most inhibitors are insoluble in water, and are applied and taken up in the same way as disperse dyestuffs.



(XXX)



(XXXI)

4. *Dyeing of Triacetate*

Since in triacetate fibers all the alcoholic hydroxyl groups are esterified, so that the fiber has a marked hydrophobic character, they behave towards dyestuffs in a similar manner to synthetic fibers and, like these, are nearly always dyed with disperse dyestuffs, medium to good all-around fastness properties being obtained.

a. Disperse Dyestuffs. The rate of absorption of disperse dyestuffs depends on the swelling power of the fibers. On triacetate fiber the rate of absorption is higher than on polyester fiber, but lower than on 2½ acetate. Disperse dyestuffs with high fastness to washing diffuse slowly into the fiber core, give ring dyeings (viewed in cross section, the fiber interior is less heavily stained than the periphery) and require higher dyeing temperatures. The use of carriers (fiber-swelling dyeing accelerators) in the dyebath increases the rate of absorption, improves penetration, and ensures a good exhaustion of the baths in normal dyeing times, even in heavy shades.

The heat setting of triacetate is best carried out after dyeing, since this process reduces the affinity of the fiber for dyestuffs. Further advantages of a heat treatment after dyeing are, *inter alia*, improvement of the dimensional stability by a permanent setting of the fiber in woven or knitted fabrics, the possibility of permanent pleating or embossing, and an improvement of the fastness properties by further diffusion of the dyestuff into the fiber.

Regenerated cellulose is formed on the surface of triacetate fiber by a superficial saponification, the so-called S-finish (silk finish), which is carried out prior to dyeing. This process offers the following advantages: a soft, silky handle, a higher ironing temperature, higher tensile strength, an antistatic effect, and an improvement of the fastness to ozone of the dyed material. The S-finish can be given only to woven and knitted fabrics in full width, since the formation of folds would result in an uneven saponification of the textile surface. Scouring of the material to remove spinning chemicals can be carried out simultaneously with the S-finish. This is best done in a short liquor ratio with about 2 g/liter of a nonionic detergent, 3 g/liter of trisodium phosphate, and 20 ml/liter of caustic soda 38°Bé for 2 hours at 95°. The degree of saponification can be determined with suitable direct dyestuffs, which cause a more or less heavy staining of regenerated cellulose.

Dyeing method: The disperse dyestuffs are stirred into about 10 times their weight of warm water containing about 2 g/liter of a dispersing agent. Further dilution is then carried out with water at 80°. The material is run at 40–50° in a liquor adjusted with formic or acetic acid to pH 4.5–5 and set with 1–4 g/liter of a dispersing agent and 0–6 g/liter of a carrier, depending on depth of shade and liquor ratio. After a good temperature and pH equilibrium has been attained in the material, the thoroughly dispersed dyestuff is added and the temperature is raised to 80–85° in 15–20 minutes. Dyeing is continued at this temperature for about 20 minutes and the liquor is then gradually brought to the boil. Depending on the required depth of shade, the dyeing process is completed at that temperature after 1–2 hours. Finally, the material is well rinsed, dried, and heat-set. This can be done (a) in dry heat for 12–15 seconds at 205–220°, or (b) in saturated steam for 30 minutes at 110–125°.

b. Disperse Dyestuffs under High Temperature Conditions. When dyeing is carried out under high temperature conditions, a carrier addition is not usually required, except in the case of heavy shades where small amounts offer an advantage. The dyebath is adjusted with formic or acetic acid to pH 4.5–5, and 0.5–1 g/liter of a heat-resistant leveling agent is added. Dyeing is started at 40°, the temperature of the bath is increased in 30 minutes to the boil, and then in a further 30 minutes to the final temperature of 120°. Depending on the required depth of shade, the high temperature process is completed in 1–2 hours. Under HT conditions, heat-setting of the material is accomplished simultaneously and no aftertreatment is therefore required in this case.

After heat-setting, or on conclusion of the HT process, scouring is recommended, while inhibitors can be added, if necessary, to improve the fastness to gas fading, as well as antistatic agents and softeners. The material is scoured with an addition of 1–3 g/liter of a nonionic detergent for 30 minutes at 50°.

c. Continuous Dyeing of Triacetate with Disperse Dyestuffs by the Thermosol Process. For this application, disperse dyestuffs in paste form are best used, since they are simpler to manipulate and, because of their lower content of diluent and dispersing agent, show a higher yield. The pad liquor contains x g/liter of dyestuff, 5–10 g/liter of a good dispersing agent, and 1–5 g/liter of a suitable thickening agent (e.g., a neutral alginate). The material is padded continuously at 40°, with a liquor pickup of about 60%. Intermediate drying is carried out at 100–140°, followed by heat setting for 60 seconds at 190–215°. Depending on the depth of shade, the dyeings are scoured or given a reduction cleaning with alkali and sodium dithionite.

B. Dyeing of Wool

1. *Discontinuous Dyeing Processes*

The absorption of dyestuffs in the case of wool is largely determined by its amphoteric nature. For this application the main dyestuff groups are acid dyestuffs, which react with the basic groups of wool, forming saltlike linkages. In small-scale application are also basic dyestuffs, whose color cation forms a bond with the wool carboxyl anion. In addition to main and secondary valency bonds, a certain amount of adsorptive binding must also be assumed. The histological structure of wool is very important for the diffusion of dyestuffs into the fiber.

The discontinuous dyeing of wool can be carried out in various processing stages, namely as (a) loose stock: on the pack system; (b) worsted wool: on the pack system, tops; (c) yarn: on the hank dyeing machine (stationary goods, liquor in motion), in the cheese dyeing machine; (d) piece goods: on the winch beck (as free from tension as possible), beam dyeing apparatus. In principle, the different machines are as described under cotton (Section I,A,1), although in the case of wool care must always be taken to ensure minimum mechanical stresses to prevent any objectionable felting and shrinkage.

a. Acid Dyestuffs. The wool fiber is dyed in an acid medium with anionic dyestuffs. Under these conditions, the dissociation of the carboxyl groups of the wool is diminished, and the amino groups are converted to ammonium groups by acceptance of a proton. The amino groups are therefore present as reactive ammonium ions in a percentage which depends on the respective pH value. The dyestuff itself is also dissociated in water and its anion is bound to the wool electrostatically by ammonium groups. The dyestuff absorption increases in this way as the pH falls, attaining a maximum at a pH which depends upon the nature of the dyestuff.

$$\begin{array}{llll}
\mathrm{HOOC{-}W{-}NH_2} + & \mathrm{H^+} & \rightarrow & \mathrm{HOOC{-}W{-}\overset{+}{N}H_3} \\
\mathrm{HOOC{-}W{-}\overset{+}{N}H_3} + & \mathrm{Dst{\cdot}SO_3^-} & \rightarrow & \mathrm{HOOC{-}W{-}\overset{+}{N}H_3[(O_3S{\cdot}Dst)^-]} \\
\text{Wool cation} & \text{Dyestuff anion} & & \text{Wool–dyestuff salt} \\
(\text{W} = \text{Wool}) & (\text{Dst} = \text{Dyestuff}) & &
\end{array}$$

Since dyeing is carried out in the presence of acids (sulfuric, formic, or acetic acid), acid anions are also present and compete with the dyestuff anions for the occupation of positively charged positions on the wool fiber. Because of their smaller molecular size, the acid anions diffuse more rapidly into the wool fiber and at first take possession of the available cationic groups. The color acid anions have a higher affinity for the charged amino groups, however, and gradually displace the smaller anions, occupying their positions.

$$\mathrm{HOOC{-}W{-}\overset{+}{N}H_3HSO_4^-} + \mathrm{(Dst{\cdot}SO_3)^-Na^+} \rightarrow \mathrm{HOOC{-}W{-}\overset{+}{N}H_3[(O_3S{\cdot}Dst)^-]} + \mathrm{NaHSO_4}$$

According to the described conditions, the affinity of wool for acid dyestuffs decreases with rising pH value. Consequently in alkaline medium acid dyestuffs are more or less removed from the wool fiber. By contrast, an acid aftertreatment of wool dyeings produced with acid dyestuffs in a neutral medium improves the wet-fastness properties.

Acid dyestuffs show considerable differences with regard to their affinity for wool. To avoid uneven shades, dyestuffs with a high affinity must be dyed in a less acid medium, so that the number of ammonium cations does not attain a high value. The application of dyestuffs with a lower affinity can be started in a more acid medium without any risk of uneven results.

Those dyestuffs which are applied in a strong acid medium are known as well-leveling dyestuffs because of the low strength of the bond formed with the wool fiber and the migrating power which this entails.

Owing to the stronger bond formed with the wool fiber by those dyestuffs which are applied in a weak acid medium, level dyeing is more difficult to achieve and care is required, i.e., dyeing must proceed slowly and with little acidity. These dyeings nevertheless possess better wet-fastness properties than those of the well-leveling dyestuffs. On the other hand, the latter brands offer the advantage of higher fastness to light.

i. Dyestuffs to be applied in a strong acid medium. These dyestuffs are used where (a) a short dyeing process is required, e.g., in the case of wool with a strong tendency to felting, or (b) where perfect penetration and levelness must be guaranteed, e.g., in the dyeing of fashionable goods on the winch beck when high wet-fastness properties are not required.

Dyeing method: The dyestuff is dissolved by pasting up in cold water and addition of hot water, and the dyebath is set with 10–20% Glauber salt and 3–4% sulfuric acid 96% (initial pH about 1.8). The percentages are calculated on the weight of the goods. The material is entered, the bath is brought to the boil and dyeing is completed at boiling temperature in ¾ to 1½ hours. The dyebath is then allowed to cool indirectly to at least 80°, after which the material is rinsed thoroughly and dried.

The addition of Glauber salt to acid baths assists in leveling. The dissociation of the dyestuff is suppressed by the large number of sodium ions, so that it remains longer in solution and is taken up more slowly.

ii. Dyestuffs to be applied in a weak acid medium. Such dyestuffs are used for knitted goods and hosiery in heavier shades, ladies' dress-goods, milled goods, etc.

Dyeing method: The dyestuff is dissolved as described above, and the dyebath is set with 10–20% Glauber salt and 3–5% acetic acid 30% (initial pH about 3.5). The material is entered at 40–50°, the bath is gradually brought to the boil and dyeing is continued at boiling temperature for a further ½ to ¾ hour. If necessary, complete exhaustion of the dyebath can be achieved by further addition of acid.

b. Chrome Dyestuffs. Certain ranges of anionic dyestuffs are capable of binding chromium in complex form. These chromium complexes show reduced solubility in water, and an improvement of the fastness to washing is therefore achieved. The electrostatic bond formed between color acid anions and ammonium ions of the wool is augmented in this case by the coordinate bond between the dyestuff–chrome complex and undissociated amino groups of the wool. A particularly good fixation of the dyestuff is therefore obtained on the fiber, so that these dyeings possess a particularly high fastness to washing. Chrome development also has a tanning effect on wool, and wools dyed in this way are to a large extent resistant to attack by microorganisms. Chrome development may be carried out by three different methods: the prechrome process, the afterchrome process, and the synchrome process (in the latter case, chrome development and dyeing are carried out simultaneously). The afterchrome process has gained most importance; it ensures optimum fastness properties and is suitable for numerous dyestuffs.

i. Afterchrome process. A suitable acid dyestuff which is capable of chrome development is first dyed on wool by the method described under Acid Dyestuffs, Section II,B,1,*a* and the dyeing is chrome-developed, after exhaustion, in the same bath. The bath must first be cooled to at least 70°, since an uneven chrome development and an oxidation of the wool may otherwise occur. Sodium bichromate, chromates, or chromic fluoride are used. Since only trivalent chromium can form a complex with the dyestuffs, chromates and bichromates must first be reduced. In the afterchrome process this is brought about by the wool itself, while in other cases organic acids with a reducing action are used. The amount of chromium salt to be used depends on the required depth of shade and is normally equal to one-half of the dyestuff percentage, but in any case not less than 0.1% and not more than 3% of chromate being used. After addition of the chromium salt, the bath is again brought to the boil and chrome development is achieved after ¾ to 1 hour at boiling temperature. The dyeings are then rinsed thoroughly and dried in the usual way.

These are the fastest dyeings on wool. They are used mainly for suitings, overcoatings, uniform cloths, and many other applications.

c. Premetallized Dyestuffs. Two groups are distinguished, namely (a) 1:1 chrome complex dyestuffs, and (b) 2:1 metal complex dyestuffs. Both groups offer the advantage of an easier application than in the case of chrome dyestuffs, since an additional chrome developing process is not required. Matching to pattern is also simplified, since there is no need to allow for the change of shade associated with chrome development.

i. 1:1 Chrome complex dyestuffs. These dyestuffs comprise the older group. They are acid dyestuffs whose chrome complexes are still so freely soluble that there are no difficulties in application. In the interest of level dyeing, they must be dyed with relatively high amounts of sulfuric acid, which may have an adverse effect on the quality of the wool, particularly where the dyeing time is prolonged. The amount of sulfuric acid can be reduced accordingly when a good leveling agent is used. The fastness properties are much better than those of acid dyestuffs, but do not attain the same level as chrome dyestuffs. 1:1 Chrome complex dyestuffs are used for the dyeing of cloths in medium shades, knitting yarns in heavy shades, bathing costumes, etc.

Dyeing method: In addition to the dyestuff, the dyebath contains 5–10% sulfuric acid 96%, according to dyestuff and liquor ratio, and also, possibly, a leveling agent. The goods are entered at 40°, the liquor is brought slowly to the boil, and dyeing is completed after about 1½ hours at boiling temperature. The dyeings are then rinsed thoroughly and dried in the usual way.

ii. 2:1 Metal complex dyestuffs. In addition to electrostatic and coordinate bonds, certain dissolving processes also play a part in the case of 2:1 metal complex dyestuffs.[51] These are generally dyestuffs whose solubility is not determined by sulfo groups, but by other hydrophilic groups, such as $-SO_2NH_2$, $-SO_2CH_3$, $-SO_2NHCH_3$, etc. 2:1 Metal complex dyestuffs are less susceptible to pH variations. Their fastness properties closely approach those of afterchrome dyestuffs, over which, however, they offer the advantage of a simple and protective method of application. They are particularly notable for good leveling and penetration.

Dyeing method: The dyebath is set with 1–3% acetic acid 60% (pH 4–6.5) and with about 10% Glauber salt. The material is briefly run at 40–50° with addition of 1–2% of a wetting auxiliary, the dyestuff is added, and after a further short run the bath is brought to the boil in 30–45 minutes. The dyeings are thoroughly rinsed and dried.

d. Reactive Dyestuffs. Selected members of the different reactive dyestuff ranges are dyed on wool by various processes which are specific to the dyestuffs. One of the main difficulties is in the production of *level* shades. Since these cotton dyestuffs contain several sulfonic acid groups, migration difficulties are experienced in the dyeing of wool, while the affinity in a neutral bath is also reduced. In principle, dyeing is therefore carried out with auxiliaries which block most of the sulfo groups, thereby facilitating the production of level shades. Stable quaternary compounds are used in conjunction with a dispersing agent. A great deal of care is, however, required, since any excess may reduce the solubility of the dyestuffs to such an extent that a troublesome precipitation occurs. A better behavior is shown by polyethylene glycol amino derivatives, which are cationic only in an acid medium and in this way also block a part of the color acid anions. The required amounts of these auxiliaries depend on the type and amount of the dyestuff and on the nature of the auxiliary.

Dyeing method: The dyebath is set with dyestuff, auxiliary, and 10% Glauber salt. The initial pH is adjusted to 4–5 with acetic acid, ammonium acetate, or a similar substance. The liquor is slowly brought

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[51] G. Schetty, *Textil-Rundschau* **11,** **216**; **263** **(1956)**.

to the boil and dyeing is continued at boiling temperature until the bath is practically exhausted. The dyebath is then cooled somewhat and the liquor is adjusted with ammonia to pH 6–8, depending on the reactive group. Dyeing is continued at this pH for about 15 minutes, an improved fixation thereby being obtained, since the reactivity of reactive dyestuffs increases with rising pH value. The thoroughness of this subsequent fixation largely determines the fastness standard attained with reactive dyestuffs. In any case, a part of the reactive dyestuff is bound in a similar manner to acid dyestuffs. Depending on the reactive group, the values vary between 5% and about 30%, which explains why certain fastness properties do not attain the expected standard, particularly alkaline perspiration, wet- and milling-fastness properties. Dyeings obtained with reactive dyestuffs are nevertheless notable for good fastness to washing at 50°, even after several washes, very good fastness to potting and brilliant shades.[52,53]

e. Wool Label. According to the specifications and fastness requirements issued by the International Wool Secretariat (IWS) in 1968, wool for articles which are fast to mechanical washing must (a) be nonfelting and nonshrinking, and (b) possess good fastness to washing at 50°, particularly after several washes. From this standpoint, a much wider use of reactive dyestuffs on wool is to be expected. The most usual method of obtaining a nonshrink finish is nowadays oxidation with potassium permanganate, chlorination, peracetic acid, Caro's acid, etc. Nonfelting finishes on wool sometimes cause a change in the affinity of wool for dyestuffs and may therefore result in changes of shade.

2. *Continuous Dyeing of Worsted Wool*

Although cellulosic and synthetic fibers have now been dyed for many years by the continuous method, wool is still mostly dyed discontinuously. The continuous dyeing of worsted wool has, however, been gaining in importance recently, firstly because suitable dyeing units are now available, and secondly, because the development of suitable auxiliaries and processes permits of perfect fixation of the dyestuffs on the fiber. Among the various possibilities, the so-called coacervation process based on the formation of a two-phase system in the impregnation liquor has attained the greatest importance.[54] The dyestuff is dissolved with addition of a suitable coacervation auxiliary (e.g., condensation products consisting of fatty acids and alkylolamines or alkylaryl polyglycol ethers with or without solubilizing groups) and the solution is separated by addition

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[52] A. Derbyshire and G. Tristram, *J. Soc. Dyers Colourists* **81,** 584 (1965).

[53] A. Hadfield and D. Lemin, *J. Textile Inst.* **51,** 1351 (1960).

[54] M. Milićevic and F. Kern, *Textil-Rundschau* **16,** 190 (1961).

of water into two aqueous phases, demixing of which is prevented by addition of thickening agents with a minimum solids content (e.g., solubilized carob bean gum products or similar substances). The oleaginous phase contains much auxiliary and the dyestuff in dissolved form, while the other—aqueous phase or equilibrium liquid—contains little auxiliary and virtually no dyestuff. The auxiliary must possess good wetting properties, improve the solubility of the dyestuffs, facilitate a rapid and uniform penetration of the dyestuff into the fiber, and prevent an objectionable frosting effect (in this case, the distribution in the wool pile is uneven, so that the tops of the fiber contain lower amounts of dyestuff). In the continuous dyeing of wool four operations are required, namely, padding, steaming, washing, and drying.

The following are a few formulas which may be modified according to the type of auxiliary and process used.

(a) Production of a pad liquor for acid and metal complex dyestuffs:

x g/liter	Dyestuff
15–30 g/liter	Auxiliary
30–40 g/liter	Acetic acid 30%
8–12 g/liter	Thickening agent
Balance water	

(b) For chrome dyestuffs which are easily chrome-developed with trivalent chromium:

x g/liter	Dyestuff
15–30 g/liter	Auxiliary
10–30 g/liter	Chromic fluoride
30 g/liter	Formic acid 85%
8–12 g/liter	Thickening agent
Balance water	

(c) For chrome dyestuffs which are not developed with trivalent chromium:

x g/liter	Dyestuff
5–12 g/liter	Sodium monochromate
20–30 g/liter	Acid donor (organic salt; in the interest of a good yield the pH must only rise slowly)
0–10 g/liter	Acetic acid 30%
8–12 g/liter	Thickening agent
Balance water	

The worsted wool is generally padded evenly with an emulsion of this type in the nip of a horizontal padding mangle and squeezed to a liquor pickup of 100–120%. The aqueous phase is absorbed into the fiber, while the oleaginous phase forms a practically homogeneous film round the fiber. Under these conditions the dyestuff-containing coacervate possesses no affinity for the wool fiber and a uniform dyestuff application to the fiber is therefore assured. Fixation of the dyestuff is obtained by treatment of the padded material with saturated steam. The dyestuff migrates to the interior of the fiber during steaming. Acid and metal complex dyestuffs are steamed for 10–30 minutes at 100° or 5–20 minutes at 108°, while chrome dyestuffs are steamed for 30–45 minutes at 100°.

To remove auxiliary, thickening, and any insufficiently fixed dyestuff, the dyeings are washed with warm water at 50° in several boxes of the back-washing machine. From the back-washing machine the worsted wool passes into a drier.

a. Vigoureux Printing. Melange yarns can be produced by mixing together differently dyed fiber material (mainly wool) as loose stock, slivers, or combed material. In vigoureux printing, cross-stripes are printed by means of relief printing rollers on worsted material which has been transformed into a fine fleece by a steel comb system. The worsted material printed in this way is steamed to obtain fixation of the dyestuff, aftertreated on the back-washer, and then doubled and stretched. The melange thus obtained is much more homogeneous, since the single fiber already contains the respective color components of the melange.

C. DYEING OF SYNTHETIC FIBERS

a. Dyeing of Polyamide Fibers with Acid Dyestuffs

For the dyeing of polyamide fibers, acid dyestuffs of various categories are used in the vast majority of cases. The dyeing mechanism is based on the diffusion of the dyestuff, which contains sulfo groups, into the polyamide fiber, where a saltlike bond is formed predominantly with terminal amino groups. When the pH is reduced below a certain level, a much higher dyestuff absorption takes place on polyamide fiber than above this limiting value. This is because the acid dyestuff at pH values above approx. 2 is bound only by the terminal amino groups and below that also by activated carbamide groups[55] (Fig. 2). Since, however, the dyestuff bound in this way under very strong acid conditions is easily released again in a weaker acid medium, the poor wet-fastness properties do not allow this method to be used.

A salient feature in the dyeing of polyamide with acid dyestuffs is that from the well-known ranges used for wool dyeing only certain members can be selected, generally monosulfonic acids which are compatible with one another and which do not lead to a mutual blocking. If dyestuffs

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[55] T. Vickerstaff, "The Physical Chemistry of Dyeing," p. 463ff. Oliver and Boyd, London (1954).

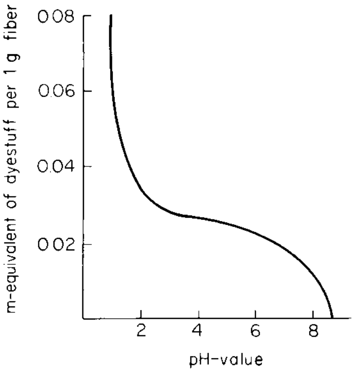

FIG. 2. Dyestuff absorption of polyamide related to pH value.

with too widely varying affinities are combined (e.g., monosulfonic acids with disulfonic acids), the dyestuff with higher affinity will block the absorption of the dyestuff with lower affinity by the fiber.

Acid dyestuffs for the dyeing of polyamide differ in their leveling capacity and in their wet-fastness properties, and it is therefore preferable to arrange in separate groups types which are similar in these two characteristics. Even under unfavorable conditions, dyestuffs with an optimum leveling effect can be level-dyed on piece goods made from perfect polyamide material, but they possess poorer wet-fastness properties than dyestuffs with a poorer leveling effect. The latter are used mainly for the dyeing of loose stock or for padding processes. Difficulties which are continually experienced by the dyer in the dyeing of polyamide, particularly warp-knit fabrics, are the streaks which occur during dyeing. This streakiness may be caused by two types of variation in the yarn: (1) differences in the physical structure of the filament (degree of stretching), (2) chemical differences (different terminal amino group content). Apart from these two main causes of streakiness, yarn denier, dulling agents, and mechanical stresses during knitting and weaving may also play a part. To a certain extent these differences can be corrected by use of well-leveling dyestuffs. Auxiliaries play an important role in the correction of these difficulties. The main auxiliaries for this application are mixtures of nonionic products (about 15 moles of ethylene oxide) with anionic substances of the alkyl sulfonate type. In any case, the effect of auxiliaries differs according to whether the varying affinity of the fiber is due to physical or to chemical influences.

Dyeing methods: Polyamide goods are mostly dyed in piece form, particularly as warp-knit fabrics. Dyeing is carried out on the winch beck in a liquor ratio of 20:1 to 30:1. The goods are entered at 40° into the bath set with about 2% (on weight of goods) of an auxiliary of the above-mentioned type and adjusted with acetic acid to about pH 4.5. After a certain interval, which is required for thorough wetting of the material, the acid dyestuff is added and the temperature is raised to the boil in 30–45 minutes, or in closed dyeing systems to about 115°. Dyeing is then completed in 1–1½ hours.

Piece goods can also be dyed in a similar manner on the jig. A very widely used method is the dyeing of warp-knit fabrics in high temperature piece-dyeing equipment (beam dyeing machine) in a liquor ratio of 4:1 to 8:1. This apparatus permits the dyeing of relatively long runs at temperatures exceeding 100°. A certain hydrosetting of polyamide warp loom goods is achieved simultaneously in this machine.

To improve the wet-fastness properties of dyeings obtained with acid dyestuffs on polyamide, an aftertreatment may be given with natural or synthetic tannins. The dyeings may be aftertreated, for example, in a bath containing 2% tannin and 1–2% acetic acid (60%), related to the fiber weight, for 20 minutes at about 65°. A subsequent aftertreatment is given with 1% tartar emetic. The effect of the tannin/tartar emetic aftertreatment is probably due to a closing of the pores of the polyamide fiber and, therefore, to a retardation of the diffusion speed of the acid dyestuffs, resulting in an improvement of the wet-fastness properties.

b. Afterchrome and Metal Complex Dyestuffs. Where a higher standard of fastness properties is required of polyamide dyeings, the dyestuffs used must be finally fixed on the fiber as chrome complexes. The fastness to light is considerably improved by the presence of chromium in the dyestuff molecule, while the coordinate bonds formed between chrome and polyamide fiber also improve the wet-fastness properties.

The procedure with afterchrome dyestuffs is to apply the initial complex-forming products, such as acid dyestuffs, to the fiber (see Section II,C,1,*a*) and then to carry out chrome development under the following conditions. The dyeing is aftertreated for 1 hour at the boil with 3–5% formic acid (85%) and ½–2% potassium bichromate. Formic acid acts as a reducing agent which converts hexavalent chromium into trivalent chromium. In contrast to wool, polyamide fiber does not contain reducing substances and the formic acid addition is therefore indispensable.

A considerable simplification of this process can be achieved by use of premetallized dyestuffs. In this case the chromium aftertreatment is not required. The material is first wetted out in a bath containing trisodium phosphate and a leveling agent of the previously mentioned type, the metal complex dyestuff is then added, and dyeing is completed at boiling temperature in 1–1½ hours. Because of their low migrating power, premetallized dyestuffs show a marked tendency to produce streaky dyeings and should therefore be used only on perfectly regular polyamide material under conditions which promote level dyeing. They are used mainly for polyamide loose stock and in the dyeing of carpets.

c. Disperse Dyestuffs. Very level shades, but only moderate wet-fastness properties, are obtained when disperse dyestuffs are used. This dyestuff group is therefore mainly used for less heavy shades where the wet-fastness properties are not too important. A wide field of application for disperse dyestuffs is in the dyeing of ladies' polyamide hose, in the charmeuse sector, and in the carpet field. On the other hand, disperse dyes are often used in conjunction with acid dyestuffs to overcome level-dyeing difficulties. Special ranges of disperse dyestuffs have been developed to meet high wet-fastness requirements.

Dyeing method: The scoured polyamide fiber is wetted in a bath containing 0.5–2 g/liter of leveling agents and the dyestuff dispersion is then added. After a uniform distribution of the dyestuff, the dye liquor is brought to the boil and dyeing is continued for 60 minutes. Where dyeing can be carried out under high temperature conditions, the optimum dyeing temperature is 105–115°.

d. Differential Dyeing Process. Design in the carpet and knitting industries has been considerably extended by the development of polyamide fibers with different dyestuff affinities.[56,57] In principle, two different types are distinguished: (1) fibers which show a different affinity for acid dyestuffs, and which therefore give different depths of shade when dyed under identical conditions, (2) polyamide fibers which are modified in such a manner that they can be dyed with basic dyestuffs and will be left practically unstained by acid dyestuffs. Both fiber types can be dyed evenly with disperse dyestuffs. Fiber mixtures consisting of two or three of these types thus permit the production of highly differential designs in a one-bath-dyeing process.

Acid dyes are taken up to a varying extent by fiber types of the first category, and basic dyes are absorbed mainly by fiber types of the second category, while also slightly staining those of the first group. These conditions show clearly that the matching to pattern of three-fiber mixtures of these fiber types with disperse, acid, and basic dyestuffs requires considerable practice and experience. For this reason, a generally applicable dyeing method will not be discussed here.

e. Space-Dyeing Processes. A pattern effect similar to that produced in the previously described differential dyeing method is achieved on polyamide in the space-dyeing process. In principle, skeins of polyamide

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[56] C. Schork, *Textilveredlung* **2,** 659 (1967).

[57] H. Egli, *Am. Dyestuff Reptr.* **57,** 1099 (1968).

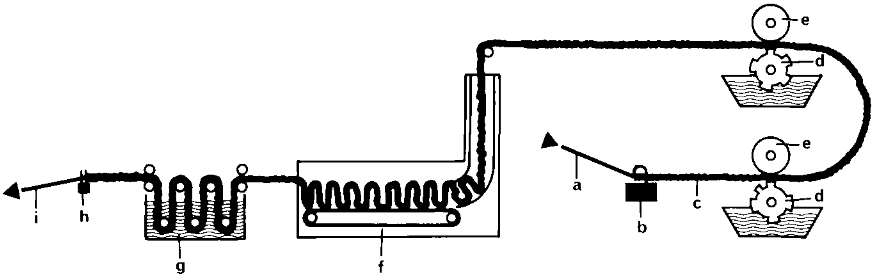


FIG. 3. Knit-deknit process: (a) yarn; (b) knitting; (c) knit goods; (d) color furnishing rollers; (e) pressure rollers; (f) aging unit; (g) washing unit; (h) deknitting; (i) yarn.

yarn are dyed lengthwise in different depths and shades, so that a very different colored pattern is obtained in the piece goods which are made of this yarn (mainly carpets and to a lesser extent knitwear for ladies' outer clothing). To carry out a space-dyeing process economically the following methods are used.

(1) *Knit-deknit process.* The polyamide yarn is first made up loosely into a flatknit structure, according to Fig. 3. This is padded free from tension with the slightly thickened dyestuff solution, then printed (several times, if required), without intermediate drying, with cross-stripes in another shade and, finally, steamed continuously for about 5 minutes. This is followed by scouring on the continuous washer and undoing of the knit piece.

(2) *Yarn printing process.* As shown in Fig. 4, in this long-known process parallel yarns are printed with cross-stripes on the vigoureux

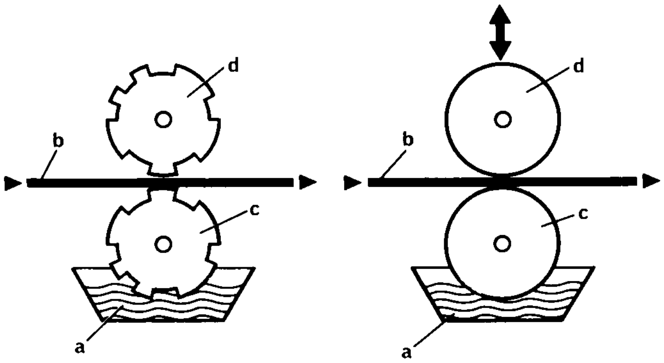


FIG. 4. Yarn printing process: (a) padding liquor; (b) yarn; (c) color furnishing rollers; (d) pressure rollers.

printing principle. Fixation of the dyestuff is obtained by steaming, in a similar manner to that described in Section II,B,2.

(3) *Injection process.* As shown in Fig 5, polyamide yarns wound onto bobbins are dyed differentially by injection of a dyestuff solution into different regions of the bobbin. In this case, fixation of the dyestuff can be achieved by steaming of the bobbin or by a cold-batch process.

(4) *Centrifugal process.* As shown in Fig. 6, the dyestuff solution is pumped inside perforated spindles which are subdivided into several partitions by means of rubber disks, which allow the dyestuff solution to penetrate only in certain segments. The dyestuff solution is forced outwards when the spools are centrifuged. Fixation is obtained as described under (3).

All these processes may be used not only on polyamide, but also on materials made from other fibers. With regard to the dye liquor, it must contain those auxiliaries which promote fixation of the dyestuffs on polyamide. By using such auxiliaries fixation can be obtained by

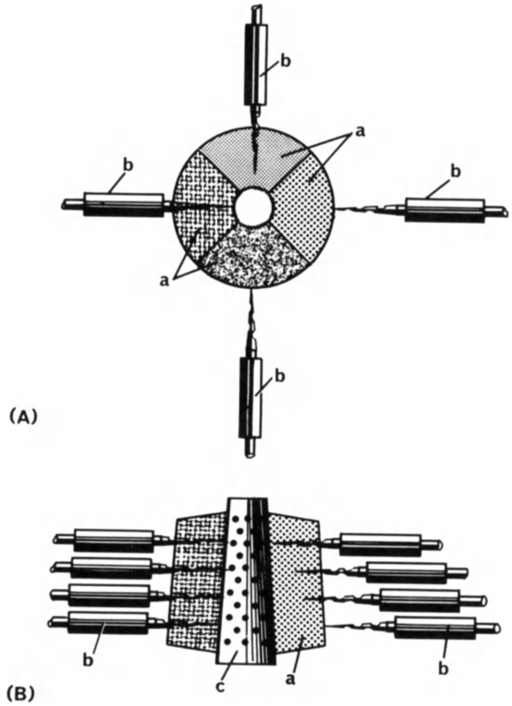


FIG. 5. Injection process (A) cross section and (B) longitudinal section: (a) textile yarn; (b) injection jets, containing different colors; (c) perforated cones.

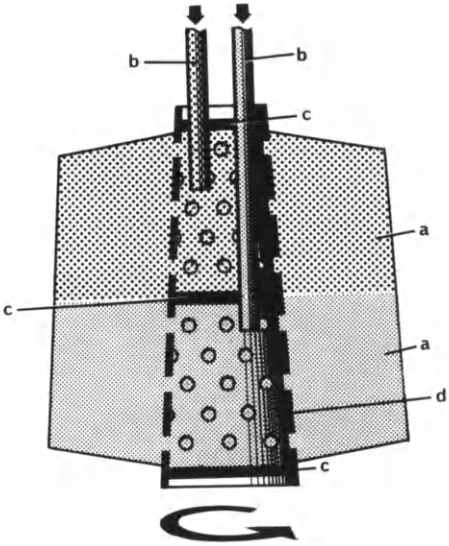


FIG. 6. Centrifugal process: (a) textile material; (b) dyestuff inlet nozzles; (c) seeking plates; (d) perforated cone, rotating at high speed.

storage at room temperature. In the case of fixations by steam, the steaming time can be reduced. Since very heavy shades are generally required and cold dye liquors are used, only highly soluble dyestuffs are suitable for this application. In processes (1) and (2) the liquor application is very high and thickening agents must therefore also be used. The dyestuff groups most generally used for these processes on polyamide are acid and metal complex dyestuffs.

f. Attempts to Dye Polyamide Continuously. Considering the high production of dyed polyamide goods, it is surprising that a satisfactory continuous dyeing process has been used in practice up to the present only in the field of polyamide tuftings. Many attempts have been made, however, some of which appear so promising that they should be mentioned here.

The possibilities of continuous dyeing have been utilized most in the dyeing of polyamide tufting goods. In this case, the dye liquor is applied to the polyamide carpet by suitable units, fixation of the dyestuff then being obtained by steaming for 8–12 minutes. The dyestuff application is difficult, because damage of the surface structure of the goods has to be prevented and a padding mangle cannot therefore be used. Two application units which have proved satisfactory in practice are illustrated in Fig. 7.

The same difficulty occurs in steaming. The goods may be led either through a suspension steamer or through a spiral steamer. Finally, steamers constructed on the basis of perforated rollers are also used.

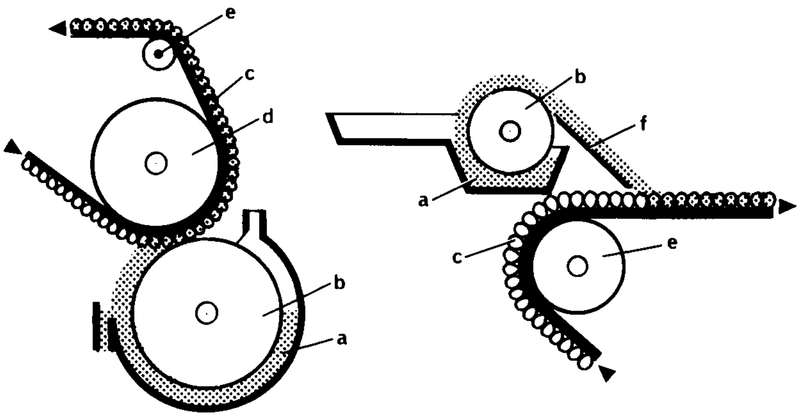


FIG. 7. Application units for continuous dyeing of tufted carpets: (a) padding liquor; (b) color furnishing rollers; (c) pile fabrics; (d) pressure roller; (e) guide rollers; (f) doctor blade.

Figure 8 shows a modern dyeing unit for tufted carpets. Dyeing takes place by a continuous exhaust process. Liquor and carpet pass through the unit at the same speed. Fixation takes place during 3–4½ minutes. No subsequent steaming process is necessary and difficulties, such as deformation of pile, can therefore be avoided.

For polyamide piece goods, e.g., warp-knit goods, these plants are naturally too expensive. In principle, it is possible to dye these goods continuously by the pad-steam process (see Section II,A,2,*a*). In this case, auxiliaries are required which permit a reduction of the steaming time. The method of dyestuff fixation in superheated steam has also been tried in practice. In this case, the steaming time can be reduced to about 1–3 minutes, but there are nevertheless considerable constructional difficulties. Up to the present, the thermosol process has given unsatisfactory

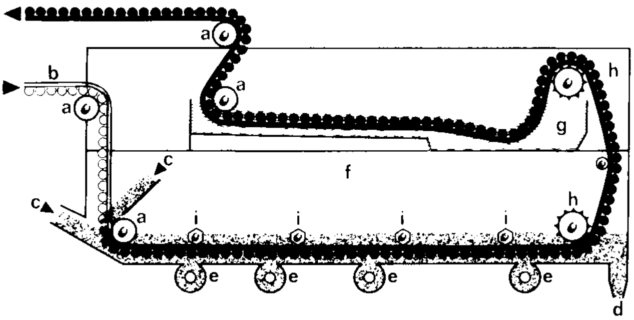
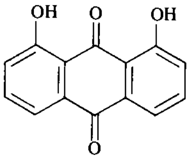
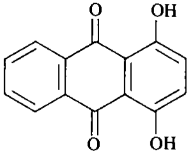
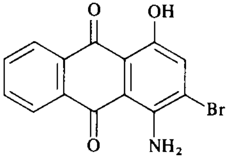
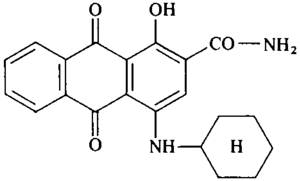
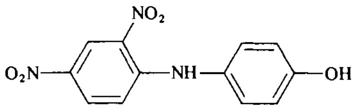
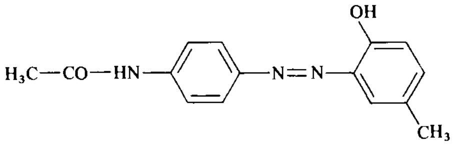
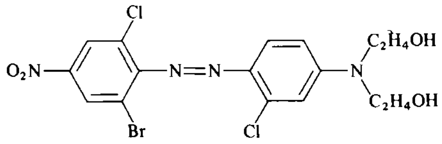
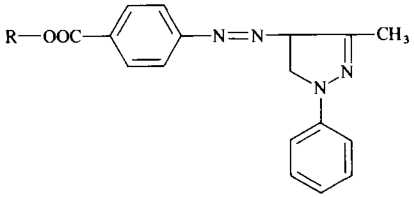


FIG. 8. Unit for continuous dyeing of tufted carpets; (a) guide rollers; (b) tufted carpet; (c) liquor feed-in; (d) liquor outlet; (e) mixing devices; (f) steam; (g) counter flow washing; (h) beater; (i) polygonal rollers.

TABLE VII

Diffusion Coefficients of Disperse Dyestuffs in Polyester

Constitution of the dyestuff	Molecular weight	Diffusion coefficients (cm^2/min) × 10^{-10}		
		without carrier	+ Benzoic acid	+ Trichloro-benzene
	240	3.7	78 ±10%	107 ±10%
	240	3.6	140 ±40%	85
	318	1.7	57	200 ±10%
	366	1.0 ± 20%	11 ±10%	9.2 ± 20%

	288	2.05	37	130 ±20%
	269	0.36	14	107 ±10%
	487	0.36	14	14 ±10%
	336	0.2 ± 40%	7 ±10%	6.5 ±10%

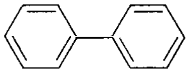
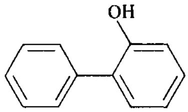
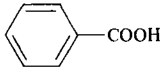
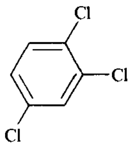
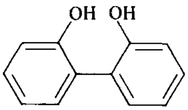
results on polyamide caused by a hardening of the fiber and a low dyestuff yield.

2. *Dyeing of Polyester Fibers with Disperse Dyestuffs*

Polyester fibers of the usual composition can be dyed only with disperse dyestuffs. In contrast to other synthetic fibers, it is indispensable to increase the rate of diffusion of the dyestuffs inside the polyester fiber structure either by raising the temperature or by addition of special auxiliaries. The diffusion coefficient of the usual disperse dyestuffs in polyester fiber generally ranges from 0.2 × 10^{-10} cm²/minute to 3.7 × 10^{-10} cm²/minute (see Table VII).

TABLE VIII

SUBSTANCES SUITABLE AS CARRIERS

	Diphenyl
	*o*-Phenylphenole
	Benzoic acid
	1,2,4-Trichlorobenzene
	2,2-Dihydroxy-diphenyl

The diffusion coefficient at 100° can be considerably increased by addition of an auxiliary (carrier) which promotes diffusion. An increase of the dyeing temperature to about 125° also increases the dyestuff diffusion very considerably and in these cases a carrier need not be used (high temperature dyeing).

Polyester fiber is dyed either as loose stock or in the form of polyester yarns on cheeses and as piece goods. Except in the case of texturized filaments (see below), pure polyester fiber is not often used. It is mostly used in mixtures with cotton or viscose staple fiber. In the dyeing of these blends, any staining of the cellulosic fibers by disperse dye is also important for the results obtained and only a selection of dyestuffs may therefore be used.

For dyeing of loose stock and yarn, the dyeing apparatus previously described in Section II,A,1 for loose stock and bobbins may be used, with a circulation of the liquor through the goods. In closed dyeing machines (autoclaves) temperatures of 125–130° can be attained, and dyeing may therefore be carried out by the high temperature method without a carrier.

Fastness to sublimation requires particular attention in the selection of dyestuffs for polyester fibers. The diffusion of disperse dyestuffs, which is required during the dyeing process, is a disadvantage during any heat treatment of the dyed polyester material, when the dyestuff, which is not bound to any active centers inside the fiber, diffuses out of the fiber again. This property is notable during any subsequent heat treatment of the dyed material either during manufacture (heat setting, pleating, decatizing) or in use (ironing, resetting of pleats).

When selecting the dyestuffs for materials which are normally subjected to a heat treatment, care should be taken to ensure that only those dyestuffs are used which possess a high fastness to sublimation: for example, CI Disperse Red 60 shows very poor, CI Disperse Red 90 medium, and CI Disperse Red 132 very good fastness to sublimation. Dyestuffs with high fastness to sublimation also naturally require higher carrier additions or prolonged dyeing times at high temperatures. Where differences exist in the density or degree of stretching of polyester material, these generally are revealed most by dystuffs with a low rate of diffusion, i.e., high fastness to sublimation. The main substances which are suitable as carriers are shown in Table VIII. These are all aromatic compounds.

As previously stated, the effectiveness of carriers is based on the increase of the diffusion speed of dyestuffs in the fiber. They differ in their degree of efficiency and in their influence on the fastness properties of dyeings, e.g., on the fastness to light. Their efficiency is associated with the distribution equilibrium between liquor and fiber, which in favorable cases must incline very markedly toward the fiber.

Dyeing methods: Regardless of the stage of processing, polyester fibers are generally dyed by one of two methods: (a) The first is the carrier method with x g/liter of disperse dyestuff, 2–3 g/liter of dispersing agent, and 2–4 g/liter of a suitable carrier. In the dyeing of heavy shades, the carrier addition must sometimes even be increased to 8 g/liter. The temperature is 98° and the pH 4.5–5. (b) The second is the high temperature dyeing method, also at pH 4.5–5, but with addition of about 1 g/liter of a special dispersing agent which remains stable under high temperature conditions. Depending on the required depth of shade, the dyeing time at 125° amounts to 1–2 hours.

a. Dyeing of Textured Polyester Filaments. As previously stated in Section I,C,2 texturized polyester filaments are taking an increasing share of the market in the outer-clothing sector. These textured materials are dyed either as yarns on bobbins which are flexible in axial direction, as cakes, in the package dyeing machine, or in piece form free from tension in the winch beck. A protective treatment of the material is required in all dyeing processes for texturized filaments, so that the high bulk of the goods is maintained.

Moreover, in the dyeing of texturized polyester material it must be remembered that any slight unevenness occurring in the presetting of the yarn or during the knitting process may be revealed very markedly, since in this case differences appear in the diffusion speed of the dyestuffs in the material. These difficulties are overcome by a selection of suitable dyestuffs, preference being given to those brands which possess a higher diffusibility. Level dyeing can also be promoted by higher temperatures and prolonged dyeing times (preferably 125°, 2½ hours).

b. The Thermosol Process. A process developed specifically for polyester fibers and now in large-scale use is the continuous dyeing of polyester fibers and their blends with other fibers by the thermosol dyeing process.[58] In the thermosol process, piece goods made from polyester fibers or polyester blends with other fibers are padded with disperse dyestuffs, dried, and then subjected to a heat treatment for 30–60 seconds at 190–215°.

During this heat treatment, in which a setting of the fiber takes place simultaneously, the disperse dyestuff diffuses into the polyester fiber. While in the dyeing of polyester fibers by the exhaustion process the rate of diffusion of the dyestuff in the fiber is the speed-determining factor for the total dyeing, the rate of diffusion in the thermosol process

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[58] F. Fourné, "Synthetische Fasern," p. 710. Wissenschaftliche Verlags-Gesellshaft, Stuttgart, 1964.

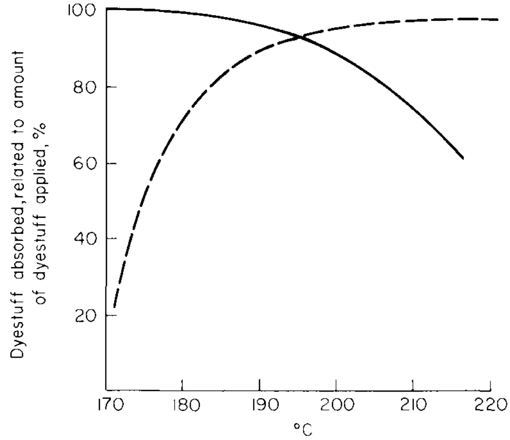

FIG. 9. Disperse dyes with different fixation optimum. (——: dyestuff A; — — — dyestuff B.)

is so high that the speed-determining factor is the penetration of the dyestuff into the fiber surface. Since the penetration speed of the dyestuff into the fiber surface depends on the dyestuff particle size, an agglomeration of the particles during the heat treatment must be avoided by use of suitable auxiliaries. The finer the dispersion of the dyestuffs at the start and the better the fine dispersion is maintained during the heat treatment, the higher is the yield achieved.[59]

When selecting a mixture of dyestuffs for the thermosol process it is important to know their fixation curves. Figure 9 shows the fixation curves (temperature against dyestuff yield) of two dyestuffs which attain their fixation optimum under very different conditions. In these cases, even slight variations of the fixation conditions between ends or between the two sides in the fixation unit will result in changes of shade. On the other hand, the two dyestuffs whose fixation curves are shown in Fig. 10 attain their fixation optimum under equal conditions and are therefore fixed in the same proportions even under unfavorable conditions of fixation.

With regard to the plant required for the thermosol process, the following observations may be made. In principle, a stenter or a hotflue may be used. However, some special thermosol equipment has been developed by the machine manufacturers. One type operates by means of perforated cylinders. The fabric, preferably polyester/cotton, after padding and predrying is led over these cylinders and hot air of 190–210° is sucked through the fabric from outside into the drums.

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[59] R. Kuth and D. Hildebrand, *Z. Ges. Textil-Ind.* **69, 329**; **405**; **473** **(1967)**.

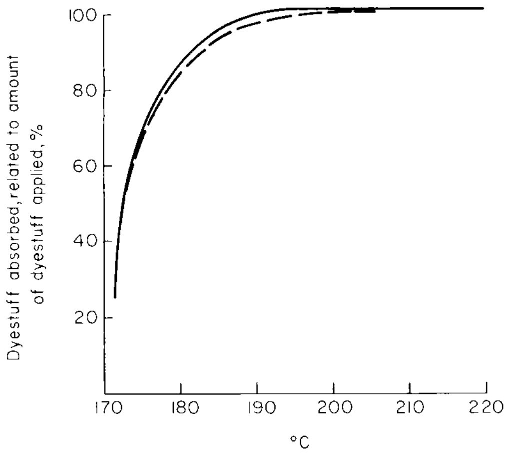

FIG. 10. Disperse dyes with similar fixation optimum. (——: dyestuff C; — — — dyestuff D.)

Fixation can also be obtained on metal rollers by contact heat, the material being led very quickly over oil-heated or gas-heated metal rollers at a temperature of 240°. One side or the other of the material contacts the hot surface alternately.

c. Dyeing of Polyester/Cotton Blends. A very large proportion of the polyester fiber production is marketed in mixtures with cotton or other cellulosic fibers. The most popular blends contain 65 parts of polyester fiber to 35 parts of cotton or viscose staple fiber, but mixtures in a ratio of 50:50 are also gaining in importance. When dyeing these blends in an exhaustion process, disperse dyestuffs are first applied to the polyester fiber, and the cellulosic fiber is then dyed with direct, reactive dyestuffs or vat dyestuffs.

In the selection of disperse dyes, care must be taken to ensure that these mainly dye the polyester fiber and leave the cellulosic fiber practically unstained, since the standard of fastness properties achieved will otherwise be affected very adversely. There are methods of dyeing both fiber types simultaneously in the exhaustion process, disperse dyestuffs and direct dyestuff being applied from the same bath. With reactive dyestuffs a two-step process is required, inasmuch as the alkali needed to obtain fixation of the reactive dyestuffs is added only after fixation of the disperse dyes.

When dyeing these blends continuously a combined thermosol–pad-steam process is applied. The plant consists of a padder for application of the dyestuff, a predrying unit, drying equipment, thermosol equipment, a chemical padding mangle, a steamer, and a washing unit. The disperse dyestuff and the dyestuff for the cellulosic fiber, generally vat or reactive dyes, are applied on the first padding mangle. After the thermosol treatment, the agent required to obtain fixation of the cellulose dyestuff is applied on the second padder. Vat dyes are fixed with alkali and sodium dithionite, reactive dyestuffs only with alkali. The goods then pass into the steamer, where fixation of the dyestuff is obtained on the cellulosic component. The aftertreatment depends on the dyestuff group used, as described for cellulosic fibers in Section II,A. A selection of specific disperse and reactive dyestuffs permits of application in a single-step process, in which disperse and reactive dyes are applied together with alkali on the first padder, fixation being obtained in the thermosol plant. The following formula is used:

0–100 g/liter	Disperse dyesuff paste
0–40 g/liter	Reactive dyestuff
5–10 g/liter	Sodium bicarbonate
60–100 g/liter	Urea

The material is padded, dried, and thermosol-treated for 60 seconds at 180–215°, depending on the type of disperse dyestuff.

d. Acid-Modified Polyester Fibers. Fiber manufacturers have developed polyester fibers incorporating an acid-group-containing component, which can therefore be dyed not only with disperse dyes, but also with basic dyestuffs. These polyester fiber types are used mainly in mixtures with normal polyester fibers, thus simplifying the different dyeing of such blends as piece goods or as yarn. A selection of basic dyestuffs developed for the dyeing of acrylic fibers is used, and it should be remembered that the fastness to light on acid-modified polyester fibers is somewhat lower than on acrylic fibers. With the aid of special dispersing agents, blends of acid-modified and normal polyester fibers may also be dyed with disperse and basic dyestuffs in the same bath.

3. *Dyeing of Polyacrylonitrile Fibers*

Polyacrylonitrile fibers are dyed mainly with basic dyestuffs. For palest shades disperse dyestuffs are used, although when the depth of pastel shades is exceeded the fastness properties, particularly the wet-fastness properties and the fastness to crocking, are not sufficient.

Polyacrylonitrile fibers are dyed in the following processing stages: (1) As loose stock—the dyeing of acrylic fibers in this form is used in particular for carpet fibers or fibers for furnishings. (2) As yarn on cheese dyeing apparatus—polyacrylonitrile fibers in cheese form are used for colored woven goods. Polyacrylonitrile filaments are also often dyed in this form. (3) As yarn in hanks—the dyeing of polyacrylonitrile yarns in hank form is widely practiced because high-bulk yarns, which are subjected to a shrinking process during or immediately before dyeing, are dyed in this form (see Section I,C,3). HB yarns are of outstanding interest, in particular, for ladies' outer clothing (pullovers, sweater, etc.). (4) Finally, polyacrylonitrile can also be dyed in the form of piece goods, e.g., on the winch beck or on a high temperature beam dyeing machine, although care must be taken to ensure that the polyacrylonitrile pieces are not subjected to tension or compression, particularly at higher temperatures, since a permanent deformation may otherwise occur.

a. Cationic Dyestuffs. The fact that polyacrylonitrile fibers take up cationic dyestuffs and form a firm bond with them is based on a saltlike binding of the dyestuffs inside of the fiber. As a result of polymerization, acid groups (sulfo or sulfate groups) are present in the fiber at the ends of the polymeric chains. Besides that, small amounts of acid monomers are used in polymerization to increase the dyestuff uptake.[60]

The maximum dyestuff absorption of the fiber has a constant relation to the number of these sulfo or sulfate groups at the chain ends, or to the chain length. The higher the number of acid groups in the fiber, the higher is the dyestuff-binding equivalent. Before the cationic dyestuff reaches the binding groups in the fiber, it must first be absorbed on the fiber surface by electrostatic forces, and in the second phase dissolved by the fiber substance, so that it can subsequently diffuse inside the fiber to the binding positions. Once the cationic dyestuff has penetrated into the fiber, its wet-fastness properties and fastness to crocking are generally very high, since it is hardly exposed at all to the influence of the respective agents.

A salient feature in the dyeing of polyacrylonitrile with cationic dyestuffs is that the fiber begins to take up the dyestuff only above a certain critical temperature. In all cases, this critical temperature exceeds 85°, and the dyebath can therefore generally be heated to this temperature very quickly, after which it is very slowly brought to the boil. The rate of absorption of cationic dyestuffs on polyacrylonitrile fibers begins to increase very quickly above the critical temperature. Level-dyeing difficulties may be encountered if the temperature increases too rapidly in comparison with the liquor circulation, so that the dyestuffs are taken up preferentially at those parts of the material where the temperature is higher compared to other parts.

A further difficulty which is experienced in the production of level shades is that any subsequent leveling by a migration of the dyestuffs inside the fiber, or from fiber to fiber, takes place only very slowly,

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[60] W. Beckmann, *J. Soc. Dyers Colourists* **77**, 616 (1961).

if at all. It is therefore necessary to run the dyeing process in a way which guarantees the equal distribution of the dyestuff on the fiber from the very beginning of the dyeing process.

The individual dyestuffs differ in their affinity for polyacrylonitrile fibers. Dyestuffs with a high affinity possess a comparatively low diffusion coefficient and cannot be leveled once they are bound to the fiber, i.e., they do not migrate at all. Dyestuffs with a low affinity remain to a certain extent in equilibrium in aqueous solution and show a slight tendency to migrate. On the other hand, high affinity dyestuffs displace those of low affinity from their positions on the fiber, so that a combination of dyestuffs which are not mutually adapted may lead to blocking or displacement effects. For this reason, special attention must be given to the suitability of dyestuff mixtures used in the dyeing of polyacrylonitrile fiber, i.e., the components must be compatible with regard to their affinity.

Leveling of the dyestuffs is improved by use of so-called retarders. A distinction is made between cationic and anionic retarders. Cationic retarders are virtually colorless basic dyestuffs. They are taken up by the fiber before or with the dyestuff, and at first block part of the anionic binding groups, which therefore become available for the dyestuff only after a certain time. The displacement of the retarder is, of course, accomplished more rapidly by high affinity dyestuffs than by dyestuffs with an affinity similar to, or even lower than, that of the retarder.

Cationic retarders have the disadvantage, however, that they cause a certain blocking effect, and very heavy shades therefore cannot be obtained on the fiber in the presence of a retarder. This phenomenon is most apparent in redyeing, where a shade of medium depth produced with the aid of a cationic retarder is to be subsequently dyed navy blue or black. A part of the sulfo groups of the fiber is then blocked by the cationic retarder and does not permit the application of additional dyestuff to the fiber to dye it a deep navy blue or black. An expedient in such cases is to strip the retarder from the fiber by means of nonionic and anionic auxiliaries and to bind it outside of the fiber in the aqueous liquor. A more elegant method is, however, to use retarders which show a certain tendency to saponify, so that they become ineffective as retarders as dyeing proceeds and give up their positions to the dyestuff.

A retarding effect can also be achieved by use of anionic retarders. These compounds, which are similar to anionic surfactants, are used together with nonionic compounds. The anionic surfactants form electrically neutral compounds with cationic dyestuffs, precipitation being prevented by the presence of nonionic substances. Depending on the degree of dissociation constants of the electrically neutral addition compounds between dyestuff and anionic auxiliary, a higher or lower proportion of the bound dyestuff is present in the liquor as cations, which are taken up by the fiber.[61]

The retarding effect of these retarders is therefore based on a constant and slow control of the quantity of cationic dyestuff in the dye liquor, from which it can then be taken up by the fiber.

An important advantage of these systems is that no blocking occurs inside the fiber. On the other hand, depending on the dissociation constant of the complex, there are extraordinary differences between the individual dyestuffs. Only a few members of the usual cationic dyestuff ranges are suitable for combination when this type of retarder system is used.

Dyeing method: For polyacrylonitrile loose stock and cheeses the following dyeing formulas may be used:

The dye-liquor is set at 70° with

x%	Cationic dyestuff
0.5–2%	Sodium acetate
3 –1%	Acetic acid 60%
4 –2%	Sodium sulfate calc.
0.5–1%	Nonionic auxiliary
2.5–0%	Retarder

The bath is run for a short time at 70°, the dyestuff is added, and the temperature is increased in 45 minutes to 115–120°. Depending on the required depth of shade, dyeing is continued at this temperature for 1–2 hours, the bath is cooled indirectly to 80°, and rinsing is carried out with overflow at 60° until the rinsing water is clear.

In the dyeing of polyacrylonitrile high-bulk yarn on hank dyeing apparatus, care must be taken to ensure suspension of the hanks in such a manner that the shrinking process has sufficient room to take place without any excessive pressure on the sticks, which would result in deformation. Shrinking and dyeing can be carried out simultaneously by the following method: The bath is set at 85° (shrinkage temperature of high-bulk yarns) with

x%	Cationic dyestuff
0.5– 2%	Sodium acetate
3 – 1%	Acetic acid 60%
10%	Glauber's salt calc.
0.5– 1%	Nonionic auxiliary
2.5– 0%	Retarder

The yarns are entered into this liquor at 85° and are run for 5 minutes. This completes the shrinking process. The bath is then heated in 45 minutes to 95–98° and, depending on the required depth of shade, dyeing

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[61] G. Sigrist, *Textil-Rundschau* **17,** 143 (1962).

is completed at that temperature in 1–2 hours. Polyacrylonitrile shows an increased thermoplasticity at temperatures exceeding 60° and the bath must therefore be cooled slowly to prevent deformation of the fiber.

Polyacrylonitrile piece goods can be dyed on the winch beck by the following method: The dye liquor is set as stated above. Dyeing is started at 50°, the temperature is increased in 10–15 minutes to 85°, and then slowly and uniformly in 40–45 minutes to 95–98°. As in the dyeing of high-bulk yarns, dyeing is completed at this temperature in ¾–2 hours and the bath is then cooled very carefully.

b. Dyeing of Polyacrylonitrile Tow. Polyacrylonitrile tow can be dyed discontinuously in cylindrical vessels, in a similar manner to worsted wool. An additional method is the continuous dyeing of polyacrylonitrile tow, for which builders of textile machinery have constructed apparatus to ensure a practically tension-free treatment of the goods. For this application, one type of plant, shown in Fig. 11, is most widely used.

The polyacrylonitrile tow is first led through a trough containing the slightly thickened dye liquor and is then squeezed by two rubber rollers to a certain liquor pickup. The tow is subsequently led from above into a steaming tunnel, where it remains for about 3–5 minutes. It is drawn off from below on a slowly traveling rack and is led through a horizontal steamer. The material is subjected to no mechanical stresses during this passage, since the tow is merely lying on the rack. After steaming for about 12 minutes, the tow is drawn off carefully, quickly cooled, and washed on the back-washing machine. This method of tow dyeing offers the advantage that the crimp of the material, which is important for subsequent spinning, is maintained. The dye liquor contains

x g/liter	Cationic dyestuff
$\frac{x}{2}$ g/liter	Auxiliary to improve the solubility of basic dyestuffs
5 g/liter	Nonionic dispersing agent
30–50 g/liter	Urea
3–5 g/liter	Thickening agent (based on carob bean gum)

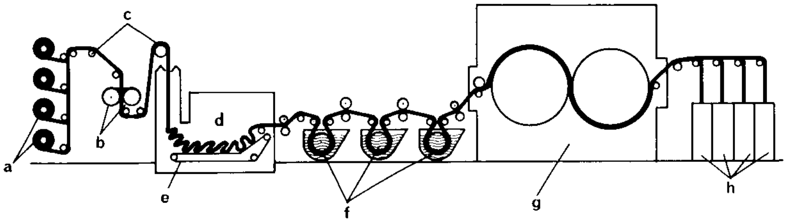

FIG. 11. Unit for continuous dyeing of polyacrylonitrile tow: (a) tow, (b) vertical padding mangle, (c) guiding rollers, (d) steaming, (e) grate, (f) washing units, (g) drying cylinders, (h) cans.

c. Dyeing of Polyacrylonitrile Fiber Blends. Polyacrylonitrile fibers are seldom used in mixtures. When they are mixed, however, the blends generally contain viscose staple fiber, and in certain cases polyester fibers or polyester and viscose or cotton staple fiber. Blends of polyacrylonitrile with viscose staple are used in ladies' dress goods. They are dyed in piece form on the winch beck or on a high temperature piece-dyeing machine, the acrylic component first being dyed with cationic dyestuffs according to the formula given in Section II,C,3,*a* and the cellulosic component then being dyed with selected direct dyestuffs.

Provided that a certain depth of shade is not exceeded, both dyestuff groups can be dyed in the same bath with an addition of suitable auxiliaries. In any case, dyeing must be carried out free from tension or pressure. Dyeing on the winch beck ensures an optimum handle of the goods. When dyeing is carried out on the high temperature beam, subsequent washing on the winch is recommended, since in this case a certain improvement of the handle is obtained.

Mixtures consisting of polyacrylonitrile and cotton, although not in one phase, are used for plush materials with a cotton backing and a pile made from polyacrylonitrile fibers. These goods are best dyed on the *star dyeing machine* where surface stresses are reduced to a minimum. This machine consists of an open vessel, similar in shape to that of a package dyeing machine, which contains the dye liquor. As for the star frame, two stainless steel spirals with hooks are connected by a center rod. One of them is adjustable to cope with the widths of the various fabrics. The cloth is pinned onto the hooks from the inside to the outside of the spirals. The loaded star frame is immersed into the dye liquor and level dyeings are ensured by gentle up and down movements of the frame throughout the dyeing cycle.

The liquor ratio on this dyeing equipment is nevertheless very unfavorable (about 40:1), so that prolonged dyeing times and high losses of unexhausted dyestuff must be expected. For this type of dyeing in particular, the one-bath dyeing process for cotton and polyacrylonitrile offers an advantage. The procedure in this case is to use basic dyestuffs and direct dyestuffs in the same bath with addition of nonionic and anionic auxiliaries.

The blend consisting of polyacrylonitrile and polyester fibers is used to a certain extent for washable materials for gentlemen's suitings and ladies' costumes. These polyacrylonitrile–polyester mixtures are best dyed on the winch beck or on a high temperature piece-dyeing machine. Up to medium depths of shade, cationic dyes and disperse dyes may be used in the same bath and applied to the fiber simultaneously. In heavier shades, it is advisable first to dye the fiber with the lower amount of dyestuff and then to dye the other fiber.

Blends made from polyacrylonitrile–polyester and cotton or viscose staple can also be obtained. The mixture ratio is 33% of each fiber. Addition of the cellulosic component results in a much more difficult behavior of the mixture compared with the pure synthetic fiber blend. These textiles, which are mostly used for ladies' outer clothing, are best dyed on the winch beck, the acrylic fiber and polyester first being dyed as previously described, and the cellulosic component then being dyed with direct dyestuffs. Where, however, a thermosol treatment is possible under protective conditions, the polyester component can also be dyed first with disperse dyestuffs by the thermosol process. In this case, however, the acrylic and cellulosic components should then be dyed on the winch to improve the handle of the goods.

4. *Polyurethane Elastomeric Filaments*

a. Polyurethane Filaments Covered with Polyamide. About 90% of the production of elastomeric filaments is now used for foundation garments, where they are generally employed in amounts of 20–30% as a "core" covered with 80–70% of polyamide. The dyeing of solid shades on polyamide and polyurethane elastomeric filaments is therefore of a certain importance. The following processes are required: (a) relaxation and steaming, (b) pretreatment, (c) dyeing or optical whitening, (d) drying, (e) finishing. The following general precautions must be taken at all stages of processing: maximum freedom from tension, temperatures over 100°, max. 105° to be avoided, no aftertreatment with metal salts, no compounds which give off chlorine, resin finishes without metal salt catalysts.

A sufficient relaxation of the goods is one of the most important factors for a satisfactory result. A shrinkage of 20–30% must be expected. The goods are either run on an endless metal belt with overspeed over a steaming table, or they are entered with overspeed into a boiling jig bath. It is particularly important to remove fiber chemicals before the dyeing process. Where anionic chemicals are present, the material is scoured in a phosphate-alkaline bath containing an anionic detergent (4–8 g/liter in a short liquor ratio) for 1–1½ hours at 85°. In the presence of cationic chemicals, the material is scoured at pH 5 with about 1–3 g/liter of a nonionic detergent for ½ hour at 85°, the process then being repeated with fresh liquor.

To dye polyurethane filaments covered with polyamide various dyestuff groups are available, particularly metal complex, disperse, and afterchrome dyes and, to a lesser extent, acid dyestuffs.

Metal complex dyestuffs are used without special auxiliaries and without special processes in the usual manner for this dyestuff group. Practically solid shades are obtained on polyamide (PA) and polyurethane elastomeric filaments (PUE). A disadvantage of this dyestuff group is the relatively strong marking of differences in filament structure. The fastness properties obtained generally meet the usual requirements.

Disperse dyestuffs are applied by the usual process and generally produce solid shades on PA and PUE. The wet-fastness properties attained by certain ranges are, however, insufficient in some cases, and these dyestuffs are therefore suitable only for pale to medium shades.

Afterchrome dyestuffs give optimum fastness properties and solid shades on PA/PUE, but have the great disadvantage of the very prolonged dyeing and chrome-development process, which adversely affects the technological properties of PUE. These dyeings cannot be stripped without destruction of the polyurethane. Moreover, afterchrome dyestuffs are not suitable for all types of PUE. Many types are able to bind chromium, and the dyestuff formation therefore does not develop to the full extent.

Acid dyestuffs present special problems with regard to the production of solid shades on PA/PUE mixtures, since the two fiber types differ in their affinity, acid-binding capacity, and rate of dyeing. These differences sometimes also result from previous processes on the Raschel machine and in the hosiery mill.

The differences of affinity between PA and PUE can often be largely corrected by a suitable selection of dyestuffs, auxiliaries, and dyeing methods. The auxiliaries used should possess an affinity for the fiber *and* the dyestuff.

To overcome the differential dyestuff-binding capacity, trials have been made to precipitate the anionic acid dyestuff with the aid of cationic auxiliaries and, in this way, to apply the dyestuff in an insoluble, dispersed form.

CHAPTER II

APPLICATION OF DYES IN TEXTILE PRINTING

Karl Neufang

FARBENFABRIKEN BAYER AG, ANWENDUNGSTECHNISCHE ABTEILUNG,
D-509 LEVERKUSEN, WEST GERMANY

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I. History

Textile printing may be considered as an ingenious further development and modification of dyeing. Without the experience and knowledge gained in dyeing, textile printing would certainly not exist today.

The first printed fabrics came from China and India. The colors were applied to the fabric with printing blocks made from wood, and sometimes also from metal. Batik printing, which originated in East Asia, is probably even older. The fabric was covered with a thin layer of wax and the required design was then applied with a style. The fabric was dipped in the dye liquor so that only those parts which had no protective layer of wax were dyed. After this operation the process was repeated. We may speak of resist dyeing: the parts to be protected are covered with a design of liquid wax and the fabric is again dipped in the dye liquor. This process of resisting and dyeing can be carried out as often as desired.

In Java this art attained an extremely high state of development. Batik printing possessed a beauty of outline and color which has not been attained even today, despite the modern and versatile printing machines.

Pigment printing, which is now so widely used, is also no recent invention. We know that in the 11th and 12th centuries German monks in the Rhineland prepared printing pastes from glue or oil and color pigments, and applied them to fabrics with hand stamps.

In the 17th century, the Dutch and English introduced calico printing into Europe from India. For a start the same methods were used as in India. An extremely high demand soon arose for these printed fabrics. At the end of the 18th century Thomas Bell invented printing with engraved copper rollers, a considerable step forward, and roller or machine printing was introduced. The invention of the steam engine did the rest. The large-scale production of inexpensive prints was now possible. Block and screen printing remained for high quality designs and expensive materials.

Up to this time natural dyestuffs had been used. The discovery of the first synthetic dyestuff by Perkin in the middle of the last century ushered in a period of extraordinary activity for textile printing. Because of differences in technical behavior, the application of these new dyestuffs permits a variety of new techniques. These are the subject of the following discussion.

II. The Principles of Textile Printing

As previously mentioned, printing can be considered as the localized dyeing of textiles. There is nevertheless an important difference. Whereas in dyeing, the dyestuffs and the required chemicals are present in the dyebath in relatively low concentrations, in a printing paste we have a very high dyestuff and chemical concentration, as well as a thickening agent which is particularly important for the printing process. As colloidal solutions, these thickening agents possess a very high swelling power. They are able to take up considerable quantities of water. If the printed textile is dried and then steamed after the printing operation, the dyestuff migrates from the paste to the fabric. The thickening agent prevents the dyestuff from flowing out into the fabric. We speak of a sharp outline. The large number of thickening agents based on starch, vegetable mucilages, and other products permits the production of printing pastes suitable for the usual requirements.

In textile printing, the dyestuff groups used for the various fiber types are the same as those employed in dyeing. These dyestuffs are often specially formulated for use in textile printing by additions of dispersing agents, solubilizing agents, etc.

Fixation of the dyestuff is obtained in a steaming process. Thickening agents and fiber swell during the steam treatment. The dyestuff migrates into the fiber, where it is bound by physical or chemical action.[1]

III. The Main Printing Processes

Direct printing is the simplest and most usual printing process. The printing blocks filled with various colors are applied in sequence to the white or already colored fabric. If the prints are superposed compound shades are obtained.

Resist printing has been known since ancient times, but has now lost its former importance. After printing the fabric with a special resist printing paste, the printed parts remain unstained during the subsequent dyeing process. Depending on the dyestuff group used, this effect is achieved by adding products to the printing paste which act as resists on a chemical or physical basis.

In *discharge printing* the dyestuff is destroyed in those parts where the discharge paste is applied to a dyed fabric. The destruction of the dyestuff is generally brought about by chemicals with a reducing action which are added to the printing paste. Salts of sulfinic acid should be given preference since they offer the advantage of not tendering the fabric. The material must, of course, be dyed with easily discharged dyestuffs. Moreover, the decomposition products must not be colored and must have no affinity for the fiber.

So-called color discharges can also be obtained by adding discharge-resistant dyestuffs to the discharge printing paste.

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[1] For a discussion of fastness tests on printed and dyed textiles, see section IX.

IV. Textile Printing Technique

A. Pretreatment of the Textile Material

The textile material to be printed must possess, in particular, a high absorption for dyestuffs and chemicals, i.e., it must be easily wetted. It is therefore pretreated to remove impurities and objectionable substances. On cotton the dyestuff absorption is considerably improved by mercerization. On wool this is achieved by acid chlorination.

In many cases the fabric must be set before the printing process. Heat-setting (treatment in dry heat) is recommended for synthetic fibers. Wool, for example, is subjected to a treatment in hot water.

B. Block Printing

Block printing, which is one of the oldest printing processes, is now used only in special cases. It is still employed for high-quality goods, such as textile wall-coverings and printed cloths.

The fabric to be printed is held firmly on long tables which are covered with a resilient felt blanket. Printing is carried out by hand. A relief printing block made of wood is applied to the fabric. Stepwise, print after print is made. Each printer applies a different color. Care is taken to ensure that the guide pins of the printing blocks are correctly engaged.

C. Roller Printing

Roller or cylinder printing was invented at the end of the 18th century. It enabled textile printing to be carried out on a large scale. As shown in Fig. 1, the roller printing machine consists of the printing cylinder over which the material is led. The actual printing rollers, which are engraved in recess, are coated with color paste from the color trough by furnishing rollers. Surplus color paste is removed with a blade (doctor) so that only the engraving is filled. The printing rollers then transfer the paste to the fabric.

Printing machines for up to 16 colors are available, but most machines are of the 8–10 color type.

D. Screen Printing

Screen printing is now probably the most widely used of the stencil printing processes. A frame, generally made of wood, is fitted with a very fine mesh screen consisting of bronze wires, silk threads, or threads made from synthetic fibers. The nonprinting areas of this screen are blocked

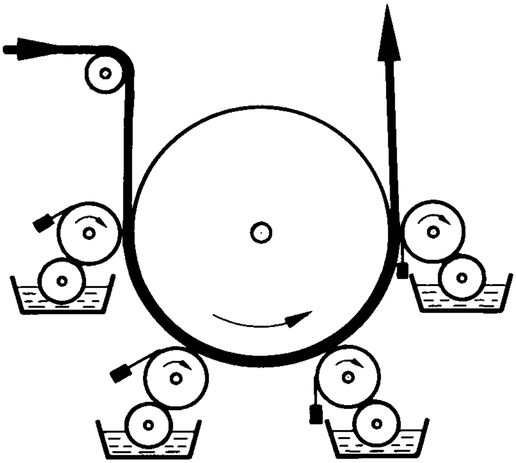

FIG. 1. Roller printing machine.

up with a lacquer. The material to be printed is held on long tables, as described under block printing. The screen is applied and the printing paste is forced through the open meshes by means of a doctor.

This printing process has been considerably improved in recent years. The latest screen printing machines are notable for a perfect alignment of the pattern and, in particular, for a high rate of production. They are usually fully automatic. The printing screens, stationary in one plane, are mounted above the table. This screen printing table consists of an endless rubber belt onto which the material to be printed is pasted. The printing process is carried out as follows: The screen descends automatically and the printing paste is applied with a doctor. The screen then rises and the conveyor belt with the pasted fabric moves forward to the next repeat. The screen descends again and the printing operation is repeated.

A very interesting development is the rotary screen-printing machine. In this case the color is applied by means of a cylindrical screen. This is a seamless, perforated metal foil cylinder with a wall thickness of about 0.1 mm. The printing paste is forced by a doctor from the interior of the cylinder through the fine perforations. The nonprinting parts of the screen are blocked up, as previously described.

Rotary screen printing machines have met a long-felt need in textile printing practice. The maximum printing speed of automatic screen printing machines is limited by the number of reciprocating doctors, the drive of the printing blanket, and the interval between the effective doctor strokes. Roller printing machines operate at high speed, but in this case

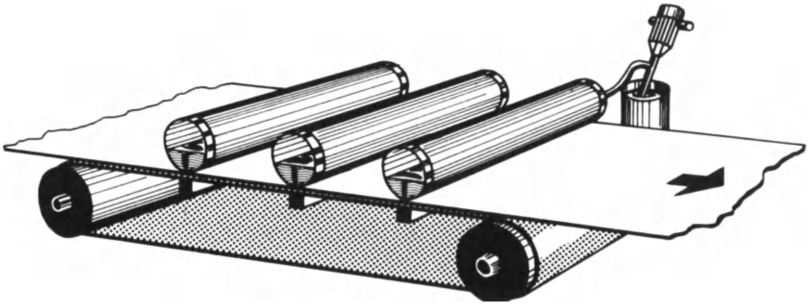

FIG. 2. Rotary screen printing machine.

prolonged setup times must be tolerated and for shorter runs, in particular, are very expensive. Rotary screen printing machines do not have these disadvantages and it appears that in the course of time they will partly replace the old roller printing machines. See Fig. 2.

E. Drying of the Prints

To prevent any flaking or smearing of the applied printing pastes, the printed materials are dried immediately. Drying is carried out with hot air in drying chambers or hotflues, which for continuous printing processes are generally attached to the printing machines.

F. Fixation of the Dyestuffs

Fixation is the next process after drying. The dyestuff must migrate from the printing paste to the fabric on which fixation is obtained. In many cases the actual formation of the dyestuff takes place in this process (e.g., Naphthol dyestuffs, Rapidogen dyestuffs, and Phthalogen dyestuffs). This important fixation process can be carried out by various methods, now to be described.[1]

1. *Steaming*

The goods are led through a steamer, i.e., through a chamber generally supplied with saturated steam at a temperature somewhat exceeding 100°. During the steaming process the following operations take place:

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[1] The following repeatedly mentioned product names are registered trademarks: Lanasol, Ciba; Levafix, Farbenfabriken Bayer AG; Verofix, Farbenfabriken Bayer AG; Naphtol-AS, Farbwerke Hoechst AG; Rapidogen, Farbenfabriken Bayer AG; Rongal, Badische Anilin- & Sodafabrik AG; Rongalit, Badische Anilin- & Sodafabrik AG; Phthalogen, Farbenfabriken Bayer AG; Polyestren, Cassella Farbwerke Mainkur AG.

Steam condenses on the fabric. The thickening therefore swells and the dyestuff diffuses into the fiber substance, together with the chemicals present in the printing paste. The high temperature promotes solution and accelerates very markedly the rate of diffusion of the dyestuff. Chemical reactions also occur at this stage (reactive dyestuffs, Phthalogen dyestuffs, etc.).

Textiles made from cotton, viscose staple, or wool, i.e., hydrophilic fibers, require steaming with only a slight superpressure (about 0.1–0.2 atmosphere). The fixation of prints on the hydrophobic synthetic fibers is best obtained by steaming with saturated steam under pressure. A temperature of about 125–130° is used. Numerous steamers of different construction are available, which, however, need not be discussed here.

2. *Fixation in Dry Heat*

The fixation of several dyestuff groups can also be obtained on various textile machines by a treatment in dry heat instead of a steaming process. On cotton and regenerated fibers this applies, in particular, to naphthol and Phthalogen dyestuffs, as well as to reactive dyestuffs. This method of fixation is often used for synthetic fibers; in this case it is known as the Thermosol process. It has proved extremely suitable in the application of disperse dyestuffs to polyester materials.

Fixation in dry heat is used on a very large scale in pigment printing, since curing and cross-linking reactions of the binders take place most satisfactorily under these conditions.

3. *Wet Development*

The fixation of certain dyestuff groups is also achieved by passing the printed fabric through a chemical solution suitable for the dyestuff group in question. This method is very interesting because no elaborate apparatus need be provided. Its field of application is nevertheless limited. It is used mainly for Naphtol AS dyestuffs. Recently, however, wet development has also been used for the fixation of reactive dyestuffs on cotton and regenerated fibers.

G. AFTERTREATMENT

After fixation, any unfixed dyestuff and also the thickening agents must be removed from the material. This is achieved in rinsing and soaping processes carried out on rope washers and full-width washing machines. To attain an optimum process, various types of machines are available, operating, for example, on the countercurrent principle, and incorporating other physical principles to ensure a thorough exchange of liquid in the goods.

V. Printing of Cellulosic Fibers

A. WITH DIRECT DYESTUFFS

With few exceptions, direct dyestuffs—also known as substantive dyestuffs—are azo dyes which contain several sulfonic groups in the molecule. They are therefore freely soluble in water. Fixation is obtained by steaming. Since the wet-fastness properties of the prints meet requirements only in the rarest cases, an aftertreatment with cationic products is recommended, as also in dyeing, whereby the solubilizing sulfonic groups are blocked to a certain extent. Where the direct dyestuffs used are of such a nature that they form a metal complex, the wet-fastness properties and fastness to washing of the prints, and also in most cases their fastness to light, can be considerably improved by an aftertreatment with dilute, slightly acid Cu II salt solutions.

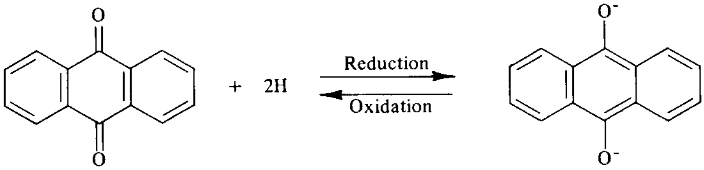
Printing with direct dyestuffs has never occupied a prominent position. The moderate wet-fastness properties sometimes lead to difficulties during processing. A staining of the white ground by the high-affinity dyestuff, for example, cannot always be avoided during rinsing.

B. WITH VAT DYESTUFFS

This dyestuff group continues to play an important part in textile printing, although in recent years it has lost ground through the introduction of reactive dyestuffs. Vat dyestuffs are versatile in application, i.e., they can be used in direct, discharge, and resist printing. They are notable for their outstanding all-around fastness properties. Their very good fastness to light and also, in certain cases, a weather resistance which is attained by no other dyestuff group render them suitable for curtains, furnishing fabrics, and awnings.

Vat dyestuffs are insoluble in water. During the steaming process they must be transformed into a soluble form so that they can diffuse into the cotton material. In the presence of alkali, such as soda ash, potash, or caustic soda, they are converted by suitable reducing agents during the steaming process into the water-soluble sodium leuco compound. In this form the dyestuff has an affinity for the fiber and also a considerable diffusibility. After the steaming process, a reoxidation must naturally take place to re-form the water-insoluble dyestuff.

Most vat dyestuffs are anthraquinone derivatives. The chemical reaction which occurs during fixation can be represented as follows:



Unfortunately, not all of the vat dyestuffs used in dyeing can also be used with equal success in textile printing. It is obvious that the leuco compound must be highly soluble in printing—a requirement which cannot always be met. Moreover, the dyestuffs must be quickly and easily reduced. The more negative the redox potential of a vat dyestuff, the more difficult it is to reduce. For use in printing, those products which undergo a chemical change—mostly associated with a change of shade—under the conditions prevailing in the steamer must also be eliminated. Certain acylamino derivatives of anthraquinone, for example, show a tendency to saponify, particularly in printing pastes or pad liquors with a high alkali content. With insufficient alkali, however, other dyestuffs may be converted from the enol form to the oxyanthrone form, which is more difficult to reoxidize.

Other anomalies, such as halogenation and over-reduction, must be considered when making a selection of suitable vat dyestuffs for textile printing.

The printing paste used in direct printing contains alkali and a suitable reducing agent in addition to the vat dyestuff. The dyestuff is printed in the unreduced state, reduction to the leuco form and fixation being obtained simultaneously during the steaming process.

The reducing agent must possess the following properties: At room temperature, i.e., in the printing paste, it must have no reducing effect, but must develop its full reducing action at steaming temperature, the redox potential being sufficiently negative to reduce all vat dyestuffs used in textile printing. These ideal requirements are difficult to fulfill.

Up to the present, sodium formaldehyde sulfoxylate [sodium hydroxymethanesulfinate, marketed under the name Rongalit C (BASF)] has proved satisfactory for this application. As an alkali, potash (potassium carbonate) is given preference since it is more easily dissolved than soda, while potassium salts of the leuco compound are in most cases particularly soluble. For these reasons direct printing is also known as the *Rongalit-potash process.*

An important disadvantage of this process is that the reducing agent may be destroyed by atmospheric moisture and oxygen during drying and storage of the prints prior to steaming.

Better behavior is shown by sodium aminomethane sulfinate, which is known as Rongalit FD (BASF). The prints show no change of shade or depth even after prolonged storage; this is a particular advantage when printing is carried out on screen printing tables. A disadvantage is that with this more stable reducing agent, because of the lower redox potential, fewer vat dyestuffs are suitable.

The prints are dried and then steamed for 8–10 minutes at 103–105° in saturated steam. The dyestuff is reduced after 10–20 seconds, the process being strongly exothermic so that an adequate supply of fresh steam is required, while a slight superpressure also prevents atmospheric oxygen from entering the steamer. Finally, the prints are rinsed, reoxidized, and soaped at the boil.

The two-phase printing process must be regarded as an important step forward. In the first phase a printing paste is applied which contains only the thickening agent and water in addition to the vat dyestuff. The printed fabric is dried and, in the second phase, is padded or impregnated with a solution containing alkali and the reducing agent. It then passes immediately into the steamer. The main advantages of this process are as follows: The stability of the printing pastes is no problem. The printed material can be stored for a practically unlimited period. The absence of alkali and reducing agent reduces wear of the undercloth. An increased depth of shade and, above all, more brilliant shades are often obtained than in direct printing. A larger selection of suitable dyestuffs is available. A selection of suitable reducing agents ensures a much higher rate of production.

In principle, the two-phase process has been known for many years; much tedious development work was, however, required to reach the present stage of production. The thickening agent must possess the following properties. It must be freely soluble at room temperature. The film of thickening agent which forms on the printed and dried fabric must be resilient and permeable, so that alkali and reducing agent can diffuse easily during the padding process. Since the prints must not smear, flake, or give up dyestuff to the pad solution during padding, the thickening agent must be able to form a coagulum to withstand these mechanical stresses. Formation of this coagulum is promoted by the use of coagulating agents, such as borax, in the pad liquor. Suitable thickening agents are carob bean gums, alginates, and alkyl cellulose ethers.

When sodium dithionite ($Na_2S_2O_4$) is used as a reducing agent, a steaming time of about 30 seconds is sufficient, i.e., considerably shorter than in direct printing. Sodium dithionite is, however, not ideal since it develops its reducing power at about 30°, which may cause the dyestuff to flake in the padding bath. Moreover, an air passage to improve penetration of the chemical solution into the fabric after padding cannot be recommended, since the reducing agent may be destroyed by atmospheric oxygen before the prints enter the steamer. These disadvantages are not experienced with the reducing agents based on hydroxyalkyl sulfinic acid and aminoalkyl sulfinic acid (Rongal A) (BASF), which have been especially developed for this process. At lower temperatures they are much more stable than sodium dithionite and also permit the same short steaming time of about 30 seconds.

Steaming of the prints is followed by thorough rinsing, oxidation, and soaping in the usual way. Certain vat dyestuffs are destroyed by reduction. This characteristic is used in *discharge printing.* In addition to the reducing agent, the discharge printing paste contains sodium hydroxymethanesulfinate, an alkylating agent, which converts the intermediate sodium leuco compounds formed during the steaming process into a water-soluble alkyl ether compound which is washed away after steaming.

Resist printing now has practically no importance. In this process, the parts of the fabric which are to remain unstained after the subsequent dyeing with vat dyestuffs are coated with a printing paste which prevents the diffusion and fixation of the dyestuff. For this application alkali binders such as zinc chloride, alum, etc., are added to the printing paste. Moreover, a thickening agent should be used which coagulates very strongly under the influence of alkali, as in the dyeing process, thus preventing penetration of the dyestuff by mechanical means.

C. WITH SULFUR DYESTUFFS

Although sulfur dyestuffs do not differ very much from vat dyes in their application technique, they are little used for textile printing, in contrast to dyeing, despite their favorable prices. The main reasons are as follows: Clear shades cannot be obtained. The dyestuffs are reduced to the soluble leuco form with sodium sulfide. In textile printing, this cheap reducing agent has the great disadvantage that it severely blackens the rollers in roller printing machines and the bronze gauze in screen printing apparatus.

D. WITH OXIDATION DYESTUFFS

In this case advantage is taken of the ability to form high molecular weight dyestuff pigments from simple, inexpensive aromatic amines by oxidation in the fiber. In textile printing, the so-called *Aniline Black* is used almost exclusively, since in addition to its economical price it also gives a full, bloomy black and possesses good light fastness and wash resistance. White and color resists under Aniline Black are much esteemed. The risk of tendering the fiber is a disadvantage. The printing formulas used depend on the available plant and, therefore, on the method of printing. A formula is suggested here for the direct printing of ferrocyanide steam black or Prud'homme Black. In addition to aniline salt, the printing paste also contains as oxidizing agents sodium chlorate and potassium ferrocyanide, which largely promote oxidation to the black dyestuff. HCl is liberated from the aniline salt during drying and steaming and is responsible for any tendering of the fiber. An addition of ammonium thiocyanate as a buffer substance is therefore recommended.

Formula (1000 g):

450 g	Starch-tragacanth thickening
90 g	Aniline salt
3 g	*p*-Phenylenediamine
10 g	Acetic acid
25 g	Sodium chlorate, dissolved in 165 g H_2O
60 g	Potassium ferrocyanide
15 g	Ammonium thiocyanate
182 g	H_2O

The prints are dried and then steamed at 100° for 2–3 minutes in saturated steam. The full black shade is attained in an alkaline aftertreatment with sodium bichromate.

Aniline Black is easily resisted by using a resist printing paste which contains acid-binding chemicals, such as alkali carbonates or sodium acetate, or reducing agents, such as sodium sulfite. When an Aniline Black liquor, formulated on the lines suggested for direct printing, is subsequently padded, the parts of the fabric coated with the printing paste resist the formation of Aniline Black.

Where color resists are required, suitable vat dyestuffs, reactive dyestuffs, Rapid Fast, and Rapidogen dyestuffs (naphthol products) can be added to the resist printing paste. Color resists can also be obtained with pigment dyestuffs and suitable binders.

Overprint resists are to be preferred to preprinted resists, since there is less danger of bleeding and sharper outlines are therefore obtained. In overprint resists the printing paste is applied to the goods after they have been padded with the Aniline Black solution and dried. Care must be taken to ensure by a careful intermediate drying that no premature oxidation to Aniline Black takes place on the fabric, since the resist would otherwise be considerably impaired.

E. WITH COUPLING DYESTUFFS

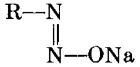
Advantage is taken of the ability to form a water-insoluble dyestuff in the fiber by coupling a diazonium component with a naphthol compound. These prints are notable for full, heavy, and, in certain cases, brilliant shades with good to very good all-around fastness properties.

In the *base printing process* the fabric to be printed is first padded with an alkaline naphthol solution and dried. As naphthols only the following products can be used: 2-hydroxy-3-naphthoic acid anilide (Naphtol AS), 2-hydroxy-3-naphthoic acid *o*-toluidide (Naphtol AS-D), 2-hydroxy-3-naphthoic acid *o*-anisidide (Naphtol AS-OL). The required diazonium salts of suitable aromatic bases are then printed. Coupling to form the dyestuff takes place immediately. Surplus naphthol is removed in an alkaline soaping process after drying. It is obvious that this process is more economical the larger the printed patterns, since in this case less surplus naphthol must be removed.

The *naphtholate printing process* is an inversion of the base printing process, although it has attained less importance. The fabric is printed with a printing paste containing a naphtholate solution. It is then dried and padded with a diazonium solution, when coupling to form the dyestuff takes place. Any surplus diazonium compound remaining on the prints is removed in a washing process with sodium bisulfite. Both of these processes must be carried out in two phases and are uneconomical where only small patterns are to be printed.

In *one-step direct printing*, the printing paste contains the naphtholate and also the diazotized base in a stabilized form. Coupling in the printing paste is thus prevented. Development to the dyestuff is effected by steaming, or else in dry heat or by a wet treatment.

Stabilized diazo compounds of types (I) or (II) are available.

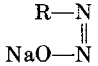


$$\mathrm{R{-}N{=}N{-}ONa}$$

(I)

anti-Diazotate

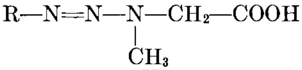
In the presence of excess caustic soda the *anti*-diazotate is much more stable than the *syn*-diazotate:



$$\mathrm{R{-}N{=}N{-}ONa}$$

and the printing pastes possess sufficient stability. Development is effected by brief steaming and a subsequent passage through an acetic acid or formic acid Glauber's salt bath, or alternatively in a so-called acid steamer. This is a steamer into which a mixture of acetic acid and formic acid is injected.

The diazo compound is stabilized with a water-soluble aliphatic or aromatic amine, e.g., with sarcosine:



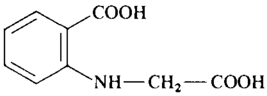
$$R{-}N{=}N{-}\underset{\displaystyle CH_3}{\underset{|}{N}}{-}CH_2{-}COOH$$

(II)

Diazoamino compound

These diazoamino compounds are notable for their outstanding stability. Development is also mainly effected by the methods described for compounds of type (I).

A further step forward was achieved with the introduction of the neutral steam brands, i.e., diazoamino compounds which are coupled with naphthol in neutral steam. This is brought about by the reaction of the diazonium compound with water-soluble amines which are slightly basic, such as *N*-phenylglycine-*o*-carboxylic acid.



Mixtures of these compounds with naphthols considerably facilitate the work of the printer, and are marketed under the following trade names: Cibaneutren, Ciba; Iratral, Geigy; Neutrogen, FMC; Rapidogen, Bayer, etc.

F. WITH REACTIVE DYESTUFFS

Because of the brilliant shades, good to very good all-around fastness properties, and simple application, this recently developed dyestuff group for cotton and regenerated fibers is very widely used in textile printing. The reaction between these dyestuffs and the fiber is described in detail in Chapter III, Vol. VI.

Careful attention must be paid to the selection of thickening agents, because as polysaccharides these may also react with the reactive dyestuff. Alginate thickening agents have proved very satisfactory.

The various reactive dyestuff ranges now available differ in their reactive components. The chemistry of these reactive components, i.e., their reaction with cellulosic fibers and the stability of the fiber–dyestuff bond, largely determines their behavior in printing and therefore the differences in application.

The present state of development of the reactive dyestuff ranges is such that each range gives optimum printing results under certain conditions, i.e., in one case with the application of dry heat, in another with a steaming process, etc. The development of the reactive dyestuff ranges is by no means concluded. The discovery of new and more economical reactive components enlarges, or at least diversifies, the fields of application.

From a technical standpoint, a reactive dyestuff range should meet the following optimum requirements for textile printing:

(a) High stability of the printing paste in the alkaline pH range.

(b) Short fixation time in a rapid steamer, or else in dry heat, either on drying cylinders or hotflues.

(c) The difference of shade and depth between cotton and regenerated fibers must be a minimum.

(d) Maximum dyestuff yield, i.e., the highest proportion of color-fast dyestuff on the fiber, related to the amount of dyestuff used.

(e) Easy removal of any unfixed dyestuff remaining on the fiber after the fixation process, using the usual washing units; no soiling of the white ground.

Requirement (e) means that the reactive dyestuff must possess a very low affinity. It may be pointed out that this affinity depends both on the chromophore component and also on the reactive component. Moreover, it is a great advantage if the fiber–dyestuff bond is stable not only in the alkaline range, but also in the acid range.

The main fields of application for reactive dyestuffs are in clothing and apron materials. For these applications, coupling and vat dyestuffs, in particular, are being replaced by the new reactive dyestuffs.

In *direct printing,* the alkali required for the chemical reaction is added direct to the printing paste. Sodium bicarbonate or soda ash is sufficient for reactive dyestuffs with short fixation times, but caustic soda is required for dyestuffs which are fixed more slowly. An addition of urea as a hydrotropic compound has proved beneficial. Fixation is obtained by neutral steaming with saturated steam for 2–8 minutes or by a dry heat passage at 150° for 2–5 minutes.

A further possibility is the pad-steam process, which may be compared with the two-phase printing process for vat dyestuffs discussed in Section V,B. The dyestuff is printed in a neutral medium, i.e., without alkali. After intermediate drying, the goods are padded with an alkali solution and immediately steamed. An advantage of this process is that the stability of the printing pastes is no problem. On the other hand, it may be a disadvantage for those reactive dyestuffs which do not show an optimum stability of the fiber–dyestuff bond in the alkaline range. In this case, with a relatively high alkali concentration on the goods, a breakdown of the bond must be expected when at a given temperature a certain steaming time is exceeded, and this may result in differences of shade and depth. In the wet development process, fixation of the prints is obtained in a hot alkali passage on a full-width washer for 10–30 seconds. Although in this case no steamer is required, this process is not always more economical since the consumption of chemicals is high. The liquor may contain, for example, per liter:

50 g	Caustic soda 32.5%
150 g	Soda ash
50 g	Potash
150 g	Common salt

In a similar manner to the popular cold pad-batch process used in dyeing (which see), textile prints produced with very reactive dyestuffs can also be developed by an alkali passage and subsequent storage. The batching time required to obtain a maximum color strength also depends, of course, on the alkali used.

Since the fixation of the dyestuff on the fiber is obtained only in the alkaline range, *resist printing* can be carried out by preprinting with a printing paste which contains nonvolatile organic acids, such as tartaric and citric acid. The reactive dyestuff is resisted in the printed parts during the subsequent padding or impregnation process. Color resists can be produced successfully by addition of pigments and binders to the acid printing paste.

G. PIGMENT PRINTING

In recent years the pigment printing process has increased enormously in importance. The very economical method of application and the ability to print all fiber types—also blended yarns containing synthetic fibers—with simple apparatus, are features which have aroused great interest.

Advantages of Pigment Printing

(a) Largely independent of the textile material, the same color strength is obtained with good fastness properties.

(b) Subject to a suitable selection of pigments, the fastness to light of pigment prints is surpassed by no other printing process.

(c) Since no aftertreatment is required, no printing process is more economical for the production of medium and heavy shades.

A disadvantage is the sensitivity to crushing of the printing pastes, which is particularly perceptible when using roller printing machines. For this reason the compound shades of overprints are also thinner and duller than the starting colors.

Another disadvantage is the heavy benzine required to produce the printing pastes, above all because of the special safety precautions which must be taken during printing and fixation.

In the pigment printing process, as the name implies, pigments are attached to the fiber by the adhesion of a thin film of synthetic resin. The pigments are members of various dyestuff groups (azo, anthraquinone, phthalocyanine dyes, etc.). Their suitability depends not only on their fastness properties, but also to a large extent on their physical and printing properties. Particle size, hardness, specific gravity, and charge of the pigment particles are characteristics which play an important part.

Modern pigment printing, which is discussed here, invariably uses the emulsion technique. A distinction is made between the aqueous phase and the organic phase, the latter generally consisting of aliphatic hydrocarbons. As binders, those hardenable synthetic resins are used which are either soluble in the organic phase, or soluble or dispersible in the aqueous phase. They must also be capable of forming an elastic film on the fabric.

As can be seen under the microscope, the great advantage of these emulsion printing pastes is that they are deposited on the fabric in the form of points or tiny islands and in this way envelope the pigment.

The textile character of the material is therefore largely maintained. In principle, two different systems are distinguished.

a. *Water-in-Oil Emulsions.* Water is dispersed in oil and forms the inner phase, while oil forms the outer phase and in quantity is also the lesser component. The binder is dissolved in the oil phase, while the pigment lies dispersed in the water/oil boundary zone.

To improve the fastness properties of the prints, the aqueous phase also often contains a hardenable carbamide resin and an acid donor. After printing and drying, fixation is obtained by a treatment in dry heat at 150°. Since oil forms the outer phase in this system, the printing rollers and screens are best cleaned with organic solvents.

b. *Oil-in-Water Emulsions.* In these printing pastes the inner oil phase is quantitatively the larger component compared with the outer aqueous phase. The binder is mainly in the aqueous phase. The binders used are polymers with reactive groups which can be cross-linked with polyfunctional compounds. These polymers may be of various structures. The behavior of the emulsion printing paste during printing and also the properties of the binder film formed on the fabric may therefore differ widely. Methylol–melamine products, as well as urea–formaldehyde resins, are used as polyfunctional compounds. The polymers are mostly based on acrylic compounds, butadiene, and other monomers.

Fixation of the dried prints, in this case also, is obtained in hot air at 150°. In no case is rinsing and soaping or any other aftertreatment of the prints required.

The oil-in-water process is more widely used than the water-in-oil process.

VI. Printing of Wool

The classic wool printing article, wool muslin, has lost much of its importance in recent years, particularly as a result of the rapid progress made by synthetic fiber materials. The following are now the main applications: combed wool, buntings, carpet yarns, plushes, and also knitted dress goods. In many cases, particularly dress goods, wool is chlorinated prior to printing. In this way, not only is the felting property of the fiber greatly reduced, but the affinity for dyestuffs is also considerably increased. In comparison with cotton and synthetic fibers, wool is a very sensitive material, and an optimum textile character can therefore be maintained only by devoting particular care to the composition of the printing paste, as well as to the drying and steaming processes. Wool undergoes a minimum amount of damage to the fiber in the isoelectric range (pH 4.5–5). In this range a minimum swelling also naturally occurs. It is beneficial to add hygroscopic agents, such as glycerine, to the printing paste, which is thereby prevented from drying up. Reducible dyestuffs can be protected against the reducing action of wool by an addition of weak oxidizing agents, such as *m*-nitrobenzenesulfonic acid.

Practically the same dyestuffs used in dyeing are also employed for printing. As acid donors, organic acids, such as acetic, tartaric, lactic, and citric acids, are used. For blotch prints it is an advantage to use ammonium salts of these acids. The slow dissociation of these salts during the steaming process considerably promotes the production of uniform prints.

Where particularly high fastness properties are required, as in the case of vigoureux printing, chrome dyestuffs are used. The presence of chromium III salts in the printing paste ensures formation of the complex during the steaming process. To attain maximum fastness properties, this complex formation must not take place until the dyestuff has diffused into the fiber. This is achieved by an addition of oxalic acid.

As in the case of acid dyestuffs, fixation is obtained by a treatment in saturated steam for 30–60 minutes.

In textile printing there has long been a keen demand for clear, brilliant shades with high all-around fastness properties. It is well known that the fastness to regular laundering on chlorinated wool does not always meet modern requirements. In any case, it is not so good as on unchlorinated wool. This oxidation process is, however, now being used on an increasing scale for hand-laundered goods to confer on woven or knitted fabrics a nonshrink finish which prevents wool from felting during domestic laundering. In recent years, the dyestuff manufacturers have closed this gap in wool printing by marketing extremely suitable reactive dyestuffs especially for the dyeing and printing of wool, i.e., Lanasol dyestuffs (Ciba), and Verofix dyestuffs (Bayer).

These dyestuffs form a firm chemical bond with the fiber and it is therefore not surprising that the fastness to washing and wet processing is not reduced on chlorinated wool. The printing process is relatively simple. Any of the thickening agents used in wool printing are suitable, particularly products based on carob bean gums. Ammonium sulfate has proved satisfactory as an acid donor. Fixation is obtained by a treatment in saturated steam, generally for about 20 minutes depending on the required depth of shade and on the nature of the goods. Although a very high degree of fixation is achieved, i.e., a high ratio of chemically bound dyestuff to the amount of dyestuff used, amounting in certain cases to 90%, the unfixed dyestuff must nevertheless be removed in an aftertreatment, particularly in the case of heavy prints and where optimum wet-fastness properties are required.

This aftertreatment is given at about 70° and at a pH value of 8–9 (adjusted with ammonia).

VII. Printing of Silk

For the printing of silk, practically the same dyestuff groups are used as for the printing of wool. Silk is more stable to alkalies than wool, however, and direct dyestuffs may therefore be applied to silk by the method used for cellulosic fibers.

Degummed silk is best used for textile printing. It must be remembered that during the entire course of manufacture the material is very sensitive to mechanical strain.

Silk printing is considerably influenced by fashion, brilliant shades being in particular demand. For this reason, cationic dyestuffs continue to be of interest. In pale shades they are printed as acid dyestuffs; in heavy shades an aftertreatment with tannin/tartar emetic is recommended to improve the wet-fastness properties.

Modern development shows that in the future reactive dyestuffs may gain in importance for silk printing. In contrast to wool, fixation is possible and recommended not only in the acid range, but also in the slightly alkaline range (sodium hydrogen carbonate).

VIII. Printing of Synthetic Fibers

A. Polyamide Fibers

The main materials for printing are woven and knitted fabrics made from Perlon (polyamide 6; caprolactam) and nylon (polyamide 6.6; hexamethylenediamine and adipic acid).

The pretreatment of the goods is on the lines recommended for dyeing, i.e., after scouring, the woven or knitted fabric is set so that it retains its shape. Depending on the nature of the goods and on the available plant, this is achieved either by hydrofixation on cotton dyeing apparatus or by treatment with hot air on a stenter. The material can be printed on roller or screen printing machines, and also on screen printing tables.

The following dyestuff groups may be used: (1) selected acid dyestuffs; (2) selected direct dyestuffs; (3) 1:2, 1:1 metal complex dyestuffs; (4) disperse dyestuffs. Reactive and vat dyestuffs play practically no rôle. Basic dyestuffs, as used in the dyeing and printing of acrylic fibers, while possessing considerable brilliance show only a moderate fastness to light and are therefore used only for a few special articles.

Of the specified dyestuff groups, (1)–(4), metal complex dyestuffs possess the highest fastness properties, but generally give subdued, thinner, and flatter shades. Acid and direct dyestuffs give clearer shades, but in heavy shades the fastness to washing and wet processing is not always sufficient. Finally, disperse dyestuffs can be used only in pale shades, since they possess poorer wet-fastness properties than the previously mentioned dyestuff groups.

Fixation is obtained in rapid steamers and star steamers, the latter being given preference for delicate materials which are liable to stretch under tension. The full depth of shade, with an optimum penetration of the capillary filaments, is generally achieved in 20–30 minutes at 103°. Where fixation is obtained in steam at 0.5 atmosphere superpressure, the diffusion speed of the dyestuff is considerably increased, so that the same color strength is obtained under these conditions as in normal steam fixation, but in half the normal time.

Disperse dyestuffs can also be fixed in dry heat at 190°. An addition of urea as a hydrotropic substance improves the yield. Less brilliant prints than in steam fixation are, however, generally achieved. A much harsher handle of the material is also obtained.

Washing of the prints to remove from the goods any unfixed dyestuff, and also thickening and chemicals, often leads to a staining of the white ground when acid dyestuffs are used. Unfixed dyestuff from the printed parts is taken up from the washer by the white, unprinted parts. This trouble can be avoided by an addition of suitable auxiliaries to the rinsing bath, such as Mesitol PNR (Bayer), Erionol NWS (Geigy), Cibatex PA (Ciba). The wet-fastness properties and fastness to perspiration of the prints are also often considerably improved. The same improvement of these properties can also be achieved by an aftertreatment with tannin/tartar emetic.

B. POLYACRYLONITRILE FIBERS

The various types of polyacrylonitrile fibers now available often differ considerably in their chemical and physical constitution. In addition to pure polyacrylonitrile fibers, there is also a wide range of copolymeric fibers, i.e., fiber types which in addition to acrylonitrile also contain small amounts of vinyl compounds. A distinction must also be made between dry-spun and wet-spun fiber.

For these reasons it is obvious that the various acrylic fibers may differ in their coloristic behavior. They can be dyed and printed in all cases with cationic dyestuffs, although there are often wide variations in the maximum depth of shade which can be obtained.

As in dyeing, cationic dyestuffs should also be given preference in textile printing. With few exceptions, they meet practically all coloristic requirements. Prints produced with them are notable for brilliant shades and outstanding wet-fastness properties and fastness to crocking. The fastness to light, and also in certain cases the weather resistance, are excellent. In this respect, the level of vat prints on cotton is often attained. The printing pastes must be acidic, since in the neutral pH range cationic dyestuffs may be precipitated. Additions of thioethylene glycol and cyclohexanol promote the solubility of the dyestuffs in the printing paste.

Fiber swelling agents improve the rate of dyestuff absorption in the steaming process, but they must be easily removed during washing and must cause no tendering of the fiber. Glyezin PFD (BASF) (dicyanogen ethyl formamide) has proved very satisfactory for this application.

Disperse dyestuffs give more subdued shades with poorer wet-fastness properties. In textile printing, however, they offer the advantage of sharper outlines than can be obtained with cationic dyestuffs. For this reason, e.g., for outline black, mixtures of disperse dyestuffs are given preference.

Fixation of the dyestuff can be achieved only by steaming, rapid steamers of the Mather Platt or Krostewitz type being unsuitable for lighter weight fabrics since the softening range of the fiber is below 100°

and tensile stresses during the steaming process result in a deformation of the fabric which cannot be subsequently corrected. For this reason, cottage steamers or star steamers should be used. The steam must not, however, be too dry since in this case certain cationic dyestuffs do not develop their full brilliance. The steaming conditions are 20–30 minutes at 0.2–0.4 atmosphere superpressure. A careful aftertreatment is indispensable for good fastness to crocking and maximum brilliance. The following method has proved satisfactory: Rinse in an ample supply of cold water, soap at 70° with an anionic detergent in the acid pH range (acetic acid), then rinse again and dry.

C. POLYESTER FIBERS

The water-soluble sizes are mostly removed during preliminary washing. The fabric is then set in dry heat at 200° for 30 seconds on a tenter frame to stabilize its shape. Printing is carried out mainly with selected disperse dyestuffs. The rate of diffusion of disperse dyestuffs into polyester fiber is considerably lower than into acetate and polyamide fiber, although polyester fiber has a higher affinity for the dyestuff. For this reason only ring-dyed goods are obtained by normal steaming without pressure. The rate of diffusion can be considerably increased by addition of so-called carriers to the printing paste. Fixation in the star steamer under pressure has proved very satisfactory. The dyestuff yield increases more or less proportionally to the steam pressure. The normal treatment is 20–30 minutes at 1.5–2.5 atmospheres superpressure. Fixation of the printed dyestuff can also be obtained by the Thermosol process at about 200° for 60 seconds, but the shades are not always so brilliant as those achieved by steaming under pressure. After steaming, the goods are rinsed, and, to obtain maximum fastness properties, particularly fastness to crocking, are given a reduction clearing treatment with caustic soda and hydrosulfite.

Polyester/cotton blended yarns are continually gaining in importance and already play a greater rôle in textile printing than materials made from pure polyester fibers. For this reason, the printing of polyester/cotton blends must be briefly discussed.

Apart from pigment printing, which possesses without doubt the larger share of the market, only selected vat dyestuffs give the same shade and same depth on both fiber types. Such products are marketed, for example, under the name Polyestren dyestuffs. Fixation of the vat dyestuff is obtained on the polyester fiber by the Thermosol process, followed by fixation on the cotton by the two-phase printing process (see Section V,B). Mixtures consisting of disperse and vat dyestuffs can also be applied in a similar manner. The disperse dyestuff is fixed by the Thermosol process, while the vat dyestuff is developed by the previously mentioned two-phase process.

Very interesting possibilities are offered by mixtures consisting of disperse and reactive dyestuffs, not only because brilliant shades can be obtained, but also because these dyestuff mixtures can be applied by simpler and, therefore, economical processes. The possibilities depend largely on the reactivity of the reactive dyestuff. Reactive dyestuffs are available which can be printed with sodium bicarbonate and fixed in dry heat, giving very good yields (e.g., Levafix P dyestuffs, Farbenfabriken Bayer). Sodium bicarbonate generally causes no interference with disperse dyestuffs and both dyestuff groups can therefore be fixed by the Thermosol process, a considerable simplification thus being achieved. Other reactive dyestuffs are best fixed by steaming or in an alkaline shock treatment. Where alkali-resistant disperse dyestuffs are available, special printing paste formulations permit fixation of the disperse dyestuff and the reactive dyestuff to be obtained in a single operation by steaming under pressure (20–30 minutes at 1.5 atmospheres superpressure).

IX. Fastness Tests on Dyestuffs

A. The Meaning of Fastness

The fastness of a dyeing or textile print signifies its resistance to a number of different influences. We distinguish between the fastness to processing and the fastness to wearing of a dyestuff. All the properties required of a dyeing or print during the various processes carried out in the manufacture of textiles (e.g., soaping, acid treatments, mercerization, decatizing) are grouped under the first-mentioned definition, whereas the resistance to the influences to which a dyeing or print is exposed during the subsequent use of textiles is known as the fastness to wearing. The latter definition includes the fastness to light, water, washing, perspiration, etc.

Since a dyestuff possessing absolute fastness is unknown, we must always consider the fastness of a dyeing as a relative value, e.g., in comparison with that of another dyeing. The textile manufacturer knows which properties are required of a given article. He therefore carefully selects the dyestuff to be used. This work is facilitated if information is available in fastness tables regarding the fastness properties of a dyestuff. An objective and, therefore, uniform evaluation naturally depends on the adoption of strict rules for the fastness tests.

B. ORGANIZATIONS

The dyestuff manufacturers had recognized the far-reaching importance of fastness evaluations as early as the last century. We therefore find evaluations of the fastness to light, water, and washing of the dyestuffs offered in the first customers' circulars and sales literature. Since, however, these fastness evaluations were not based on uniform test methods, an objective comparison of the dyestuffs offered by the various manufacturers was extremely difficult. Both dyestuff manufacturers and users were equally interested in the solution of this problem. In Europe, for example, before and after the First World War, national and international associations were formed to draw up strict rules for determining the fastness properties.

In 1914, the Deutsche Echtheitskommission (DEK) was formed. Then, in 1934, a fastness commission was also founded by the British Society of Dyers and Colourists (SDC). After the Second World War, international associations were formed by amalgamation, i.e., the Fastness Convention for the Continent of Europe (ECE) and ISO (International Organization for Standardization). In the U.S.A. a fastness commission was also formed by the American Association of Textile Chemists and Colorists (AATCC). An active exchange of experience exists between these organizations with a view to the unification, *inter alia,* of the fastness evaluations and test methods.

C. EVALUATION OF THE FASTNESS PROPERTIES

The fastness to light is evaluated in eight fastness steps, whereas five steps are provided for the other fastness properties. Step 1 denotes the lowest, and Steps 5 and 8 the highest fastness evaluations.

It is well known that the fastness of a dyeing depends on the depth of shade. For this reason, an exact comparison of the fastness evaluations of dyeings is possible only in the same depth of shade. To facilitate comparison a range of 20 shades has been provided, all in the same medium depth. These so-called "auxiliary types" give a good idea of the depth of shade in which the comparative testing of dyestuffs must be carried out in all shades.

For evaluation of the fastness to light, a scale consisting of eight blue wool dyeings with a graduated fastness to light has been provided. If a dyeing which is exposed to light in comparison with this "blue scale" shows, for example, the same degree of destruction as dyeing "5" of the scale, then its fastness to light is evaluated "5."

The other fastness properties are evaluated by the following method: The change of shade and depth of the dyeing, and the staining of accompanying fabrics occurring during the fastness test, e.g., fastness to water, are evaluated. The fastness is evaluated in figures with the aid of the "gray scale." The gray scale to determine the "change of shade" is distinguished from the gray scale to determine the "staining of adjacent fabrics." The scale "change of shade" has five neutral gray dyeings corresponding to the five fastness steps, the difference in depth to the deepest gray dyeing corresponding to the specified degrees of fastness.

The scale for the "staining of adjacent fabrics" is also a five-step scale. It consists of the white fabric together with a neutral, pale gray dyeing for each single step. As shown in Fig. 3, these gray dyeings are deeper stepwise. To evaluate the fastness, the test piece is placed beside the gray scale "change of shade" or "for the staining," and the change of shade or staining is compared with the steps of the respective scale.

D. Test Methods

The test method or laboratory tests must be arranged in such a manner that the dyeing to be tested satisfies the requirements which it is expected to meet in practice during subsequent processing and use. In addition to a test for the fastness to light, there are nearly 30 different test methods which can be used to determine the suitability of a dyestuff for definite requirements. There is a test method to determine the fastness to water, and others for the fastness to acids, ironing, perspiration, etc.

To ensure unvarying test results, and also to accelerate the tests, testing apparatus is being used on an increasing scale.

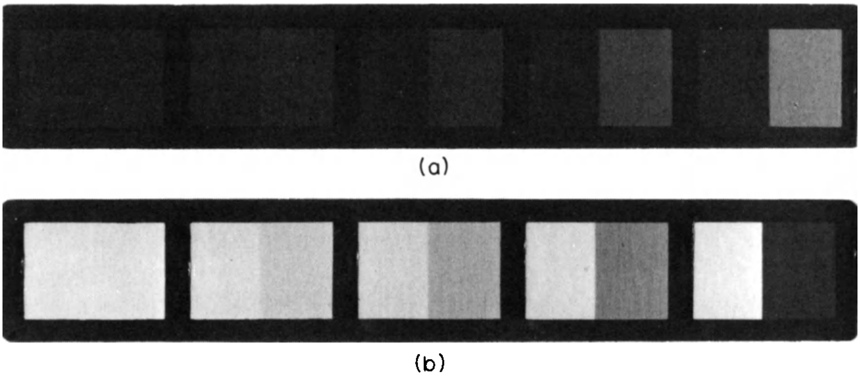


FIG. 3. Gray scale.

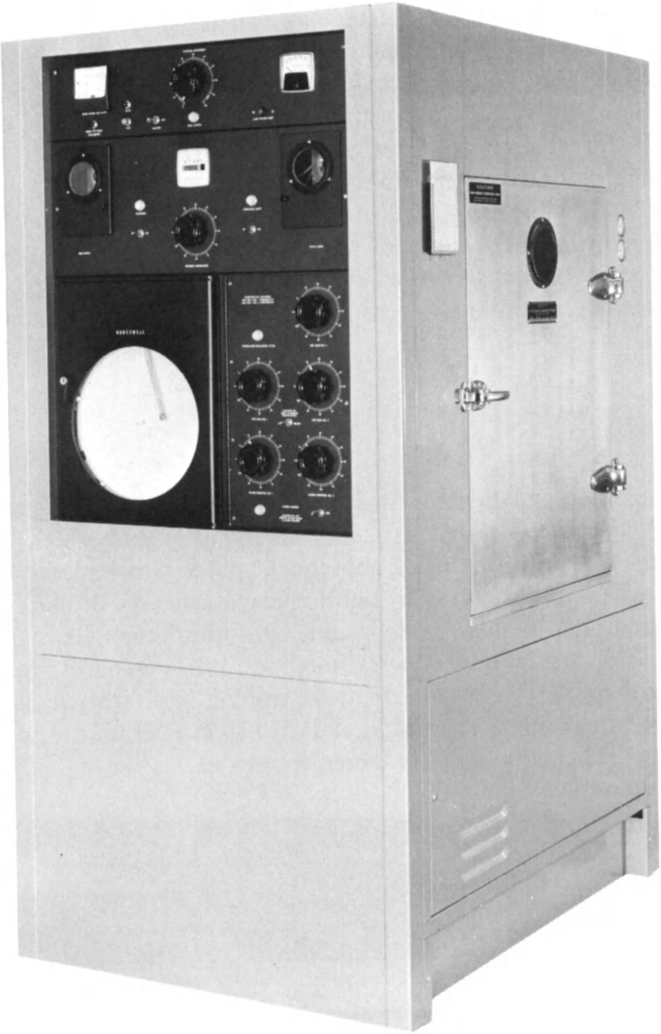


FIG. 4. Fade-Ometer of Atlas Electric Devices Co. (U. S. A.) to determine the fastness to light of a dyeing. It involves xenon or enclosed carbon arc light source with thermistor temperature controls, controlled humidity from 20% to 60%, program controller, two pen wet and dry bulb temperature recorder and other user-oriented features.

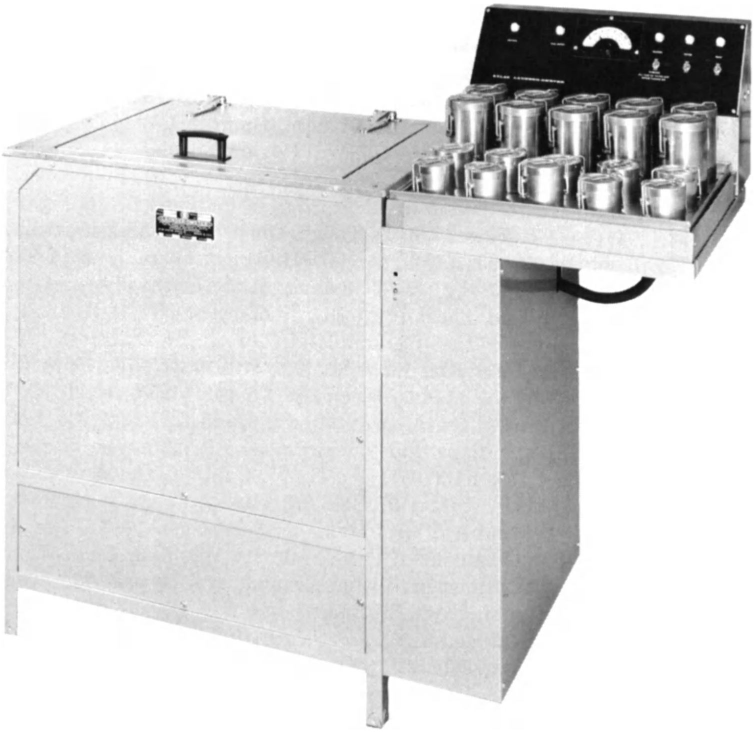


FIG. 5. Launder-Ometer of Atlas Electric Devices Co. to test the wet-fastness properties, dyeing, dry cleaning, and detergency, with controlled temperature and motion.

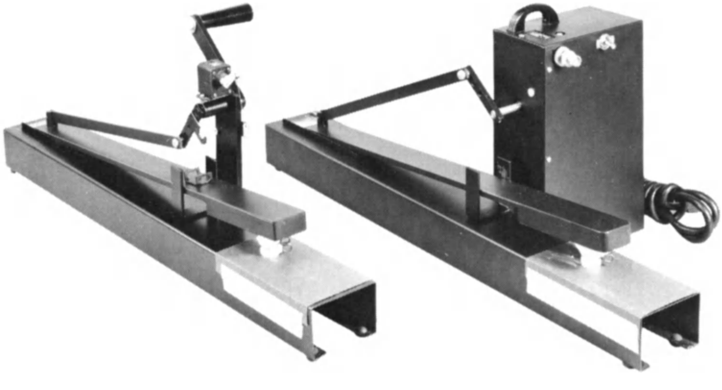


FIG. 6. Crockmeter apparatus. Manual and motorized versions provide standard motion and pressure to determine colorfastness to crocking in addition to other rubbing tests.

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CHAPTER III

BASIC DYES

N. R. Ayyangar and B. D. Tilak

NATIONAL CHEMICAL LABORATORY, POONA 8, INDIA

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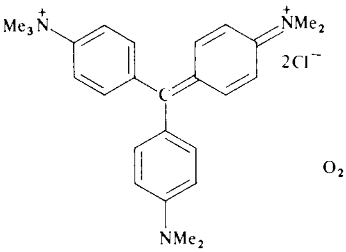
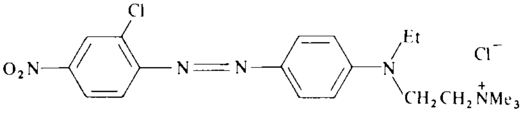
I. Introduction

Historically, basic dyes are important because the first synthetic dye, Mauvein (CI 50245), which was discovered in 1856 by William Perkin in the oxidation products of crude aniline, belongs to this class of dyes. The discovery of technically important dyes such as Malachite Green and Magenta followed soon after. Except for a few isolated examples, practically all the well-known basic dyes were discovered before the beginning of this century. Literature on basic dyes up to 1951 has been discussed in Chapters XXIII, XXIV, and XXV of *CSD II*. The basic azo dyes, such as Bismarck Brown (CI 21000, Basic Brown 1), are described in Chapter XII of *CSD I*. By definition, basic dyes are cationic dyes, which have substantivity for tannin-mordanted cotton. Basic dyes ionize in solution whereby the chromophore present carries a positive charge. The charge is generally delocalized throughout the chromophoric system, although it is probably more localized on the nitrogen atoms. A few dyes such as Methyl Green (CI 42585, Basic Blue 20) (I) have multivalent cationic chromophores. The dye bases are colorless and the color appears only after the salt formation. Basic dyes are used only to a limited extent now for dyeing cotton. Most of the recent activity in basic dyes consists in the development of new dyes for polyacrylonitrile fibers. An example of such a dye is Astrazol Red GTL (FBy; CI 11085, Basic Red 18) (Sevron Red GL, DuP) (II), which gives dyeings with good wet-fastness and excellent fastness to light.[1] The chemistry of these dyes is dealt with in the chapter on cationic dyes for synthetic fibers (see D. R. Baer, Chapter IV). The present chapter covers developments in classical basic dyes which have taken place since 1951.

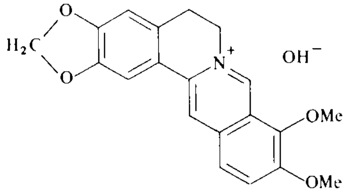


(Zinc double chloride)

(I)



(II)



(III)

The alkaloid berberine[2] (CI 75160, Natural Yellow 18) (III) is the only example of a basic dye isolated from nature which finds place in the *Colour Index*, although it has limited value for coloring textiles.

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[1] D. Haigh, *Dyer* **132**, 111 (1964).

[2] J. A. Napier, "A Manual of the Art of Dyeing." Griffin, Glasgow, 1853, and subsequent eds.; J. J. Hummel, "Dyeing of Textile Fabrics," 3rd ed. Cassel, London, 1888; F. Mayer and A. H. Cook, "The Chemistry of Natural Colouring Matters," A.C.S. Monograph, Series No. 89, New York, 1943.

Basic dyes have been classified according to their chemical constitution as well as dyeing properties (see *CSD II*).

After a brief general description of their dyeing and other properties, the more recent work on basic dyes will be reviewed in the following pages.

II. Properties

Basic dyes do not dissolve readily in water. In fact, special attention has to be paid to dissolve them in water to avoid formation of a sticky mass, which, if formed, is difficult to dissolve. The best method to dissolve a basic dye is to make it into a paste with about its own weight of ethanol or dilute acetic acid (30%). Addition of sufficient hot water with proper agitation yields a clear solution. Auramine (CI 41000, Basic Yellow 2) is decomposed, when treated with boiling water. It should be dissolved in water at temperatures below 65°. Other basic dyes also decompose slightly, if boiled with water for a long time. Basic dyes are sensitive to alkali and they liberate colorless dye bases, when treated with alkali solutions. For example, Pararosaniline (CI 42500, Basic Red 9) (IV) gives the corresponding carbinol base (V), which regenerates the dye salt (IV) on treatment with acid. Further treatment of (IV) in alcoholic solution with acid results in salt formation at another nitrogen atom with consequent color change. In triphenylated Pararosaniline (CI 42760, Solvent Blue 23) (VI), which can be obtained by heating (V) with excess aniline at 180° in the presence of benzoic acid, the NH group may be expected to be much less basic. However, the carbinol bases of both (IV) and (VI) give the corresponding dye salts, when treated with weak acids such as acetic, boric, or carbonic acids. This shows that the basicities of the carbinols are practically of the same order, in spite of the low basicity of the NH groups in (VI). It may therefore be concluded that these dyes exist as carbonium ions in acidic solutions and that their color may be likened to the salt obtained from triphenyl carbinol with acid.[3]

Trisulfonation of (VI) gives Ink Blue (S) or Helvetia Blue (Ciba) (CI 42780, Acid Blue 93), the heavy metal lakes of which are used as pigments for printing inks. Many of the carbinol bases derived from basic dyes are sparingly soluble in water, and they are precipitated out when the dye solutions are treated with alkali. Hence water containing alkali or temporary hardness should be first treated with acetic acid before using it for dissolving the basic dyes.

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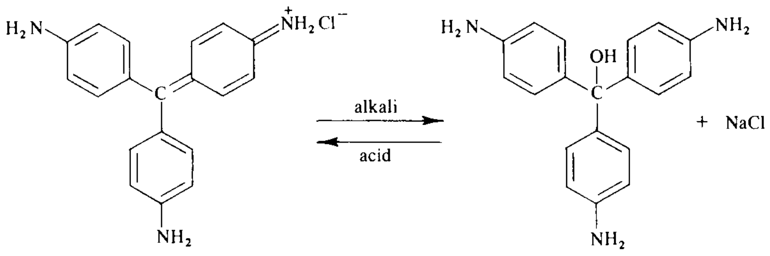
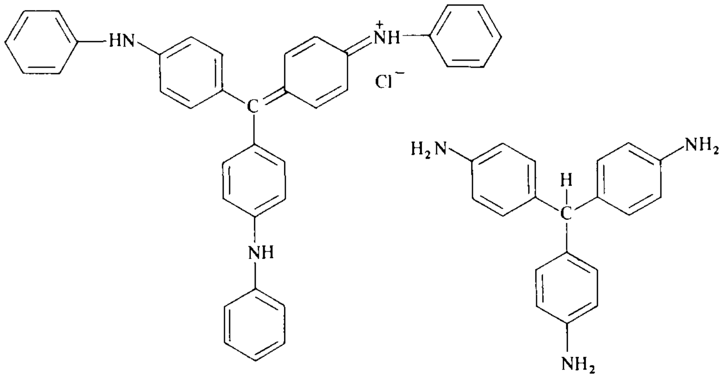
[3] V. F. Lavrushin, T. M. Shmaeva, and I. M. Nikolaeva, *Dokl. Akad. Nauk SSSR* **105**, 492 (1955).



(IV) (V)



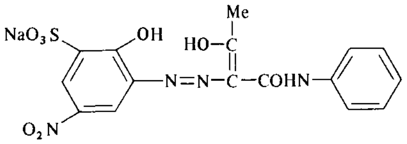
(VI) (VII)

Reducing agents convert the basic dyes to the corresponding colorless leuco bases, which, in turn, are readily reoxidized to the original dyes. On reduction, Pararosaniline yields the leuco base (VII).

Like other aromatic compounds, basic dyes can also be sulfonated with sulfuric acid; they are thus converted to the corresponding acid dyes by sulfonation.

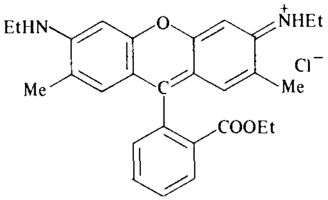
Most basic dyes are beautiful shiny crystalline compounds and their most outstanding property is brilliance and high intensity of color, which is unmatched by any other class of synthetic dyes. However, basic dyes are fugitive to light, which limits their use in dyeing.

Basic dyes, being cationic, are precipitated by anionic dyes such as acid and direct dyes. This property has been made use of in the aftertreatment with basic dyes of cellulosic materials, which have been dyed previously with direct colors. Bright shades are thus obtained. Azosol Fast Brilliant Red BA (G, Solvent Red 36) is a dye complex obtained from Acid Yellow 99 (CI 13900) (VIII) and Basic Red 1 (CI 45160) (IX). The insoluble salts between dye bases and dye acids are useful as colorants for ink pastes used in ballpoint pens. For example, the insolu-

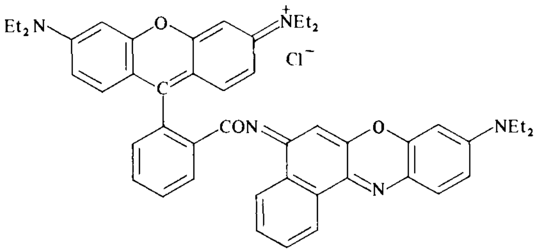


(Chromium complex)

(VIII)



(IX)



(X)

ble salt obtained by heating a mixture of Rhodamine 6G or 6GDN (CI 45160, Basic Red 1) (IX) and Benzo Orange S (CI 29150, Direct Orange 26) can be used as a red colorant for ballpoint pen inks. The resulting pigment is very fast to light and is insoluble in ethanol or acetone.[4] The property of mutual precipitation of cationic and anionic dyes has been used for the production of new biological stains and histochemical reagents such as Rhodanile Blue, to which an unacceptable covalently linked structure (X) has been assigned.[5] This dye is obtained by reacting Rhodamine B (CI 45170, Basic Violet 10) with Nile Blue (CI 51180, Basic Blue 12). Covalent structures, such as (X), for these pigments have been the subject of controversy and it has been shown that Rhodanile Blue is nothing but a mixture of Rhodamine B and Nile Blue.[6] Basic dyes are also precipitated with tannic acid and this property is the basis of dyeing cellulosic fiber with basic dyes.

III. Uses of Basic Dyes

Basic dyes can be applied to wool, silk, and leather and also to tannin-mordanted cotton. The high tinctorial power of the basic dyes and the

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[4] B. von Zychlinsky, *BP* 1,062,321.

[5] E. Gurr, *Lab. Pract.* **15,** 1128 (1966); "The Rational Use of Dyes in Biology," p. 49. Leonard Hill, London, 1965.

[6] R. Consden, J. Dorling, and J. E. Scott, *Chem. Brit.* **3,** 407 (1967).

brilliance of their shades is unsurpassed. However, they have very poor fastness properties, particularly to light, and have been more or less completely replaced by dyes belonging to other classes as regards their use for coloring textiles. However, with the advent of polyacrylonitrile fibers for which basic dyes are extremely useful, these dyes are now used extensively for dyeing textiles derived from this fiber. Basic dyes can be applied to these synthetic fibers by conventional methods to give bright dyeings of good fastness to light. The other present day usage of basic dyes is confined mainly to nontextile purposes. Thus basic dyes are used extensively for coloring paper, transfer sheet materials for hectographs, typewriter inks, and plexographic printing. Basic dyes have also been shown to be of potential interest in photography. Some basic dyes also find use as biological stains and as colorants for inks.

IV. Application of Basic Dyes

Protein fibers such as wool, silk, and leather can be dyed with basic dyes under faintly acid conditions. The free carboxylic acid groups present in such fibers have a tendency to form salts with dye cations, showing that the affinity between the cationic dyes and protein fibers is of a chemical nature. The fastness of basic dyes on animal fibers can be improved by aftertreatment with tannic acid and antimony salts such as tartar emetic (potassium antimony tartrate). The high affinity of basic dyes for protein fibers necessitates the use of retarding agents during dyeing. A small amount of acetic acid serves the purpose. The free hydrogen ions compete with the dye cations for the electronegative sites in the fibers and slow down the rate of absorption of the dye. Absorption of Methylene Blue by wool decreases considerably below pH 6 and becomes very small at pH 4.5.[7] Crystal Violet[8] also behaves similarly. Thus the exhaustion of basic dyes appears to be very sensitive to change in pH in the region 4–6.[9] Acrylic fibers, which contain acidic sulfonic acid groups[10] (Orlon 42 and Courtelle), have much higher affinity for basic dyes, with consequent better wet-fastness of the dyeings and somewhat poor leveling properties. In this case exhaustion of the dyebath appears to be less sensitive to pH change. Hence unions of acrylic fiber and wool can be dyed with some basic dyes at higher temperatures around pH 4–5, without heavy staining of wool taking place. The exhaustion on acrylic fibers of basic dyes is slow below 80°, but increases rapidly above that

[7] T. R. Briggs and A. W. Bull, *J. Phys. Chem.* **26**, 845 (1922).

[8] E. Elöd, *Trans. Faraday Soc.* **29**, 327 (1933).

[9] C. L. Bird and G. P. Stancey, *J. Soc. Dyers Colourists* **77**, 244 (1961).

[10] S. Rosenbaum, *Textile Res. J.* **33**, 899 (1963).

temperature and is maximum at 100°. The rapid uptake of basic dyes on acrylic fibers has led to the development of dye retarders,[11] which are of two types: (i) those which react with the dyes in the dyebath and form a complex, which breaks only slowly at the boil; and (ii) those which are cationic in nature and compete with the cationic dyes for dyeing sites. Most of the water-soluble quaternary ammonium salts such as benzylphenyldimethylammonium chloride have a retarding action and are good leveling agents in the dyeing of polyacrylonitrile fibers with basic dyes.[12] The I-T Process employs an anionic leveling agent (Irgasol DA), which forms a complex with basic dyes. They are maintained in a fine state of dispersion by a nonionic agent (Tinegal NA). During dyeing, the complex breaks down slowly yielding even distribution of the dye.[13]

It has been shown that the equilibrium adsorption of a cationic dye increases with an increase in sulfonic acid sites in the polyacrylonitrile fibers, although the effect is not linear.[14] The acidic groups which control the sorption of basic dyes, are introduced in the polyacrylonitrile polymers, when persulfates and bisulfites are used as polymerization catalysts.[15] It has also been shown that acrylic fibers contain a mixture of strong and weak acidic groups, the latter having ionizing constants comparable with those of carboxylic acids. The changes in dye absorption with increasing pH are due to the number and strength of these weakly acidic groups.[16]

Cellulosic fibers have no affinity for basic dyes. These fibers have to be mordanted before dyeing with basic dyes. The usual mordant used is tannic acid, which is subsequently fixed by treatment with tartar emetic. This tedious operation can sometimes be avoided by using synthetic mordants, such as Katanol, Katanol O, Resistone, or Tanninol BM. They are usually prepared from phenol by heating with sulfur and a trace of an iron compound. The substances are of complex composition and their chemical structures are not known. The mordanted cotton is then dyed with the dye solution in the presence of acetic acid.[17]

Offset or lithographic prints of good fastness to washing and rubbing

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[11] Chemstrand Corp., *USP* 2,740,687; W. Beckman, *Chemiefasern* p. 452, (1958).

[12] S. Cohen and A. S. Endler, *Am. Dyestuff Reptr.* **47,** 325 (1958); BASF, *BP* 884,157; FBy, *BP* 897,742.

[13] J. A. Leddy, *Am. Dyestuff Reptr.* **49,** 272 (1960); see also W. Beckman [*J. Soc. Dyers Colourists* **77,** 616 (1961)] for an excellent review on dyeing polyacrylonitrile fibers with basic dyes.

[14] S. Rosenbaum, *Textile Res. J.* **34,** 52, 159, and 291 (1964).

[15] W. Hees, *Melliand Textilber.* **42,** 87 (1961).

[16] D. Balmforth, C. A. Bowers, and T. H. Guion, *J. Soc. Dyers Colourists* **80,** 577 (1964).

[17] E. R. Trotman, "Dyeing and Chemical Technology of Textile Fibres," p. 333. Griffin, London, 1964.

TABLE I

FASTNESS TO WASHING AND LIGHT OF SOME BASIC DYES ON WOOL AND COTTON[1]

	Fastness to			
	Washing		*Light*	
Dye	*Wool*	*Cotton*	*Wool*	*Cotton*
Auramine O	1–2	2	1–2	1–2
Auramine G	1–2	2	2	2
Malachite Green	4–5	4–5	1	1
Brilliant Green	2–3	4–5	1[2]	1–2[2]
Fuchsine (Magenta)	3–4	4–5	1	1
Crystal Violet	2–3	3	1	1
Ethyl Violet	2	2	1	1
Methyl Green	1	2	1	1
Victoria Pure Blue BO	2	2–3	1	1
Rhodamine 6G	3–4	2–3	1	1
Rhodamine B	3	1	3	1
Meldola's Blue	1–2	2	1	1
Methylene Blue	1–2	3	1	3
Methylene Green	4 (silk)	3[2]	2 (silk)	5[2]

[1] Based on Continental or DEK (Deutsche Echtheitskommission) tests.

[2] Based on American (AATCC) tests.

can be obtained by forming water-insoluble salts of basic dyes with aliphatic carboxylic acids. These are applied and fixed by steaming and soaping.[18]

V. Fastness Properties

Basic dyes as a class are either poor or only moderately fast to washing and their poor lightfastness (rarely exceeding 2 on a scale of 1–8) is their biggest drawback. The fastness properties of some of the well-known basic dyes are recorded in Table I. The diaminotriphenylmethane dye, Malachite Green (XXIV; see below) has superior wash-fastness to that of Crystal Violet (XXIX), a triaminotriphenylmethane dye. Similarly Brilliant Green, the diethyl analog of Malachite Green is superior in wash-fastness to Ethyl Green, the diethylamino analog of Crystal Violet. Methyl Green (I), which has two cationic charges, has poor wash-fastness properties. Rhodamine B has moderate wash- and lightfastness properties on wool. It is of interest to note that Methylene Green (CI 52020, Basic Green 5), a nitro derivative of Methylene Blue (CX) has

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[18] A. Messerli, *BP* 686,231.

superior lightfastness compared to that of Methylene Blue. However, its dull bluish green shade is not so attractive.

The "onium" nature of basic dyes is the main cause of their photosensitivity. The light-fugitiveness of these dyes can be influenced only to a small extent by making other alterations in the chemical structure of the dye. Sulfonated basic dyes, which are acid dyes, exhibit improved lightfastness, and such dyes are preferable to basic dyes for dyeing wool. The main reason for the fading of basic dyes may be the autoxidation of the dye or oxidation by hydrogen peroxide formed by the photochemical oxidation of traces of water in the fiber. A detailed account of lightfastness of basic dyes will be found in CSD II (p. 1223). The importance of basic dyes for textiles is increasing since the commercial introduction of polyacrylonitrile fibers in 1953. Basic dyes can readily be applied to these fibers and bright dyeings of very good fastness to light are obtained. Unlike the natural fibers, polyacrylonitrile fibers are hydrophobic in nature and the dyed sites in the fiber are not easily accessible to moisture and oxygen, which are supposed to be responsible for the fading processes. This may account for the good lightfastness of basic dyes on acrylic fibers.[19]

As regards the dyeings of basic dyes on acid-modified poly(ethylene terephthalate) (Dacron) fibers, it has been found that some substituted hydroxybenzophenones, such as 2,2′-dihydroxy-4,4′-dimethoxybenzophenone, act as light screeners and improve fastness to light of the dyeings.[20] These compounds can be applied by the normal dyeing techniques. Dyeings with basic dyes, such as Rhodamine 6G or 6GDN (CI 45160, Basic Red 1) (IX) and Crystal violet (CI 42555, Basic Violet 3) (XXIX), of cellulose film modified by treatment with cyanuric chloride and further with *p*-aminophenol, or of cellulose film having directly bound *p*-aminophenol, had improved fastness to light.[21] However, the reverse was the case when Rhodamine B (CI 45170, Basic Violet 10) was used.

VI. Diphenylmethane Dyes

Dyes of this subclass are ketonimine derivatives and only two such dyes have been listed in the second edition of the *Colour Index*. They are Auramine O (CI 41000, Basic Yellow 2) (XI) and Auramine G (CI 41005, Basic Yellow 3) (XII). They are still manufactured on a large scale, because of their cheapness and the brilliance of their shades, and

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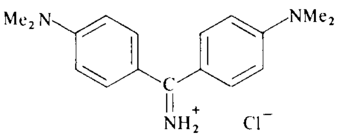
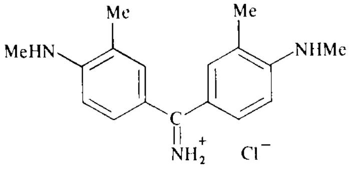
[19] F. Jones, *Rev. Textile Progr.* **14**, 303 (1962).

[20] S. B. Macrov and H. Kobsa, *Textile Res. J.* **31**, 697 (1961).

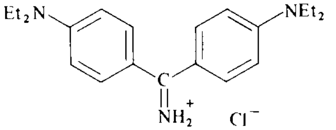
[21] H. Kling and F. Galil, *Textil-Praxis* **22**, 261 (1967).



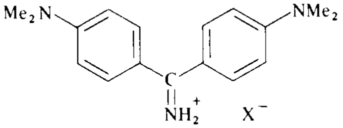
(XI)



(XII)

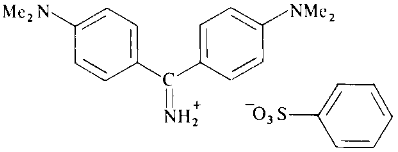


(XIII)



(X = NO_3^- or NO_2^-)

(XIV)



(XV)

find extensive use in the coloration of paper, silk, jute, and leather and for the preparation of lakes. The greenish yellow diethyl analog (XIII) of Auramine O is also now available commercially as Calcozine Yellow FW (CCC) (CI 41001, Basic Yellow 37).[22] It has been found that use of urea in the preparation of these dyes by the Sandmeyer process improves the yields of these dyes.[23] Thus, when Auramine was prepared by passing anhydrous ammonia through 4,4′-bis(dimethylaminodiphenyl)-methane, sulfur, ammonium chloride, and large amount of common salt at 170° for 6 hours, a 61% yield was obtained. Replacement of half the sodium chloride by urea increased the yield to 85%. Incorporation of sulfamic acid in the above process, improves the yield further and gives a purer product.[24] Thus, urea and 4,4′-bis(dimethylaminodiphenyl)methane are heated to 120° in an atmosphere of ammonia. Sulfamic acid, urea, and sulfur are added and the mixture heated at 175° for 5½ hours. The melt is then poured into water and the dye salted out. A yield of

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[22] CCC, *USP* 3,132,178.

[23] CCC, *BP* 975,844.

[24] CCC, *BP* 1,033,169.

91% is realized. The auramine sulfamate formed in the reaction may be directly used for dyeing and coloring or can be readily converted into Auramine base.[25]

Generally, dyes of the Auramine series are isolated as hydrochlorides. They have good water solubility, but are not sufficiently soluble in alcohols and hence could not be used in lacquers and plexographic printing colors. The usual Auramine hydrochlorides, when treated with the nitrates of calcium, ammonium, sodium, or potassium or the nitrites of sodium, potassium, or barium in water at 60° to 80° give Auramine nitrates or nitrites (XIV), which have excellent solubility in alcohols and could be used for making lacquers and making plexographic printing colors.[26] Similarly, Auramine salts with alkyl sulfonic acids, aralkyl sulfonic acids, or aryl sulfonic acids have good solubility in alcoholic solvents and in aqueous alcohols, which facilitate their use in offset printing. Details of a typical preparation are as follows: Auramine O (152 parts) is stirred under reflux for 1 hour with finely ground sodium benzenesulfonate (80 parts) in 99% to 100% ethanol (1200 parts). The mass is filtered at 35°, washed with a little ethanol, and the filtrate evaporated to give an Auramine dye (XV), practically free from sodium chloride and quite soluble in aqueous alcohols.[27]

Leuco-Auramine derivatives such as (XVI) and (XVII) are stable, colorless, crystalline materials, which turn dark blue or blue green when brought in contact with acidic inorganic compounds such as aluminum sulfate, zinc sulfide, bentonite, attapulgite, or kaolin; and they are suitable for printing bluish shades on paper containing such acidic substances. The lightfastness of the prints is very good. These alkyl and halogen derivatives are better for transfer coatings in manifold record systems than the unhalogenated *N*-phenyl leuco Auramine, because they are less volatile and have more oil solubility. They are prepared by condensing the substituted arylamines with Michler's hydrol. By refluxing for 4 hours on a steam bath a mixture of 2-methyl-5-chloroaniline (70.8), Michler's hydrol (135), and ethyl alcohol (500), crystals of (XVI) were obtained, which were practically colorless.[28,29] The leuco derivative (XVIII), prepared from Michler's hydrol and 5-trifluoromethyl-2-chloroaniline, on contact with kaolin turns blue-violet and is useful in the preparation of copy paper.[30] Similarly, the quaternary leuco-Auramine

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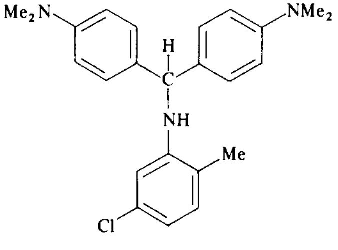
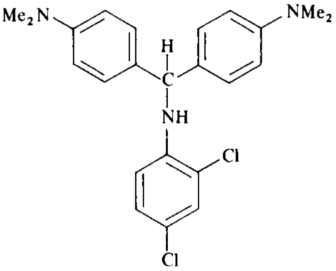
[25] CCC, *USP* 3,268,585.
[26] BASF, *BP* 815,966.
[27] BASF, *BP* 884,882.
[28] National Cash Register Co., *BP* 788,427.
[29] National Cash Register Co., *BP* 804,087.
[30] Nippon Kayaku Co. Ltd., *JP* 15,026.



(XVI)



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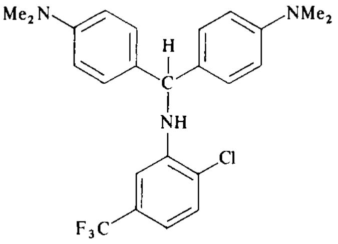
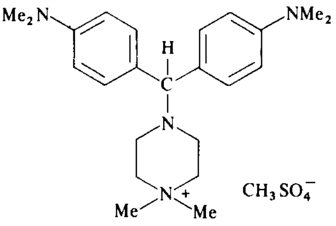


(XVIII)



(XIX)

compounds, such as N-bis-(p-dimethylaminophenyl)methyl-N', N'-dimethylpiperazinium methosulfate (XIX) colors papers impregnated with acidic components, such as succinic acid, and gives an intense bluish violet shade. They can be used in colorless carbon papers.[31] The compound p-dodecylphenylamino-bis(p-dimethylaminophenyl)methane (XX) and similar leuco derivatives with alkyl chains of 8 to 20 carbon atoms are also useful in the production of colorless transfer sheets, which when used in conjunction with an acid-reacting copying sheet, yield blue characters on the copying sheet as a result of pressure. They are readily soluble in tricresylphosphate and mineral oil.[32] Michler's hydrol has also been condensed with alkyl esters of o- and p-aminobenzoic acids[33] and compounds like 10-(p-aminobenzoyl)-3,7-bis(dimethylamino)phenothiazine.[34] Aliphatic amino derivatives such as (XXI) of leuco Auramine also have improved stability in colorless carbon papers.[35] Sulfinic or hydrazoic acid salts of the diphenylmethane derivative (XXII) are colorless

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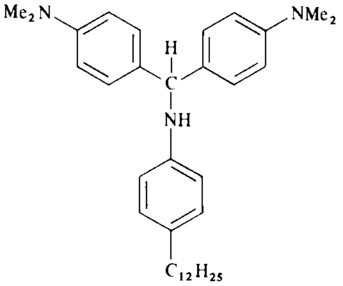
[31] NAC, *BP* 1,082,918.

[32] ICI, *BP* 1,050,468.

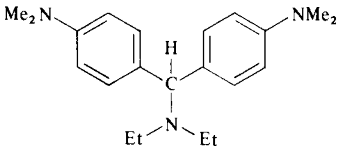
[33] Coribonum Ltd., *BP* 831,852.

[34] Coribonum Ltd., *BP* 817,564.

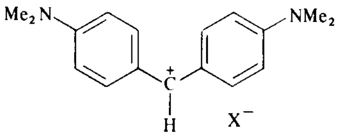
[35] NAC, *BP* 873,186.



(XX)



(XXI)



(XXII)

($X^- = N_3^-$, $4\text{-}MeC_6H_4SO_2^-$ or $EtSO_2^-$)

when associated, but are highly colored when dissociated. They are prepared by dissolving Michler's hydrol in acetic acid, adding sulfinate or azide, and precipitating the salt by the addition of water. Kaolin-coated paper gives highly colored images when printed with a solution of such salts.[36]

Highly concentrated solutions of Auramine dyes can be prepared by treating the corresponding bases with acid salts in water-miscible solvents such as formamide.[37] Thus, Auramine O base (134), suspended in formamide (280), is treated with sodium bisulfate (63), with stirring, for a long time. After filtration, a 40% solution of Auramine O was obtained, which finds use in paper industry. The solution can be diluted with water, as desired.

VII. Triphenylmethane Dyes

Triphenylmethane dyes form a major subclass of basic dyes; and in spite of the advent of new superior dyes of other classes, many of them

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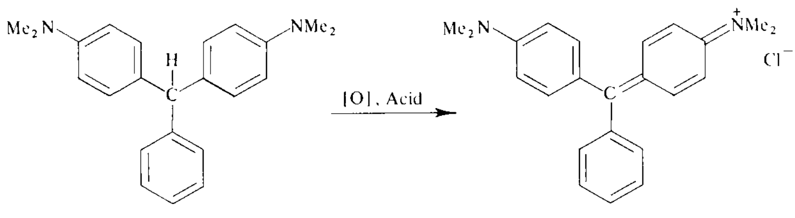
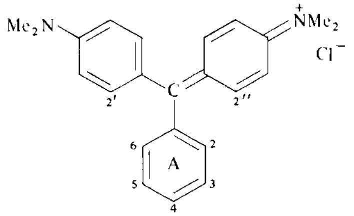
[36] Chester Davis, *USP* 3,193,404.

[37] BASF, *BP* 995,954.



(XXIII) (XXIV)



(XXV)

have still retained their importance. Details of the methods of their preparation are given in Chapter XXIII of *CSD II*.

Malachite Green (CI 42000, Basic Green 4) (XXIV) is prepared by condensation of two molecules of dimethylaniline with one of benzaldehyde. The leuco base (XXIII), which is thus obtained, is then oxidized with oxidizing agents of high electrochemical potential such as lead dioxide to give the dye salt (XXIV) with acid. It has been observed that the yield of the resultant Malachite Green was dependent on the rate of addition of the oxidant to the 4,4′-dimethylaminotriphenylmethane (XXIII). Rapid addition of the oxidant produced almost quantitative yield of (XXIV), whereas slow addition of the oxidant resulted in yields below 35%.[38] The lower yields are due to the formation of a hydrated form, which is susceptible to oxidation and decomposition.

Derivatives of Malachite Green, substituted by fluorine at the 2,3-; 2,4-; 2,5-; and 2,6-positions in the phenyl ring A [see (XXV)] can be prepared by the condensation of the corresponding fluorine-substituted benzaldehydes with more than twice the molar quantity of dimethylaniline in the presence of zinc chloride, followed by oxidation and acidification.[39] Similarly the 2′,2″-difluoro derivative [(XXV), fluorine at 2′ and 2″] can be obtained by reacting two molecules of 3-fluorodimethylaniline with a molecule of benzaldehyde in the presence of zinc chloride. The derivatives with fluorine atoms in ring A of (XXV) gave blue to

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[38] V. Hanousek and M. Matrka, *Chem. Listy* **50,** 1969 (1956).

[39] K. Inukai and Y. Maki, *Kogyo Kagaku Zasshi* **59,** 1160 (1956).

bluish green dyeings of fairly good fastness to light, but the 2′,2″-difluoro derivative was yellowish and rather fugitive to light. Other substituents such as chloro, nitro, and hydroxy groups in the ortho position with respect to the central carbon atom of triphenylmethane dyes were also responsible for the reduced lightfastness of such dyes.[40]

Water-soluble diaminotriphenylmethane derivatives such as (XXVII) can be conveniently prepared from the corresponding dimethoxy carbinol (XXVI) by condensation with an appropriate aromatic amine sulfonic acid.[41] The discovery that basic dyes could be applied to polyacrylonitrile fibers has revived the interest in these dyes and their methods of preparation. Methyl Violet (CI 42535, Basic Violet 1) (XXVIII), which is generally prepared by the oxidation of dimethylaniline by air with copper sulfate as catalyst in the presence of diluents such as phenol and salt (see CSD II, p. 719), could be obtained in pure form and in good yield by carrying out the oxidation of dimethylaniline in the presence of an emulsifying agent.[42] Compounds such as sodium alkyl naphthalenesulfonate (Alkanol B), octyl alcohol, dibutyl phthalate, and dodecyltrimethylammonium chloride (Onyxsan S, Arganad 12) can be used as emulsifying agents. The details of the process are as follows: A solution of copper sulfate (160 parts) and sodium chloride (53) in water (540) is treated with siliceous filter aid (24). An emulsifying agent (3) is added, followed by dimethylaniline (224). The mixture is heated to 60° and stirred. A solution of sodium chlorate (56) in water (120) is added gradually and vigorously stirred until the reaction is almost completed. The mixture is further heated to 85° and then cooled to room temperature. Copper is removed as copper sulfide and Methyl Violet is salted out from the aqueous solution. Formation of Crystal Violet (CI 42555, Basic Violet 3) (XXIX) by the reaction of dimethylaniline vapors with aluminum chloride *in vacuo* has been reported.[43] The triphenylmethane dye (XXX), prepared by the condensation of Michler's hydrol and *N*-ethyl-*N*-benzyl-*m*-toluidine in the presence of sulfuric acid, and oxidation with lead dioxide, gives a brilliant blue shade on unbleached sulfite-treated cellulose, wood pulp, and ethyl cellulose.[44]

Dyes suitable for dyeing and printing acrylic fibers can be obtained by treating ammonia or primary aryl amines with 4,4′,4″-trihalogenotriphenyl carbinol (XXXI).[45] The carbinol (XXXI), m.p., 85°, is obtained

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[40] V. F. Borodkin, *Tr. Ivanovsk. Khim.-Tekhnol. Inst.* **8,** 116 (1958).

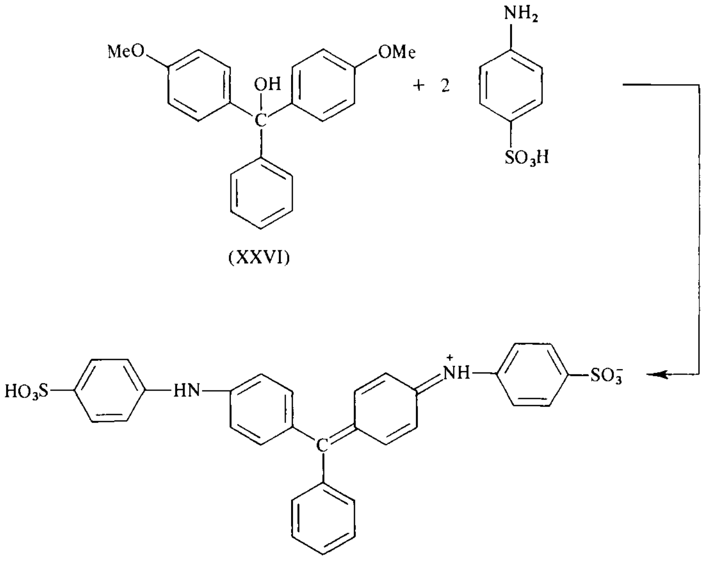
[41] Ferrania Societa per Azioni, *FP* 1,407,962; 1,411,442.

[42] CCC, *USP* 2,816,900.

[43] H. Sato, *Bull. Chem. Soc. Japan* **38,** 1719 (1965).

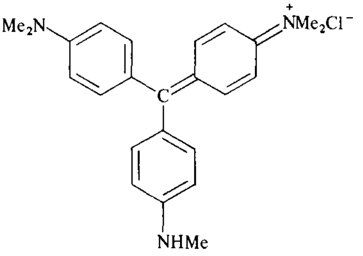
[44] FBy, *BeP* 648,866.

[45] CIBA, *BP* 800,857.

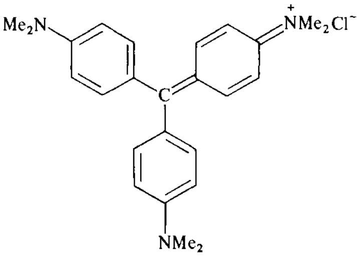


(XXVI)

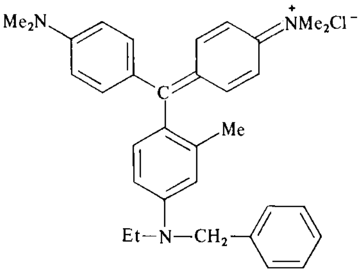
(XXVII)



(XXVIII)

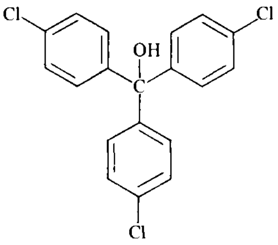


(XXIX)

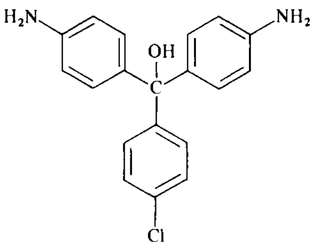


(XXX)

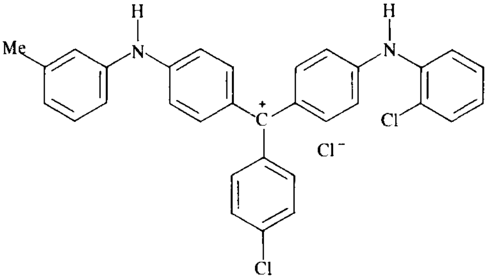
by condensing *p*-chlorobenzotrichloride with two molecules of chlorobenzene in the presence of aluminum chloride or ferric chloride at 80° to 100°. By heating a mixture of (XXXI) (182), copper powder (2), copper sulfate (10), and 25% ammonia (600 parts) in an autoclave at 195° to 200° for 10–12 hours, the diaminocarbinol (XXXII) is obtained as a pale colored powder. It gives a red-violet dye salt with acid, which gives a bordeaux shade on polyacrylonitrile, when applied from dilute acetic acid bath at the boil. Similarly triphenylrosaniline (VI) can be obtained from (XXXI) and aniline. The dyes obtained from the carbinol (XXXI) are symmetrically substituted. Both symmetrical and unsymmetrical 4-halogeno-4′,4″-diarylaminotriphenylmethane halides, such as (XXXIII), can be prepared from the aluminum chloride complex of 4,4′,4″-trihalogenotriphenylmethyl chloride (XXXIV), which unlike the carbinol (XXXI) can react with arylamines in successive single steps.[46] Thus, by reacting the aluminum chloride complex of (XXXIV) with one molecule of *m*-toluidine at 95–110°, in an inert organic solvent, the complex metal salt of 4,4′-dihalogeno-4″-(3″- methylphenylamino)triphenylmethane is obtained. By further reacting this with an excess of a second arylamine (e.g., *o*-chloroaniline) and finally by treating the product with dilute



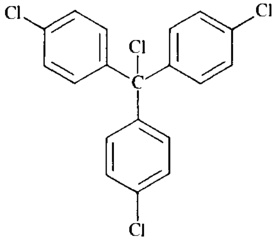
(XXXI)



(XXXII)



(XXXIII)



(XXXIV)

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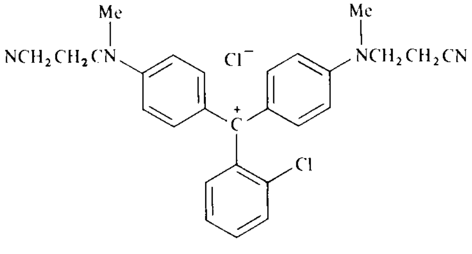
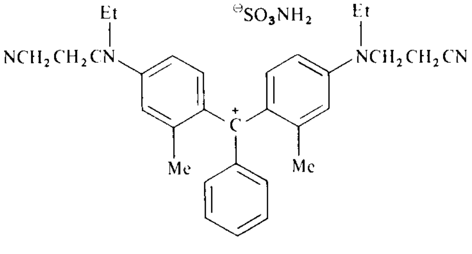
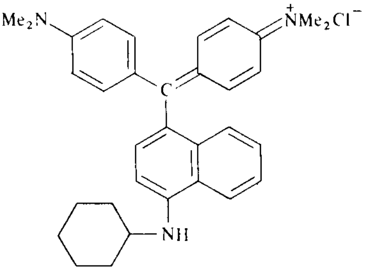
[46] FH, *BP* 1,000,664; 1,003,684.



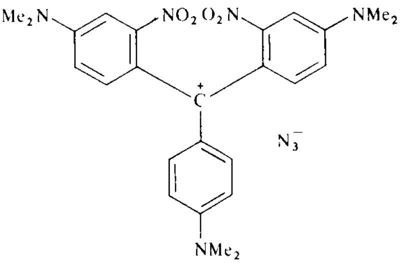
(XXXV)



(XXXVI)



(XXXVII)



(XXXVIII)

acid, the unsymmetrical dye (XXXIII) is obtained. A bright greenish blue dye (XXXV) for acid-modified acrylic fiber has been prepared by heating a mixture of *o*-chlorobenzaldehyde with two molecules of *N*-methyl-*N*-(2-cyanoethyl)aniline in isopropanol in the presence of sulfuric acid or *p*-toluenesulfonic acid and urea. The leuco derivative, so obtained, is oxidized with lead dioxide and the resulting carbinol is treated with acid.[47] The dyeings with this dye are stable to changes in pH. A similar dye (XXXVI), prepared from benzaldehyde and *N*-ethyl-

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[47] DuP, *USP* 3,021,344.

N-(2-cyanoethyl)-*m*-toluidine, dyes polyacrylonitrile a yellowish green shade.[48]

Many of the new triphenylmethane derivatives find potential use in photography, transfer sheet materials, and plexographic printing. Blue alcohol-soluble dyes such as (XXXVII) are useful in the manufacture of carbon papers and offset printing inks and for coloring nitrocellulose lacquers, waxes, and plastics. This dye is prepared by the condensation of Michler's ketone with *N*-cyclohexyl-1-naphthylamine in the presence of phosphorus oxychloride. The cyclohexyl ring may be further substituted by aliphatic groups. These reddish blue dyes are better than Victoria Blue B (CI 44045, Basic Blue 26) and are not precipitated from alcoholic solutions even on long standing.[49] A paper printed with a solution of dinitro Crystal Violet azide (XXXVIII), when developed by contact with 25% water in acetone or with kaolin, yields highly colored images.[36]

Neutral or slightly alkaline solutions of tris- 4[bis(4-dimethylaminophenyl)methylamino]phenylmethane (XXXIX) are colorless. If such a solution is incorporated in coatings of transfer sheet materials or in a typewriter ribbon, and used with an acid-receptive sheet, a dark blue color is immediately developed. In the presence of an oxidizing agent, a reddish color is obtained, which along with the blue gives a violet shade. Thus, it is possible to obtain copies in blue and violet shades. Compound (XXXIX) is prepared by condensing three parts of Michler's hydrol with one of tris(*p*-aminophenyl)methane (VII), obtained by the reduction of Pararosaniline.[50] The cyano derivatives of dyes such as New Magenta (CI 42520, Basic Violet 2) (XL) are photosensitive products and are useful in actinometry and for photographic and photoduplication processes.[51] The colorless compound (XL) is prepared by treating New Magenta (25 parts) in water (350) at 45° with 95% sodium cyanide (5.3) in water (25).[52] The product is purified by dissolving in triethyl phosphate and diluting with water at 25°. All the operations should be carried out in the absence of UV light. The colorless, photosensitive cyano derivatives of triphenylmethane dyes can also be prepared by heating the parent dyes with excess sodium or potassium cyanide in sealed containers at 100°.[53] Photosensitive gray to black triphenylmethane derivatives such as (XLI) and (XLII), which are useful in textiles and other graphic

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[48] MCI, *FP* 1,470,451.

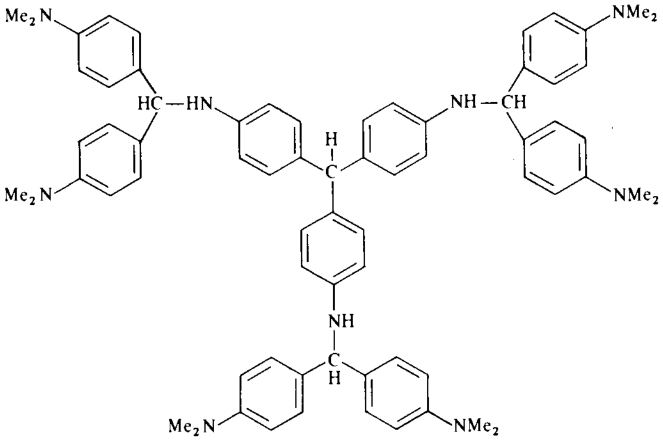
[49] BASF, *BP* 978,739.

[50] Caribonum Ltd., *BP* 835,809.

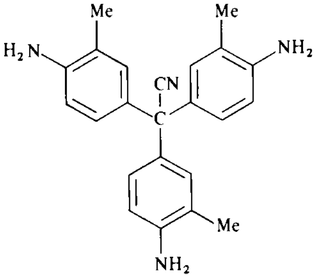
[51] L. Chalkley, *USP* 2,829,148.

[52] L. Chalkley, *USP* 2,829,149.

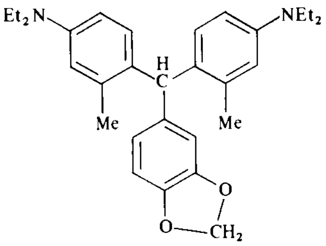
[53] L. Chalkley, *USP* 2,839,543.



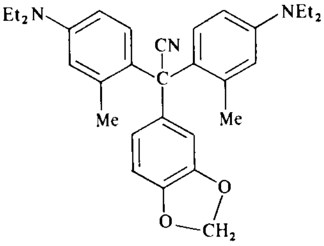
(XXXIX)



(XL)



(XLI)



(XLII)

arts, can be prepared by condensation of piperonal with twice the molar quantity of *N*,*N*-diethyl-*m*-toluidine in the presence of an acid catalyst. The cyano derivative (XLII) is obtained by treatment of (XLI) with sodium cyanide. If a mixture of (XLI), 2-(*o*-chlorophenyl)-4,5-diphenylimidazolyl dimer, methanol, and dimethylformamide is dyed on paper,

TABLE II
SPECTRA OF MALACHITE GREEN, ITS *p*-METHOXY DERIVATIVE AND ITS FERROCENYL DERIVATIVE

Dye	λ_{max}, mμ (10^{-4} ϵ)
Malachite Green (XXIV)	621 (10.4); 427 (2.0)
p-OMe deriv. of (XXIV)	608 (10.6); 465 (3.4)
(XLVI)	607 (5.2); 457.5 (1.8)

dried with infrared light, and irradiated with 2537–4200 Å light, a gray to black shade is obtained on the irradiated portion.[54] Similar results are obtained with the cyano compound (XLII).

Triphenylmethane derivatives with heterocyclic systems, such as (XLIII), which can be prepared from furfural and *N,N*-diethyl-*m*-toluidine, are useful for photographic processes. The dye is prepared by the oxidation of the resultant leuco derivative. The dye from (XLIII) is a fast dark green dye.[55] Triphenylmethane derivatives containing naphthotriazole groups were prepared by diazotizing a triphenylmethane derivative containing a free amino group, coupling with 2-naphthylamine, oxidizing with copper acetate in pyridine to obtain the triazole, and further oxidation with lead dioxide to the carbinol, which with acid gave the dye salt. Thus, (XLIV) gave the dye salt of (XLV).[56] A ferrocene analog of Malachite Green (XLVI) was prepared by the action of *p*-dimethylaminophenyllithium (obtained from *p*-bromo-*N,N*-dimethylaniline) on methyl ferrocenoate in ether.[57] The dye base, m.p. 155–156°, with acetic acid gave the dye salt (XLVI); but the color of the dye faded rapidly (half-life ~10 minutes). Addition of 10% ethanol to the acetic acid stabilized the dye considerably.

The replacement of the phenyl group of Malachite Green (XXIV) by a ferrocenyl group results in a hypsochromic shift of the first band and a marked bathochromic shift of the second band. Introduction of a strongly electron donating methoxyl group in the free para position of Malachite Green brings about a similar effect (see Table II).[58] The thiophene analog (XLVII) of Malachite Green, was prepared by the condensation of 2-thenaldehyde and dimethylaniline in presence of zinc chloride.[59] The resulting leuco base was oxidized to the dye (XLVII).

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[54] DuP, *BP* 1,047,796.

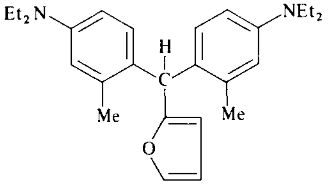
[55] K.-H. Yun and Y.-P. Chao, *Chem. Abstr.* **56,** 6125 (1962).

[56] J. Arient and J. Dvorak, *Chem. Listy* **52,** 109 (1958).

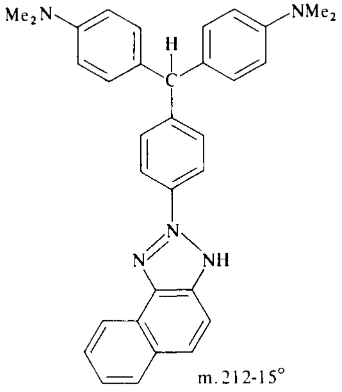
[57] C. C. Barker, G. Hallas, and M. N. Thornber, *J. Chem. Soc.* p. 5759 (1965).

[58] C. C. Barker, M. H. Bride, G. Hallas, and A. Stamp, *J. Chem. Soc.* p. 1285 (1961).

[59] L. Levi, *Ber.* **20,** 513 (1887).

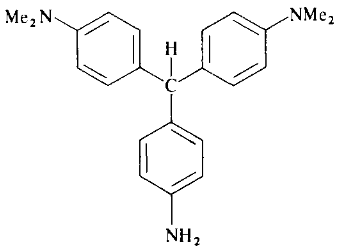


(XLIII)

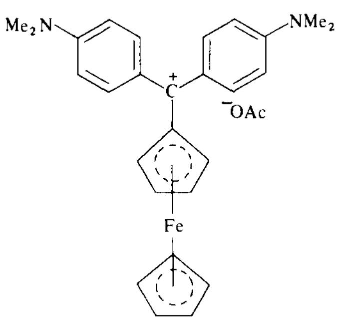


m.212-15°

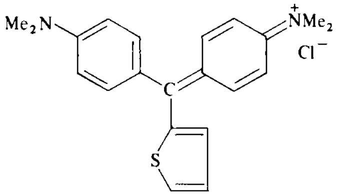
(XLV)



(XLIV)



(XLVI)



(XLVII)

Alkyl or halogeno-substituted 2-thenaldehydes gave the corresponding triarylmethane dyes.[60,61] Replacement of a phenyl group in (XXIV) with the 2-thienyl group produces a most pronounced bathochromic shift in the second band (*y* band) of the absorption spectrum of these dyes (Table III). The main absorption band of Malachite Green (*x* band) is

[60] C. D. Mason and F. F. Nord, *J. Org. Chem.* **16**, 722 (1951).

[61] C. D. Mason and F. F. Nord, *J. Org. Chem.* **17**, 778 (1952).

TABLE III
ABSORPTION MAXIMA IN ACETIC ACID

Dye	λ x (mμ)	$\epsilon \times 10^{-4}$	λ y (mμ)	$\epsilon \times 10^{-4}$	λ x′ (mμ)	$\epsilon \times 10^{-4}$
Malachite Green (XXIV)	620	9.58	428	1.88	320	1.76
Thiophene Malachite Green (XLVII)	629	8.60	469	2.85	312	1.46

due to the oscillation of an electron cloud across the molecule between the two auxochromes. The second, *y* band corresponds to an oscillation through the phenyl group and the third, *x′* band is associated with a secondary oscillation of higher amplitude. The bathochromic effect due to the introduction of the 2-thienyl group in place of phenyl group in Malachite Green is supposed to be due to the superior electron-releasing power of the thiophene ring compared to the benzene ring. By donating electrons to the central carbon atom, the thiophene ring is responsible for increasing the basicity of the nitrogen atoms with consequent lowering of absorption frequency. The electron-donating power of the thiophene ring can be visualized from the resonating structures (XLVIII,a,b,c). The 3-thiophene, 2-thianaphthene, and 3-thianaphthene analogs of Malachite Green (XLIX, L, and LI, respectively) can be prepared from the corresponding aldehydes.[62]

Similarly many other triarylmethane dyes containing two substituted phenyl groups and one heterocyclic group derived from pyridine, quinoline, 2-methylindole, carbazole, benzothiazole, benzoselenazole, phenothiazine, phenoxazine, phenoselenazine, and sulfonyldiphenylamines have been prepared.[63] Several of these dyes are suitable for filter and antihalation layers for photographic materials. Condensation of carbazole and *N*-methylcarbazole with Michler's ketone in the presence of phosphorus oxychloride gave violet dyes (LII; R = H or Me) which were suitable for dyeing silk and cotton.[64] A few triarylmethane dyes containing heterocyclic systems have been listed in the second edition of the *Colour Index.* Wool Fast Blue FBL (CI 44510, Acid Blue 123) (see *CSD II,* p. 729) is an indole derivative; whereas Chromoxane Brown 5R (CI 44525, Mordant Brown 26) (LIII), which is prepared by condensing formaldehyde with 2,3-cresotic acid and then co-oxidizing the product

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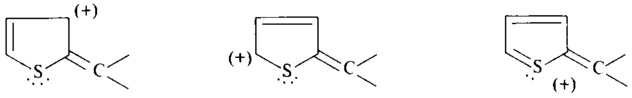
[62] V. V. Ghaisas, B. J. Kane, and F. F. Nord, *J. Org. Chem.* **23,** 560 (1958).

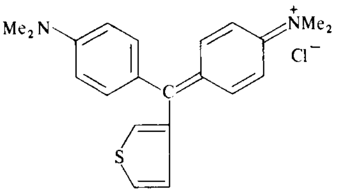
[63] L. Roosens, *Compt. Rend. Congr. Intern. Chim. Ind.* 27th *Brussels, 1954;* see *Ind. Chim. Belge* **20,** Spec. No. 641 (1955); *Chem. Abstr.* **50,** 9909 g (1956).

[64] S. I. Omel'chenko, Z. V. Pushkareva, and V. I. Shishkina, *Tr. Ural'sk. Politekhn. Inst.* **94,** 45 (1960); *Chem. Abstr.* **56,** 6123 (1962).

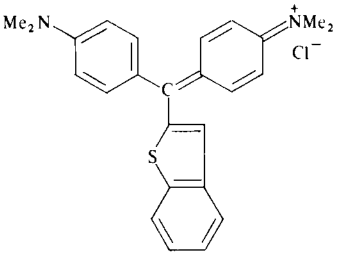


(a) (b) (c)

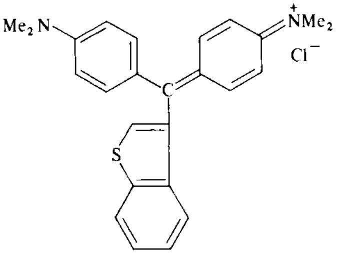
(XLVIII)



(XLIX)



(L)



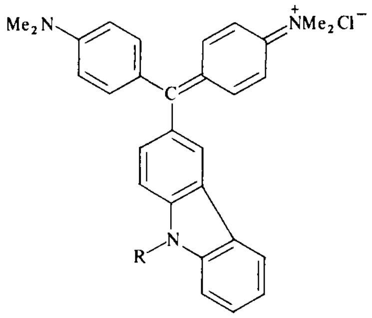
(LI)

with 3-methyl-1-phenyl-5-pyrazolone in nitrous acid, is a pyrazolone derivative.[65] Because of the high cost, these dyes have limited commercial utilization.

The silicon analog of Crystal Violet (LIV), m.p. 230–232°, was prepared by reacting controlled amounts of *p*-dimethylaminophenyllithium with silicon chloride.[66] In liquid sulfur dioxide and organic solvents (LIV) underwent reactions involving displacement of chlorine, but no compounds containing the R_3Si^+ cation could be isolated. Ultraviolet and infrared spectra reveal that (LIV) is markedly different; and the physical properties are also different, because, unlike Crystal Violet, (LIV) is not ionic in character. However, the sulfur analog of Crystal Violet

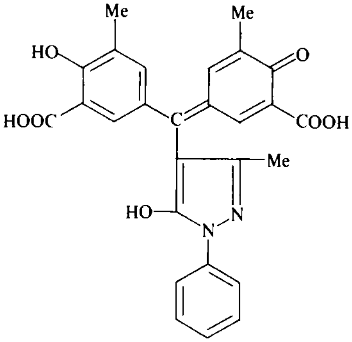
[65] BIOS *1433*, 124; FIAT *1313, 2*, 358,367; FIAT *764*.

[66] U. Wannagat and F. Brandmair, *Z. Anorg. Allgem. Chem.* **280**, 223 (1955).

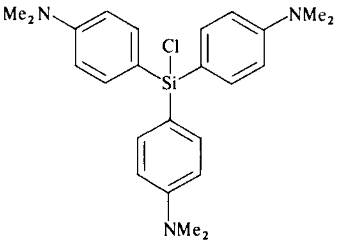


R=H or Me

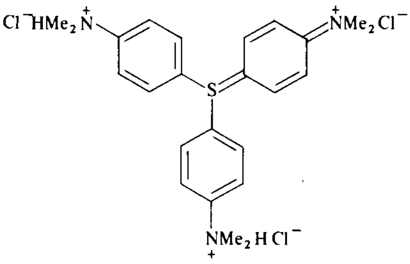
(LII)



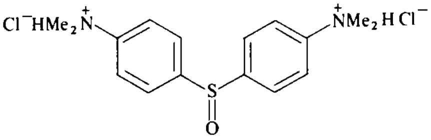
(LIII)



(LIV)



(LV)



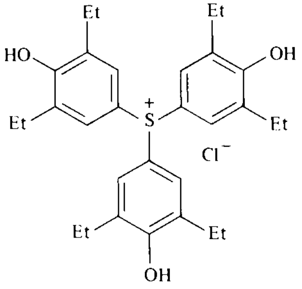
(LVI)

(LV) was a blue dye and was structurally similar to the triphenylmethane dye. The dye (LV) was prepared by interaction of the sulfoxide (LVI) with dimethylaniline in the presence of phosphorus oxychloride.[67] It dyed a pure blue shade on tannin-mordanted cotton and silk; but the lightfastness on cotton was, as usual, poor. With alkali it gave a dye base, which could be reconverted to the dye with acid. Other triphenyl-

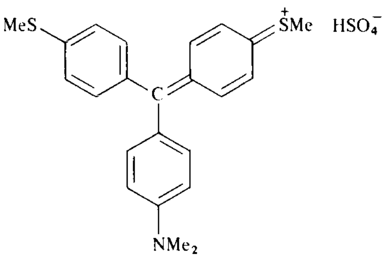
[67] J. D. Billimoria, A. N. Kothare, and V. V. Nadkarny, *J. Indian Chem. Soc.* **22**, 91 (1945).

sulfonium chlorides such as (LVII), can be prepared by reacting suitably substituted phenols with thionyl chloride and anhydrous aluminum chloride.[68] The sulfonium chlorides formed insoluble salts with acid dyes and could be incorporated into bentonite.

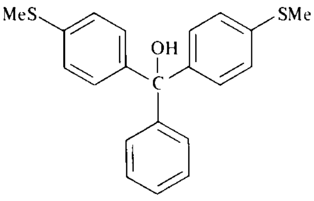
A Crystal Violet analog containing two methylmercapto groups in place of dimethylamino groups, was prepared by the reaction of two molecules of thioanisylmagnesium bromide with one of *p*-dimethylaminobenzoic acid ester and treatment with dilute sulfuric acid.[69] The dye with structure (LVIII) was obtained. In color and other properties, it showed strong resemblance to Crystal Violet (XXIX); and it was quite stable to hydrolysis. It had been observed earlier that the carbinols (LIX) and (LX) gave colored salts with strong acids, and they were easily hydrolyzable.[70] Thus it appears that the replacement of a methylmercapto group by a dimethylamino group in (LX) resulted in the stabilization of the salt owing to an increased mesomeric effect.



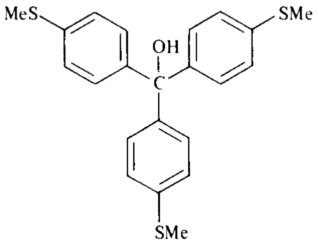
(LVII)



(LVIII)



(LIX)



(LX)

The novel triarylmethane dye (LXIII), m.p. 141°, in which two aryl

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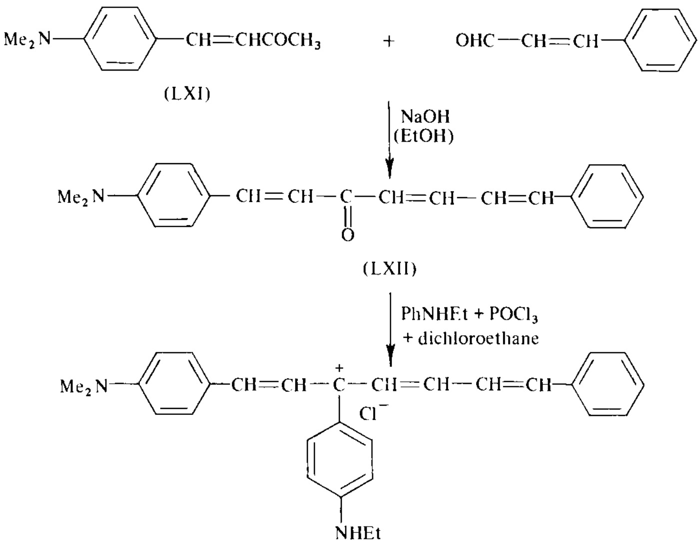
[68] FBy, *USP* 2,833,827.

[69] O. Neunhoeffer and A. Nowak, *Naturwissenschaften* **45,** 491 (1958).

[70] K. Brand and O. Stallman, *J. Prakt. Chem.* **107,** 358 (1924).



(LXIII)

groups are separated from the central carbon atom by ethylenic linkages, has been prepared, starting from (LXI) and cinnamaldehyde. It dyed tannin-mordanted cotton a lightfast brownish red shade. The dye (LXIV), which was similarly prepared, dyed a blue shade on tannin-mordanted cotton.[71] Condensation of benzaldehyde and (LXI) gave (LXV), which on further condensation with dimethylaniline and phosphorus oxychloride gave the dye (LXVI). It dyed tannin-mordanted cotton a claret shade with a violet tinge.[72] These dyes are stable to water and light.

The unsubstituted phenyl ring of Malachite Green can be replaced by an unsaturated polymer. Thus, the reaction of Michler's ketone with metallated 1,4-*cis*-polybutadiene gave a carbinol (LXVII), which changed to a deep red powder (LXVIII) with iodine. The carbinol polymer had a nitrogen content of 5.83%, corresponding to 25.6 units of the dye per hundred monomer units of polybutadiene.[73]

The biphenyl homologs of Malachite Green and Crystal Violet, (LXIX) and (LXX) were prepared from (LXXI) and (LXXII), respectively, by reaction with 4′-dimethylaminobiphenyl-4-magnesium iodide.[74] The Malachite Green homolog (LXIX) gave a green color in

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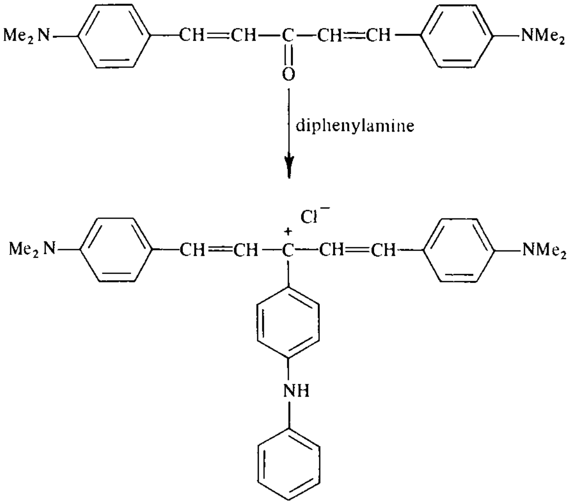
[71] B. N. Dashkevich and I. V. Smolanka, *Ukr. Khim. Zh.* **22,** 347 (1956).

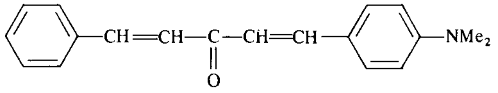
[72] B. N. Dashkevich and I. V. Smolanka, *Ukr. Khim. Zh.* **21,** 619 (1955).

[73] Y. Minoura, K. Shiina, and H. Harada, *J. Polymer Sci., Part A-1* **6,** 559 (1968).

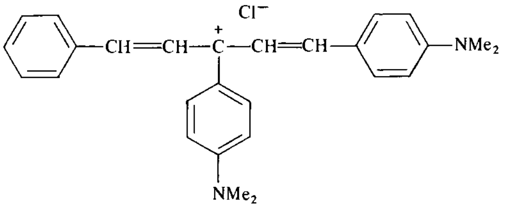
[74] W. Thielacker, W. Berger, and P. Popper, *Ber.* **89,** 970 (1956).



(LXIV)



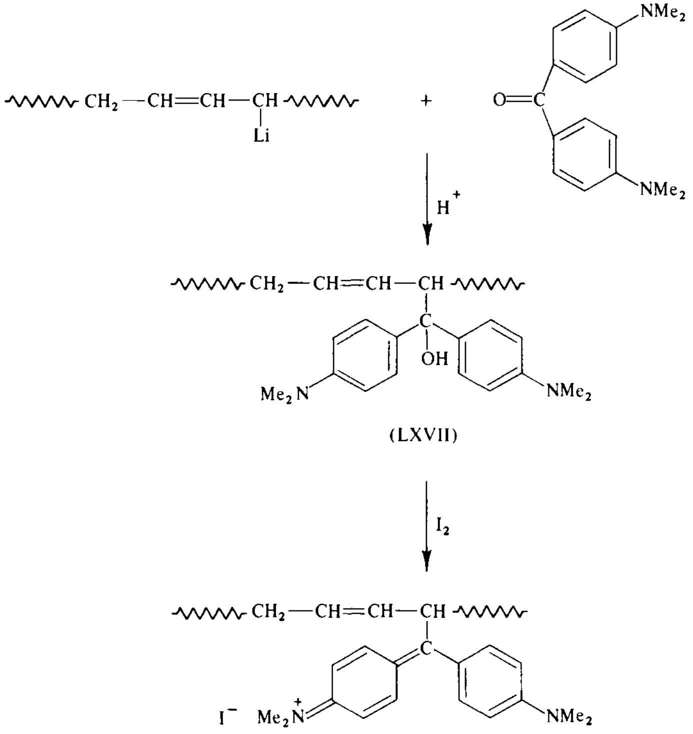
(LXV)



(LXVI)

hot acetic acid, whereas, the Crystal Violet homolog (LXX) was deep red in sulfuric and perchloric acids.

Fluorene analogs (LXXIII) and (LXXIV) of Malachite Green base and Crystal Violet base were prepared from 3,6-bis(dimethylamino)-fluorenone (LXXV) by reaction with phenylmagnesium bromide and *p*-


(LXVII)

(LXVIII)

dimethylaminophenyllithium, respectively.[75] The unsymmetrical analog of Malachite Green base (LXXVI) was prepared from (LXXVII). These analogs of Malachite Green and Crystal Violet show a very large bathochromic shift, when compared with the corresponding triphenylmethane dyes. The fluorene analog of Crystal Violet base (LXXIV) can be conveniently prepared from Crystal Violet (XXIX) by heating in 98% sulfuric acid with a little trisodium phosphate at 205–210.° The leuco derivative so obtained is then oxidized with lead dioxide in acetic acid. The dye salt of (LXXIV) dyes textiles, indigo blue shades and stains skin.[76] Fluorene quinones having structures such as (LXXVIII) have been prepared. The compound (LXXVIII) has been prepared by heating pyrocatecholsulfonphthalein (LXXIX) with ethylamine. The sulfonphthalein (LXXIX) is obtained by heating equimolar amounts of

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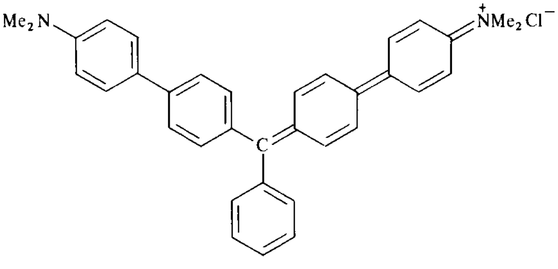
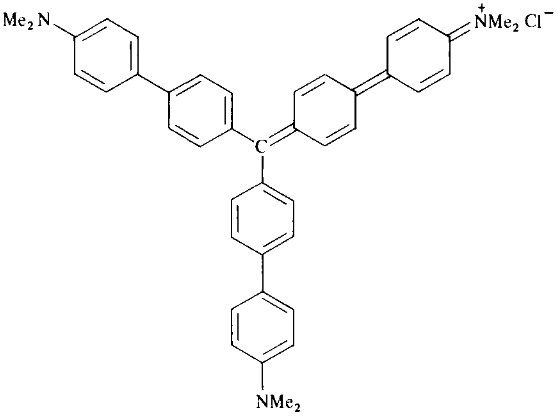
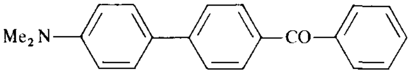
[75] A. Barker and C. C. Barker, *J. Chem. Soc.* p. 1307 (1954).
[76] Chester Davis, *USP* 3,344,189.



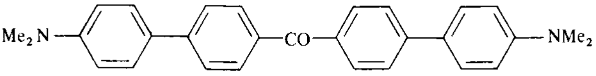
(LXIX)



(LXX)



(LXXI)

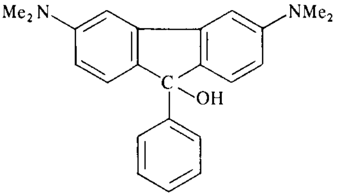


(LXXII)

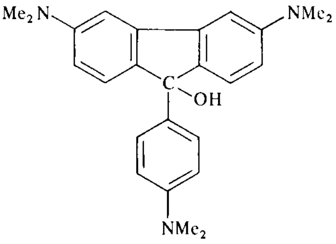
pyrocatechol and *o*-sulfobenzoic anhydride.[77] These are deeply colored compounds, which show very little color change in the pH range 3–14.

Indicator dyes containing substituents such as $-CH_2N(CH_2COOH)_2$ in the ortho position to the phenolic hydroxyl groups in triphenylmethane

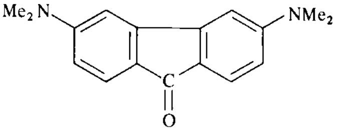
[77] G. Schwarzenbach and P. Waldvogel, *Helv. Chim. Acta* **43,** 1086 (1960).



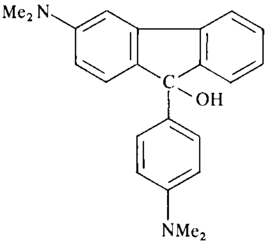
(LXXIII)



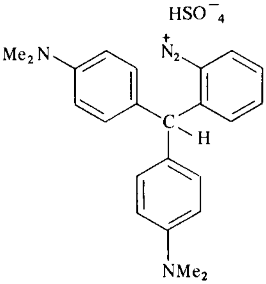
(LXXIV)



(LXXV)



(LXXVI)



(LXXVII)

systems change color on forming complexes with metal ions; and they can be used in colorimetric and titrimetric determinations. 3′,3″,5′,5″-Tetrakis{[bis(carboxymethyl)amino]methyl}phenolphthalein (LXXX) is prepared by treating a solution of phenolphthalein with iminodiacetic acid and formaldehyde in the presence of alkali.[78] For the determination of barium or strontium, the solution is adjusted to pH slightly more than 10 with ammonia and ammonium chloride and titrated in the presence of (LXXX) with 0.1 *N* disodium salt of EDTA. The color changes from

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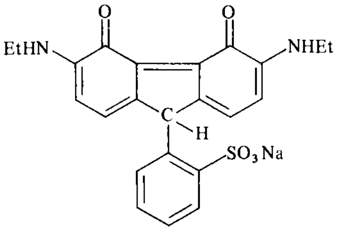
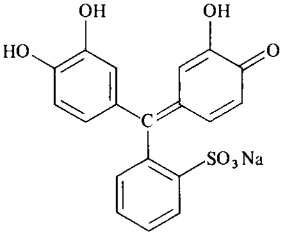
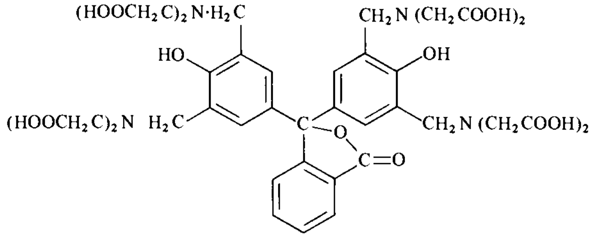
[78] CIBA, *SP* 298,194; *BP* 761,044.



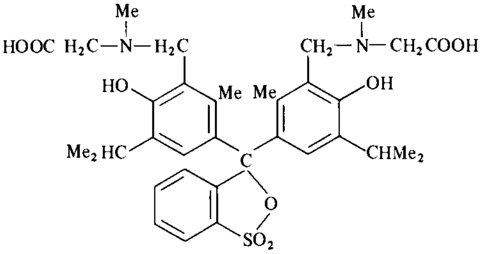
(LXXVIII)



(LXXIX)



(LXXX)



(LXXXI)

violet red to pink at the end point. Similar highly specific metallochromic indicators can be obtained from phenolphthalein, sulfonphthalein, and fluorescein. An example is (LXXXI), which is obtained by reacting Thymol Blue with *N*-methylglycine and formaldehyde in the presence of sodium acetate and acetic acid.[79] They are useful as indicators for copper, nickel, and cadmium ions and as little as 10^{-6} mole of copper can be detected.

As in the case of Auramine dyes, triphenylmethane dyes such as Malachite Green and Brilliant Green (CI, 42040, Basic Green 1) having aryl sulfonic acid as anions have improved solubility in alcohols and they

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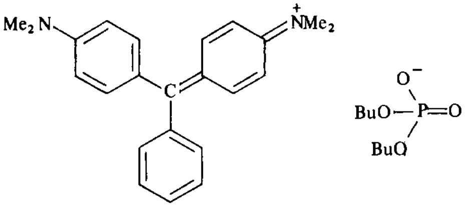
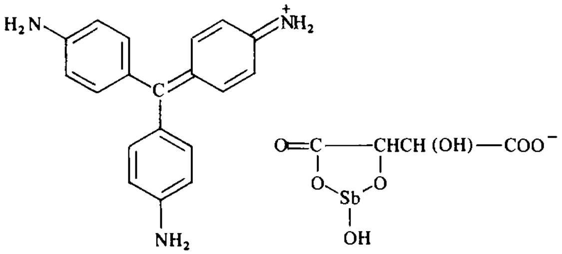
[79] D. Terzijska, V. Svoboda, and J. Korbl, *USP* 3,301,870; see also *BP* 889,801; 896,260.

can be used for coloring inks and coating compositions of high tinctorial strength for duplicating carbon papers.[80,81] They are prepared by reacting the usual basic dyes with aryl sulfonic acids, such as 5-sulfo-2-hydroxybenzoic acid. The nitrate of Brilliant Green, prepared by treating Brilliant Green crystals with aqueous sodium nitrate at 20°, also has good solubility in alcohols. Basic dyes such as (LXXXII) containing oleophilic anions can be used for dyeing polyolefinic materials. The dibutylphosphoric acid salt of Malachite Green Base (CI Solvent Green 1), obtained by heating the base with dibutylphosphoric acid in aqueous solution, dyes polyolefin a deep green shade.[82] Pararosaniline antimonyl tartrate (LXXXIII), prepared by treating an aqueous solution of Pararosaniline with antimony potassium tartrate, is useful as an antischistosomal agent.[83]



(LXXXII)



(LXXXIII)

Stable concentrated solutions of triphenylmethane dyes such as Malachite Green and Methyl Violet, which have demand in the paper industry, because of the convenience in handling and adding to the

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[80] LBH, *BP* 1,036,436.

[81] ICI, *BP* 931,438.

[82] Domenick D. Gagliardi, *USP* 3,169,824.

[83] Parke Davis Co., *USP* 3,342,844.

beater,[84,85] can be obtained by stirring the dyes in liquids such as β-hydroxypropionitrile.[86]

VIII. Mechanism of Formation of Triphenylmethane Dyes

It was generally assumed that the oxidation of leuco bases of triphenylmethane dyes to the corresponding dye salts proceeds through the intermediate formation of carbinol bases and that these carbinols yield dyes by acid-catalyzed dehydration. Thus, in the formation of Malachite Green (XXIV) the intermediate formation of the carbinol (LXXXIV) was envisaged.[87] However, this assumption was not substantiated by experimental proof (see CSD II, p. 712). On the other hand, experimental evidence rules out the mechanism involving a carbinol intermediate, since it was shown that under comparable conditions, the carbinol base is converted to the dye by acid more slowly than the leuco base by an oxidizing agent and acid. On the basis of this observation, a new mechanism, whereby the leuco base is converted to the dye by deprotonation of a tertiary hydrogen atom $(-\overset{\diagdown}{\underset{\diagup}{\mathrm{C}}}-\mathrm{H})$ by water and removal of two electrons from the nitrogen atom by the oxidizing agent (such as ceric sulfate) was proposed [(LXXXV)-(LXXXVI)].[88] Thus the dye cation is first formed, which may give the carbinol base if the medium is not acidic. Ritchie *et al.*[89] observed that a hydride transfer from the tertiary carbon atom of the leuco base should be considered as one of the probable mechanisms in the conversion of the leuco base to the dye salt by chloranil [(LXXXVII)-(LXXXVIII)]. They, however, did not rule out the earlier mechanism.

Experimental evidence was provided in favor of the hydride-transfer mechanism.[90,91] It was shown that in the reaction of the leuco bases of Malachite Green (XXIV) and Crystal Violet (XXIX) with triphenylmethyl chloride (trityl chloride) (LXXXIX), the dye cations (LXXXVI) and triphenylmethane (XC) were formed in quantitative yields. The latter was isolated and identified. The driving force for the hydride transfer is

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[84] ICI, Tech. Inform. Leaflet No. 734 (1965).

[85] ICI, Tech. Inform. Leaflet No. 751 (1965).

[86] FBy, *BP* 1,072,448.

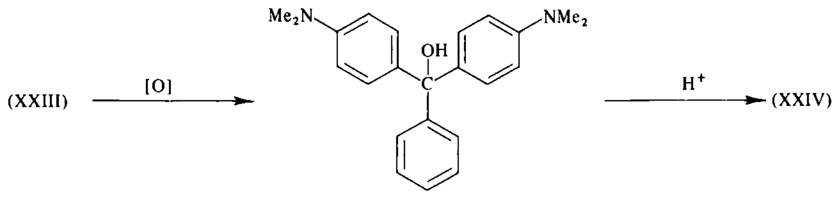
[87] J. B. Conant and A. H. Blatt, "The Chemistry of Organic Compounds," 4th ed., pp. 524–525. Macmillan, New York, 1952.

[88] C. J. Swain and K. Hedberg, *J. Am. Chem. Soc.* **72**, 3373 (1950).

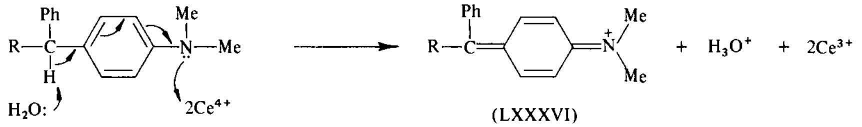
[89] C. D. Ritchie, W. F. Sager, and E. S. Lewis, *J. Am. Chem. Soc.* **84**, 2349 (1962).

[90] B. D. Tilak, *Chimia* (*Aarau*) **20**, 272 (1966).

[91] B. D. Tilak and K. Ravindranathan, unpublished work (1966).

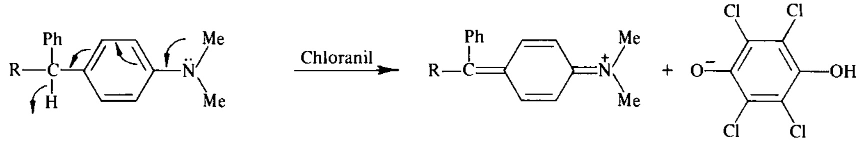


(LXXXIV)

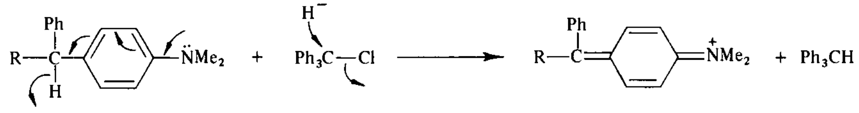


(LXXXV) (LXXXVI)

(R = *p*-dimethylaminophenyl)

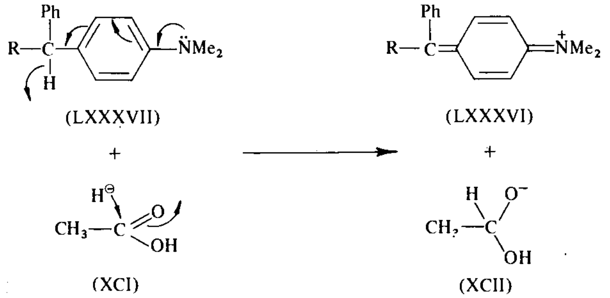


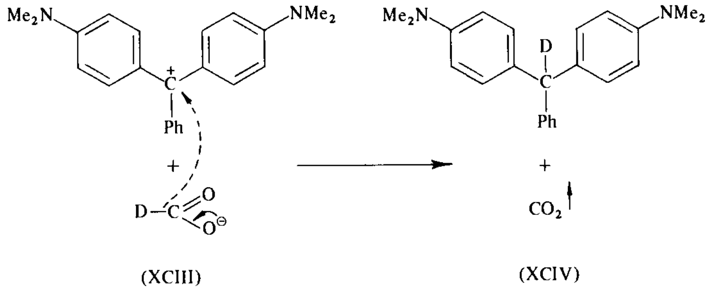
(LXXXVII) (LXXXVI) (LXXXVIII)

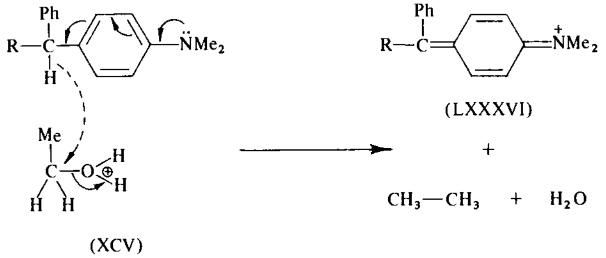


(LXXXVII) (LXXXIX) (LXXXVI) (XC)

derived from the greater stability of the newly formed dye cation (LXXXVI). Thus, the leuco bases of triphenylmethane dyes may be regarded as excellent hydride donors on account of the stabilization achieved by their conversion to the corresponding dye cations by hydride loss. The mechanism (LXXXV)–(LXXXVI), which suggests deprotonation followed by electron loss, appears improbable, since nitrogen is not likely to take up an electron pair and expand its valency shell, the nitrogen atom being an electron donor. Hydride transfer of the leuco bases of Malachite Green and Crystal Violet to weak hydride acceptors such as carboxylic acids of varying acidity (acetic acid and chloroacetic acids) and their esters, under conditions where dialkylamino groups are either not protonated or protonated to a very small extent, was also in accordance with


(LXXXVII) + (XCI) → (LXXXVI) + (XCII)


(XCIII) → (XCIV)

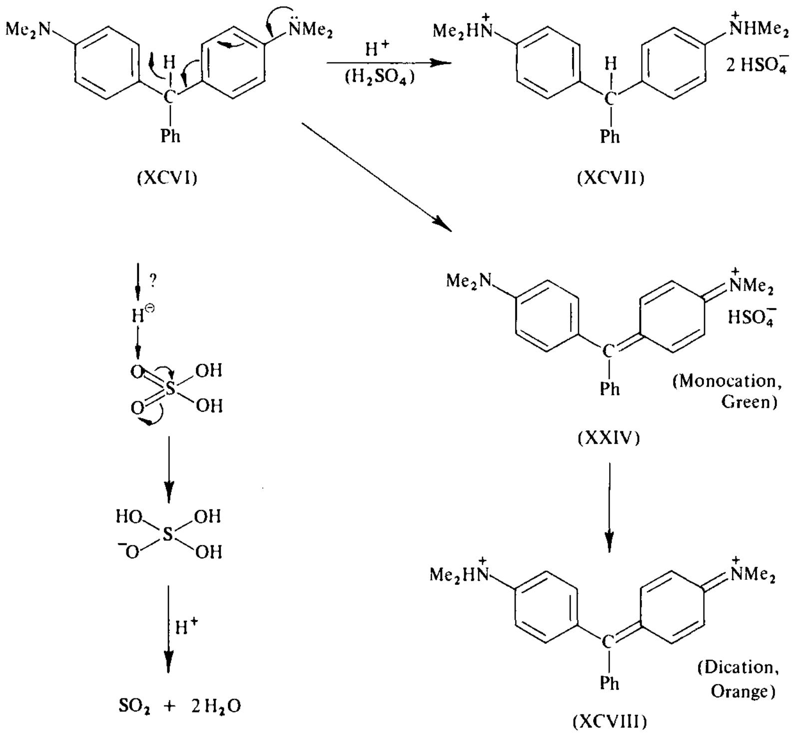

(XCV) → (LXXXVI) + $CH_3—CH_3$ + H_2O

the proposed mechanism. As expected, the hydride-abstracting capacity of trichloroacetic acid is much greater than that of acetic acid because of the greater electron pull of the trichloromethyl group on the hydride-abstracting carbon of the carboxylic acid [see (XCI)–(XCII)]. The reverse change is also possible and Malachite Green can be quantitatively reduced by the formate ion [(XCIII)–(XCIV)].[92] Incipient carbonium ions derived from protonated ethanol can also function as hydride acceptors. Thus, a one hundred molar excess of ethanolic hydrogen chloride converted the leuco base of Malachite Green into the dye in very good yield at high dilutions. The dye formation appears to be possible only if the

[92] R. Stewart, *Can. J. Chem.* **37,** 766 (1957).

corresponding quantity of protonated ethanol gets itself converted to ethane in the process (XCV)–(LXXXVI). A very large excess of hydrogen chloride may effectively protonate the dimethylamino groups in the leuco base (XCV) and prevent the electron relay towards the central carbon atom, which is necessary for hydride loss.

In the manufacture of Malachite Green (XXIV) by the condensation of benzaldehyde with a small excess of dimethylaniline in the presence of sulfuric acid, a small amount (~2%) of Malachite Green was observed to have been formed along with the leuco base (XXIII), *without use of any oxidizing agent.*[93] This result was also confirmed by treating the leuco base of Malachite Green itself with sulfuric acid. This can be explained only on the basis of hydride loss [see (XCVI)]. The very small percentage of the dye formed can be explained on the basis of protonation of the leuco base with sulfuric acid, thus losing the driving force for hydride loss (XCVII). Whereas the leuco bases were readily converted to the respective dyes by interaction with above reagents, the ex-



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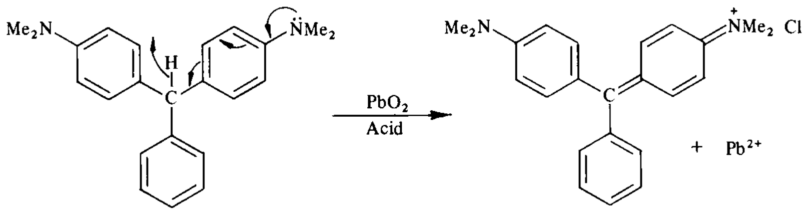
[93] German Microfilm, PB 74026 (Frame No. 2087).



(XXIII) (XXIV)

tent of the dye formation was found to be dependent on several parameters such as temperature, time, and degree of protonation of the leuco bases. In the light of the above discussion the oxidation of the leuco base of Malachite Green (XXIII) by lead dioxide in hydrochloric acid to the dye salt (XXIV) may be visualized as involving hydride transfer. The lead dioxide is reduced to the lower oxidation level (Pb^{4+} to Pb^{2+}).

IX. Steric Effects in Triphenylmethane Dyes

The extensive work of Barker and his co-workers[94-99] has mainly contributed to our knowledge on the steric effects of substituents in triphenylmethane dyes. Brooker[100] had earlier established that crowding substituents in electrically symmetrical charge resonance systems increases the wavelength of the first frequency absorption and decreases their maximum intensity (CSD I, p. 377). The progressive bathochromic shifts and the reductions in intensity of the first frequency bands shown by the *o*-methyl derivatives of Crystal Violet (XCIXa) and Michler's Hydrol Blue (Ca) are in conformity with Brooker's observation. Dewar[101] had shown that the effect of electron-withdrawing ortho substituents should be bathochromic and that of electron-donating substituents, hypsochromic. Thus, with an *o*-methyl substituent, the steric and electronic effects oppose each other, although the steric effects predominate. The scale drawings and molecular models of (XCIXa) and (Ca) clearly

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[94] C. C. Barker, *in* "Steric Effects in Conjugated Systems" (G. W. Gray, ed.), p. 34. Butterworth, London and Washington, D.C., 1958.

[95] C. C. Barker, M. H. Bride, and A. Stamp, *J. Chem. Soc.* p. 3957 (1959).

[96] C. C. Barker, G. Hallas, and A. Stamp, *J. Chem. Soc.* p. 3790 (1960).

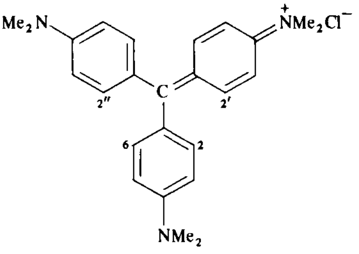
[97] C. C. Barker *et al.*, *J. Chem. Soc.* pp. 1285, 1529, 2642, and 3445 (1961).

[98] C. Aaron and C. C. Barker, *J. Chem. Soc.* p. 2655 (1963).

[99] G. Hallas, *J. Soc. Dyers Colourists* **83**, 368 (1967).

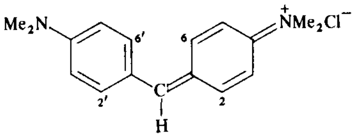
[100] L. G. S. Brooker, F. L. White, R. H. Sprague, S. G. Dent, Jr., and G. VanZandt, *Chem. Rev.* **41**, 325 (1947).

[101] M. J. S. Dewar, *J. Chem. Soc.* p. 2329 (1950).



(XCIX)

Substituent	λ_{max}(mμ)	$10^{-4}\ \epsilon_{max}$
a None	589	11.7
b 2-Me	597	11.0
c 2,2'-diMe	605	10.3
d 2,2',2''-triMe	614	10.0
e 2,6-diMe	616	11.2

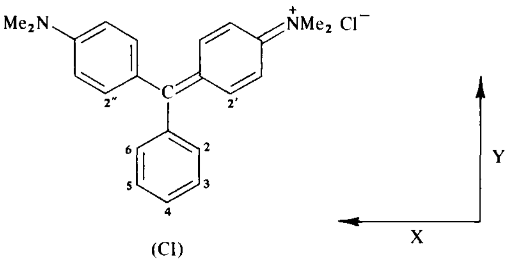


(C)

Substituent	λ_{max}(mμ)	$10^{-4}\ \epsilon_{max}$
a None	607.5	14.75
b 2-Me	614.5	13.0
c 2,2'-diMe	623	12.1
d 2,2',6,6' tetraMe	649	5.5

show that the hydrogen atoms in the ortho position to the central carbon atom overlap to a great extent. This leads to the assumption that the phenyl rings in the dye (XCIXa) are not coplanar, but are twisted in such a fashion that the shape of the dye resembles that of a three-bladed propeller. The overlap of the *o*-hydrogen atoms in the diphenylmethane dye (Ca) may be reduced by increasing the phenyl–carbon–phenyl angle, and the two phenyl rings of (Ca) may be more or less coplanar. In Michler's Hydrol Blue (Ca), the ortho positions at 2,2' and 6,6' are not identical and bulky substituents may take up the *outside* 2,2' positions with relatively less overlap. In such a case, the hypsochromic shift due to the electronic effects of the methyl substituents in (Cb) and (Cc) should be produced. The observed bathochromic shift shows that the steric response is predominant. The compound (Cd) shows a much larger bathochromic shift due to the additional interaction of methyl groups in the 6,6'-positions.

The uniform bathochromic shift (about 8 mμ per methyl group) and reduction in the intensity of the first frequency band in (XCIXa), (XCIXb), (XCIXc), and (XCIXd) suggest that the axial rotational adjustment needed to accommodate the *o*-methyl groups is shared uniformly by the three phenyl rings. The 2,6-dimethyl derivative (XCIXe) shows a much larger bathochromic shift per methyl group, and it is suggested that the dimethylaminoxylyl group undergoes most of the rotational twist so that the charge is localized on the other two dimethylaminophenyl rings, with consequent increase in the bathochromic shift. A similar argument was advanced in the case of (XCIXd), the first-frequency absorption band of which resembles more closely the corresponding absorption band of Malachite Green (CIa) than that of Crystal Violet (XCIXa). This means that as in the case of Malachite Green, one of the dimethylaminophenyl rings does not participate in the resonance of the charge; on this basis, Theilacker and Berger[102] suggested that the dye (XCIXd) has a molecular form in which one of the dimethylaminophenyl rings has been highly twisted compared to the other two and hence effectively deconjugated. The dye (XCIXb) is marketed as Crystal Violet 10B (BASF, CI 42557; Basic Violet 23) and is very similar in properties to Crystal Violet (XCIXa).



(CI)

Substituent	X-band		Y-band	
	$\lambda_{max}(m\mu)$	$10^{-4}\ \epsilon_{max}$	$\lambda_{max}(m\mu)$	$10^{-4}\ \epsilon_{max}$
a None	621	10.4	427.5	2.0
b 2-Me	622.5	12.3	420	1.5
c 3-Me	619	10.6	433	2.2
d 4-Me	616.5	10.6	437.5	2.5
e 2,6-diMe	624	13.2	410	1.2
f 2'-Me	635	7.5	437.5	2.0
g 2,2'diMe	634	8.4	431	1.8
h 2',2''-diMe	648	6.7	445	1.8
i 2,2',2''-triMe	647.5	7.4	440	1.6

Unlike the cation of Crystal Violet, the cation of Malachite Green

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[102] W. Theilacker and W. Berger, *Ber.* **89**, **965** (**1956**).

(CIa) is not symmetrical along the x and y axes. Whereas, in the visible region, there is only one absorption maxima band at 589 mμ in Crystal Violet, there are two bands in the case of Malachite Green (621 and 427.5 mμ), corresponding to polarizations along the symmetrical x axis and the unsymmetrical y axis, respectively.[103] Since the dye (CIa) is symmetrical along the x axis, an ortho substituent in the phenyl ring should respond with a bathochromic shift of the x band. The dye is not symmetrical along the y axis, and hence the y band should show hypsochromic response to the crowding substituents (Brooker had shown that unsymmetrical dyes respond to crowding substituents by decrease in the wavelength of the absorption band and also its maximum intensity).[100] Both x and y bands should show reduction in the maximum intensity. Methyl substituents in the 3- and 4-positions in the phenyl ring of (CIc) and (CId) do not produce steric effects but only electronic effects, since the spectral shifts brought about by these substituents are directly proportional to the appropriate Hammett substituent constants.[104] However, a methyl substituent in the ortho position of (CIb) produces a small bathochromic shift of the x band and a marked increase of its intensity. This increase is magnified in the 2,6-dimethyl derivative (CIe). The bathochromic shift of the symmetrical x band is consistent with expectations, but it should then be accompanied by a reduction of its intensity. The unsymmetrical y band, as expected, responds to the introduction of 2-methyl substituent with a hypsochromic shift and a marked reduction of the intensity of the band. This observation suggests that the *o*-tolyl group in (CIb) and *o*-xylyl group in (CIe) have undergone marked rotation about the central carbon bonds. The bathochromic shifts of their x bands suggest a rotation of the dimethylaminophenyl groups about the central bonds. The progressive increase in the intensities of the x bands of (CIb) and (CIe) suggests that the electronic effects outweigh the combined effects of rotation of the dimethylaminophenyl groups and general molecular distortion. The 2′-methyl, 2,2′-dimethyl, 2′,2″-dimethyl, and 2,2′,2″-trimethyl derivatives of Malachite Green [(CIf), (CIg), (CIh), and (CIi), respectively] show bathochromic shifts and reduction in intensity of the x bands compared to (CIa). This effect is consistent with rotation of the dimethylaminophenyl groups about the central bonds. The increased departure from coplanarity of the two dimethylaminophenyl rings results in greater electronic symmetry along the y axis, thus showing bathochromic shifts of the y bands of (CIf), (CIg), (CIh) and (CIi).

The manifestation of the steric hindrance at the central carbon atom

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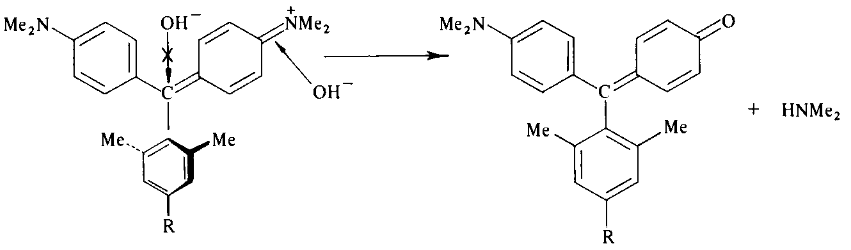
[103] J. Bigeleison and G. N. Lewis, *J. Am. Chem. Soc.* **65**, 2102 (1943).

[104] H. H. Jaffé, *Chem. Rev.* **53**, 191 (1953).

of dyes such as the 2,6-dimethyl derivatives of Crystal Violet and Malachite Green [(XCIXe) and (CIe), respectively] is evident from the observation that the action of a base on these dyes does not yield the corresponding carbinols, but gives the fuchsone derivatives (CII). The replacement of a terminal dimethylamino group is facilitated, because of steric hindrance. Comparison of the hydration reactions of Malachite Green (CIa) and its methyl derivatives (CIb), (CIc), and (CId) shows that there is very little influence of methyl groups in meta or para



(R = NMe_2 or H)

(CII)

positions of the phenyl ring of Malachite Green. However, when the methyl group is in the ortho position, the hydration reactions are strongly hindered, because of the steric influence of the *o*-methyl substituent.[105]

X. Other Basic Dyes

Practically no new basic dyes of the xanthene, acridine, azine, oxazine, and thiazine types have been reported during the last sixteen years. A few azine and oxazine dyes useful for polyacrylontrile fiber are described in the chapter on cationic dyes for synthetic fibers (Chapter IV).

The xanthene dye, Pyronine B (CI 45010) (CIII) is prepared commercially by condensing two molecules of *m*-diethylaminophenol with formaldehyde, followed by oxidation with ferric chloride in hydrochloric acid (see Pyronine G, CSD II, p. 745). Elemental and polarographic analyses, UV absorption spectra, and X-ray diffraction studies led to the conclusion that commercial Pyronine B has structure (CIV).[106] The iron must have originated from the oxidizing agent such as ferric chloride, used in the manufacture of the dye.

Isothiocyanate derivatives of Fluorescein and Rhodamine B [(CV) and (CVI), respectively] find use as biological staining agents for detecting

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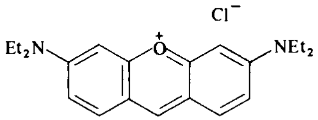
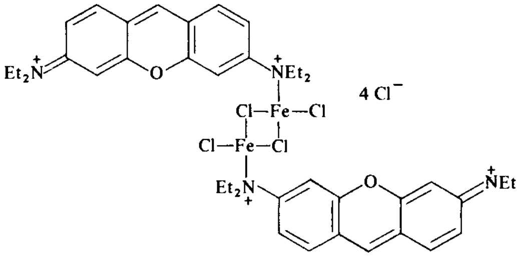
[105] C. G. Ekstrom, *Acta Chem. Scand.* **19**, 1381 (1965).

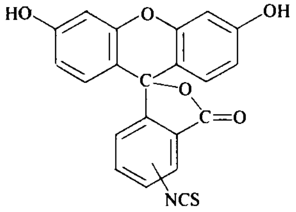
[106] E. M. Chamberlin, B. F. Powell, D. E. Williams, and J. Cohn, *J. Org. Chem.* **27**, 2263 (1962).



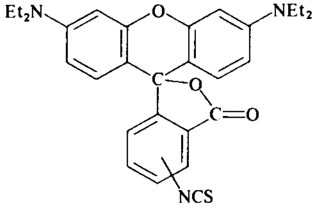
(CIII)



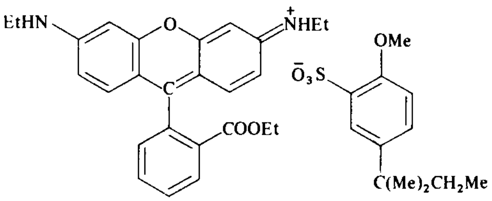
(CIV)



(CV)



(CVI)



(CVII)

the presence of antigens and antiacting substances. They are obtained by the action of aqueous alkaline carbon disulfide on the corresponding amino derivatives and treating the resulting dithiocarbonate with a solution of salts of iron, mercury, copper, or lead.[107]

Polymeric analogs of Rhodamine B (CI 45170, Basic Violet 10) having low toxicity can be obtained by using vinyl-substituted phthalic anhydride in the preparation of Rhodamine B (see *CSD II,* p. 751), followed by polymerization or copolymerization with vinyl monomers.[108]

Basic dyes of the Rhodamine type, having aryl sulfonic acid groups as anions, such as (CVII), have very good solubility in ethanol and can be used for coloring nitrocellulose lacquers and printing inks.[109] The alcohol-soluble *o*-nitrobenzoate of Rhodamine B, prepared by treating

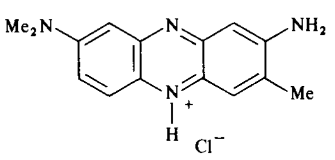
[107] Spofa Sdruzeni Podniku pro Zdravotnickou vyrobu, *BP* 1,090,159.

[108] Tanabe Seiyaku Co. Ltd., *JP* 5415 (1967); *JP* 68 08,956 (1968).

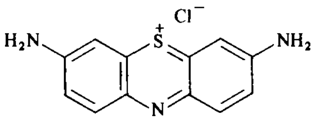
[109] Gy, *BP* 1,110,372.

the basic dye with *o*-nitrobenzoic acid in the presence of alkali, is also useful in the production of printing inks.[110]

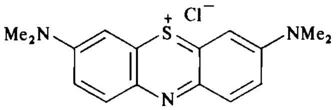
Loiseleur[111,112] showed that dyes such as Neutral Red (CI 50040; Basic Red 5) (CVIII), Lauth's Violet (CI 52000) (CIX), and Methylene Blue (CI 52015; Basic Blue 9) (CX) can be synthesized by irradiation of appropriate intermediates with ultraviolet light or X-rays. Thus, irradiation for half an hour of a mixture of *N,N*-dimethyl-*p*-phenylenediamine and toluene-2,4-diamine in dilute hydrochloric acid containing traces of copper sulfate yielded (CVIII). Similarly the radio syntheses of Lauth's violet and Methylene Blue were achieved by the X-ray irradiation of *p*-phenylenediamine and *N,N*-dimetyl-*p*-phenylenediamine, respectively, in the presence of ammonium sulfide, hydrochloric acid, and copper sulfate at pH 7. It was observed that the yields of the dyes could be increased by raising the temperature of the solution irradiated and also by bubbling air through the reaction mixture. The pure dyes could be isolated in good yields from the irradiated solutions.[113] Lauth's Violet and Methylene Blue were also prepared by the ^{60}Co γ-irradiation of *p*-phenylenediamine and *N,N*-dimethyl-*p*-phenylenediamine, respectively, under



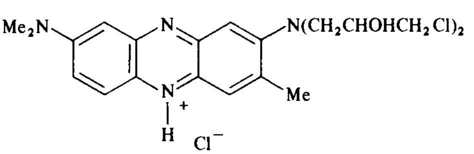
(CVIII)



(CIX)



(CX)



(CXI)

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[110] BASF, *BP* 1,095,086.

[111] J. Loiseleur, *J. Chim. Phys.* **52**, 630 (1955).

[112] J. Loiseleur and M. Petit, *Compt. Rend.* **250**, 2573 (1960).

[113] P. Balestic and M. Magat, *J. Phys. Chem.* **63**, 976 (1959).

similar conditions.[114] Radio synthesis of other dyes such as Aniline Black (CI 50440; Pigment Black 1), Fuchsine (CI 42510; Basic Violet 14), Malachite Green (CI 42000; Basic Green 4), Safranine B extra (CI 50200), Acridine Yellow G (CI 46025), and Indophenol Blue (CI 49700; Vat dye) is also possible.[112]

Dyes such as Neutral Red (CI 50040; Basic Red 5) (CVIII) can be reacted with epichlorohydrin to yield products such as (CXI), which dye protein, polyamide, and cellulosic fibers by forming covalent bonds with them, and markedly improve the wet-fastness.[115]

Examination of the electron spin resonance spectra of some of the azine, oxazine, and thiazine dyes, such as Lauth's Violet (CIX), Methylene Blue (CX), Methylene Green (CI 52020; Basic Green 5), Gallocyanine (CI 51030; Mordant Blue 10), and Safranine B extra after X-ray irradiation for 5 to 40 minutes in strong sulfuric acid, in the presence of ethanol or benzoic acid, reveals that the dyes are reduced to the same paramagnetic species as are obtained by the chemical reduction with titanous chloride. At least one acidic proton is attached to the central nitrogen atom and the unpaired electron may be found with equal probability on the sulfur (or oxygen) and on the nitrogen. The structure of the ions obtained by the radiolytic reduction of Lauth's Violet can be represented in resonance terms as (CXII), (CXIII), and (CXIV).[116]

Besides the known absorption band at 660 mμ, a band at about 500 mμ is also noticed in the spectra of Methylene Blue solutions in the visible range. The intensity of the latter band is considerably increased in some solid samples, which appear red. It is suggested that the dimethylamino groups in the red samples are forced out of the molecular plane.[117] It has also been observed that Methylene Blue (CX), dissolved in anhydrous aliphatic amines or in ethanol containing sodium ethoxide, gave red solutions, which turned blue again on addition of water.[118] The existence of the red form depends on the basic nature of the amine. In the blue form of the dye, the positive charge is distributed symmetrically throughout the chromophoric system. The red form in the amine solutions is attributed to the interaction of the dye ions with strongly basic anions. This interaction reduces the fraction of the positive charge,

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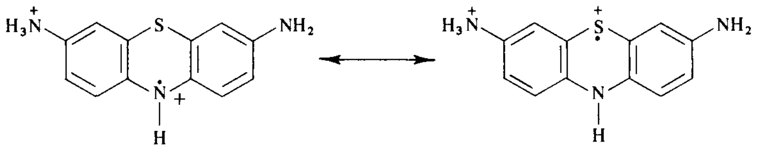
[114] P. Balestic and M. Magat, *Large Radiation Sources Ind., Proc. Conf., Warsaw, 1959* Vol. 2, p. 149. IAEA, Vienna, 1960; *Chem. Abstr.* **55,** 23542 (1961).

[115] A. A. Kharkharov and L. P. Kovzhina, *Izv. Vysshikh Uchebn. Zavedenii, Tekhnol. Tekstil'n. Prom.* No. 1, 115 (1966); *Chem. Abstr.* **65,** 18727 (1966).

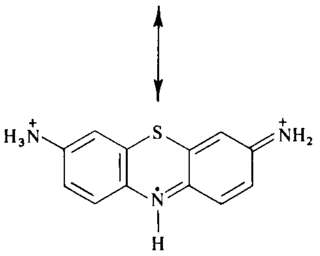
[116] P. B. Ayscough and C. Thompson, *J. Chem. Soc.* p. 2055 (1962); see also F. W. Heineken, M. Bruin, and F. Bruin, *J. Chem. Phys.* **37,** 1479 (1962).

[117] S. Daehne, *Z. Physik. Chem.* (*Leipzig*) **220,** 187 (1962).

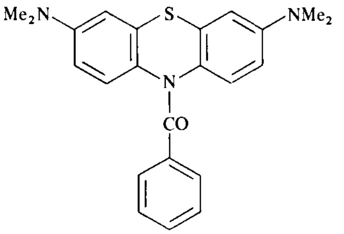
[118] R. B. McKay, *Nature* **210,** 296 (1966).



(CXII) (CXIII)



(CXIV)



(CXV)

shared by the terminal positions; and this results in the hypsochromic spectral shift.

From the application point of view, it has been claimed that phenothiazine derivatives such as (CXV) find use in the photoconductive layer of electrophotographic materials[119] and also in transfer sheet materials.[120]

Plausible mechanisms of formation of dyes, such as Pyronine G (CI 45005) (CXVI), Methylene Blue (CX), and Meldola's Blue (CI 51175; Basic Blue 6) (CXVII), in which hydride transfer is involved, have been suggested by Tilak.[90]

XI. Some Reactions of Basic Dyes

It was found that Malachite Green, Brilliant Green (CI 42040, Basic Green 1), and Crystal Violet and their derivatives decompose when their 0.0001 *M* aqueous solutions are refluxed over a period ranging from 50 to 90 hours. The decomposition was much slower in 0.01 *N* sulfuric acid or in water at room temperature. Formaldehyde and acetic acid were detected in the decomposition products; and it has been suggested that

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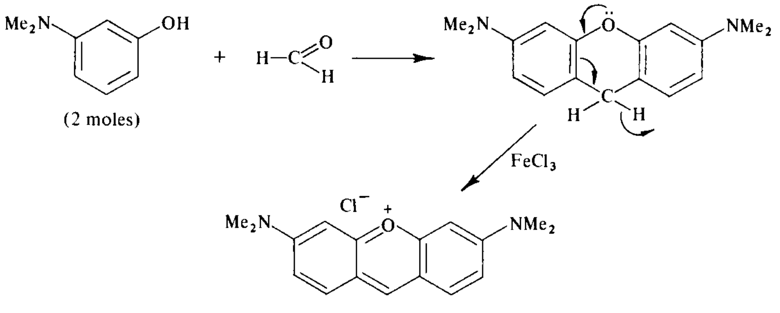
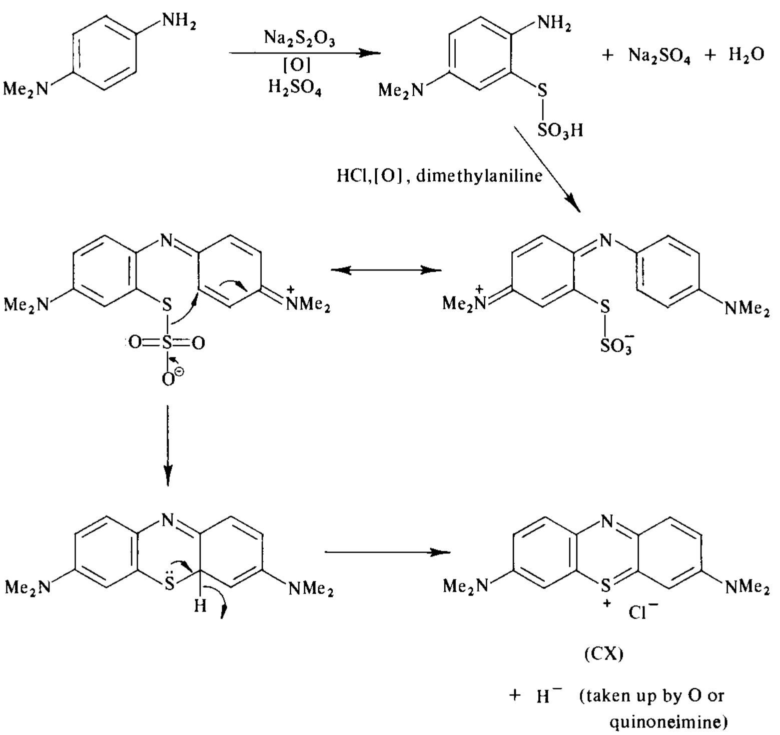
[119] Gevaert Photo-Producten N. V., *BeP* 587,794.

[120] National Cash Register Co., *USP* 2,548,364; 2,548,365.



(CXVI)



(CX)

the presence of formaldehyde is responsible for the antiseptic properties of Crystal Violet.[121] It is well known that the color of a dye such as Malachite Green fades when it is dissolved in acid solutions. The measurement of the rate of fading of Malachite Green in acid solutions shows

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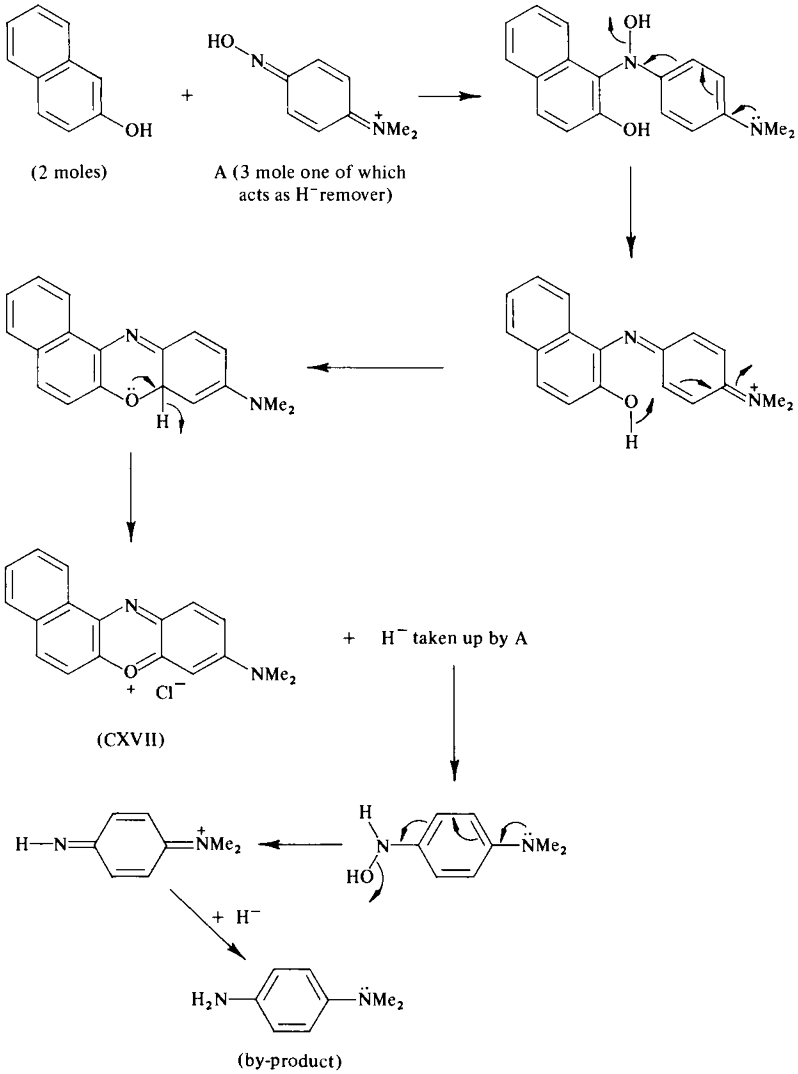
[121] M. Matrka, Z. Sagner, V. Sterba, and J. Arient, *Chem. Prumysl.* **11**, 574 (1961).



that the rate-controlling step in the fading process is the reaction between the dye cation and a proton [see (CXVIIIc)].[122] It was observed that in dilute sulfuric acid solution of the carbinol of Malachite Green

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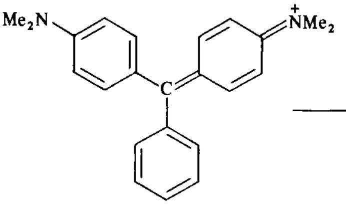
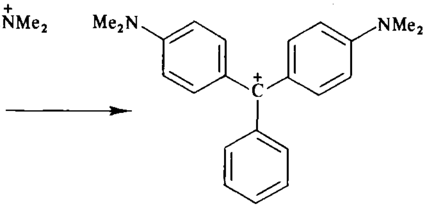
[122] S. S. Katiyar, *Naturwissenschaften* **49**, 325 (1962); *Bull. Chem. Soc. Japan* **35**, 1772 (1962).



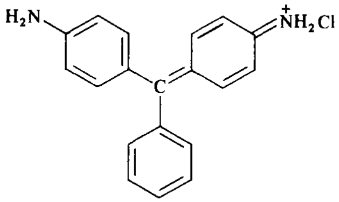
(in dilute acid)

(CXVIII a)

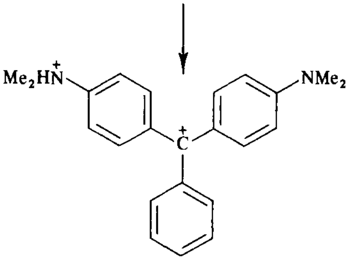


(in acid of higher concentration)

(CXVIII b)

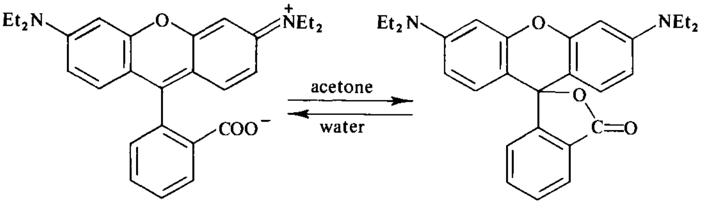


(CXIX)



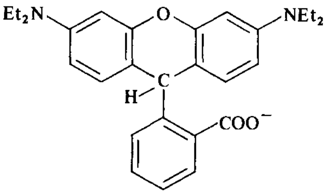
(at very high concentration of acid)

(CXVIII c)



(CXX a)

(CXX b)



(CXXI)

(LXXXIV), the content of the ammonium ion (CXVIIIa) is considerably greater than that of the conjugated carbonium ion (CXVIIIb), having the same charge. As the acid concentration increases, the proportion of the ammonium cation decreases, until it finally becomes zero. At still higher acid concentration, the carbonium ion takes up a proton to give (CXVIIIc).[123] Similar observations have been recorded in the case of Doebner's Violet (CXIX) and Pararosaniline (IV).[124] However, ortho-substituted Malachite Greens have considerably more of the conjugated carbonium ion species in dilute sulfuric acid.

The color of Rhodamine B (CI 45170; Basic Violet 10) (CXXa) in aqueous solutions does not fade even on exposure to light. It is found that when a solvent of low dielectric constant such as acetone is added to the above solution and then exposed to light, a reversible isomerization takes place and the dye is converted into the colorless uncharged lactone form (CXXb).[125] Since the color of the decolorized pure acetone solution is not restored by freezing, it is concluded that the fading process leads to the permanent saturation of the central carbon atom to give the leuco form of the dye (CXXI). Both (CXXa) and (CXXb) have been isolated. The calculated dipole moment of (CXXa) is 25 Debye units, showing the separation of unit charge to be 5 Å, which is consistent with the valence bond representation given above.[126]

Colorless solutions of leuco sulfite derivatives of triphenylmethane dyes developed color when heated. Thus, Malachite Green leuco-sulfonic acid (CXXII) showed thermochromism. This thermochromism was due to the formation of colored species (CXXIII). It was observed that aqueous Malachite Green leuco sulfonic acid fatigued or became nonthermochromic, when heated in presence of aqueous bisulfite solution. This is due to the reduction of the colored species (CXXIII) to the leuco Malachite Green (XXIII), accompanied by the evolution of sulfur dioxide.[127] The hydrogen for the reduction is obtained from the sodium bisulfite according to

$$NaSO_3H + H_2O \xrightarrow{\text{Heat}} NaHSO_4 + H_2$$

An increase in the amount of bisulfite showed an increase in the yield of the leuco base. This was particularly the case with Crystal Violet.

Triphenylmethane carbinol bases such as the Crystal Violet carbinol base (CXXIV) and their methyl ethers react with excess of a Grignard reagent. The initially formed dye ion (CXXVI) reacts further with the reagent at higher temperatures and yields the ethane derivative such

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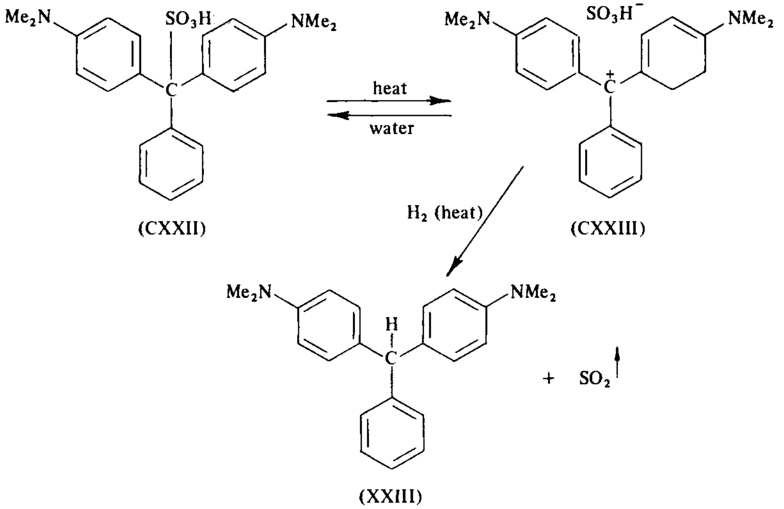
[123] N. G. Belotserkovskaya and O. F. Ginzberg, *Zh. Obshch. Khim.* 34, 2275 (1964).

[124] N. G. Belotserkovskaya and O. F. Ginzberg, *Zh. Obshch. Khim.* 34, 3274 (1964).

[125] B. Stevens and W. S. W. Bingham, *J. Soc. Dyers Colourists* 79, 632 (1963).

[126] B. Stevens, N. Connelly, and P. Suppan, *Spectrochim. Acta* 22, 2121 (1966).

[127] R. N. Macnair, *J. Org. Chem.* 33, 1945 (1968).



as (CXXVII) m.p. 134°, which could not be oxidized to a dye with lead dioxide.[128,129] Malachite Green carbinol base (LXXXIV), likewise, yields the triphenylmethane derivative (CXXVIII), m.p., 209–210°. These carbinol bases and their methyl ethers react smoothly with 1-phenyl-3-methyl-5-pyrazolone and yield condensation products such as (CXXIX).[130] However, the triphenylmethane dye (XXIX) is displaced from (CXXIX) by the action of a diazonium solution with the resultant formation of the azo dye (CXXX).

XII. Organic Pigments from Basic Dyes

A general description of the lakes of basic dyes has appeared earlier (*CSD II*, p. 736), and has also been covered in an excellent review by Williams and Conley.[131] The complex heteropoly acids such as phosphomolybdic acid (PMA), phosphotungstomolybdic acid (PTMA), and phosphotungstic acid (PTA) can be used as precipitating agents for many basic dyes. The basic dyes which can be used in the manufacture of PMA and PTMA colors include Methyl Violet, Malachite Green, Brilliant Green, Ethyl Violet (CI 42600; Basic Violet 4), Victoria Pure

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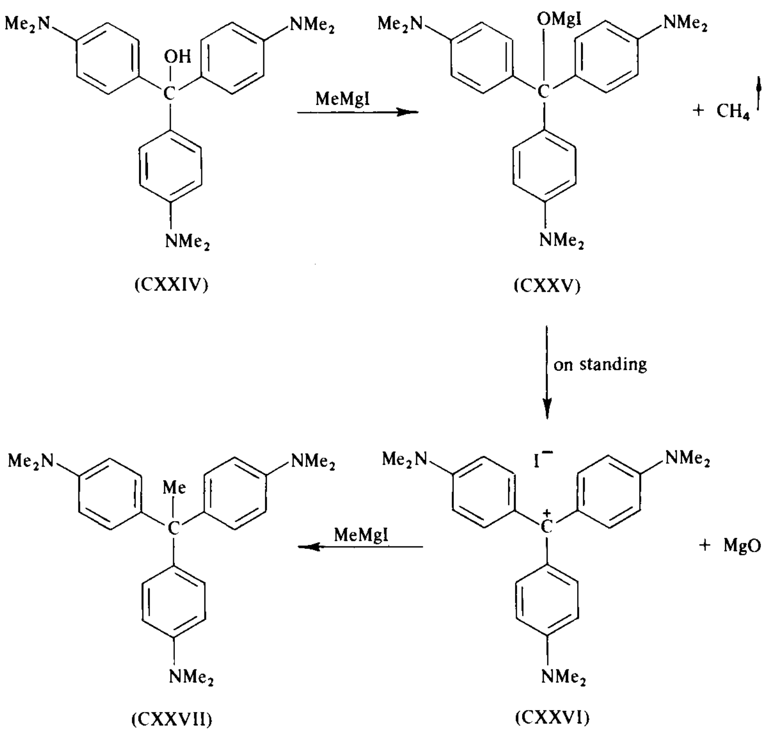
[128] O. F. Ginzburg, *Zh. Obshch. Khim.* **23**, 1682 (1953).

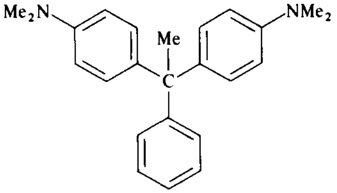
[129] O. F. Ginzburg, A. S. Sopova, and E. Yu. Shvarts, *Sb. Statei Obshch. Khim.* **2**, 1100 (1953).

[130] O. F. Ginzburg, *Zh. Obshch. Khim.* **23**, 1890 (1953).

[131] W. W. Williams and J. W. Conley, *Ind. Eng. Chem.* **47**, 1507 (1955).



(CXXIV) (CXXV) (CXXVII) (CXXVI)



(CXXVIII)

Blue BO (CI 42595; Basic Blue 7), Setoglaucine (CI 42025, Basic Blue 1), Rhodamine B, and Rhodamine 6G (CI 45160; Basic Red 1).

The principal formula for the complex phosphomolybdic acids is the one containing a 1:24 ratio of phosphoric anhydride and molybdenum oxide ($3H_2O \cdot P_2O_5 \cdot 24MoO_3$). X-Ray data indicate[132] that the preferable formula is $H_3PO_4 \cdot 12MoO_3 \cdot XH_2O$. The composition of phosphomolybdic acid pigments from Methyl Violet (CXXXI), Victoria Pure Blue BO

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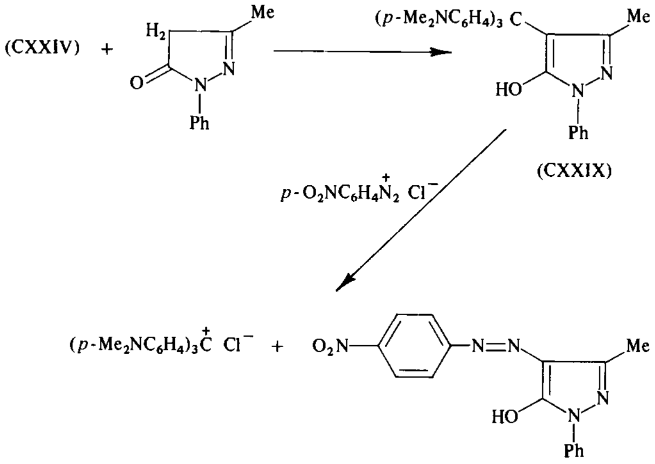
[132] L. Pauling, *in* "Molybdenum Compounds" (D. H. Killefer and A. Linz, eds.), p. 95. Wiley (Interscience), New York, 1952.

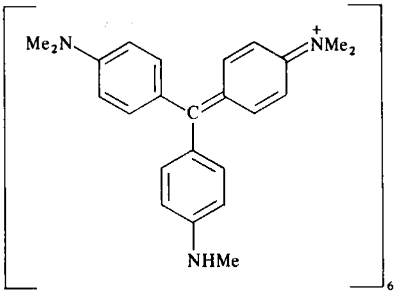


(XXIX) (CXXX)

(CXXXII), Brilliant Green (CXXXIII), and Rhodamine 6G (CXXXIV) indicate the general structure of these pigments. The basic dyes exist as salts, usually chlorides or sulfates. The formation of phosphomolybdate or phosphotungstate colors comprises simply the replacement of the more soluble anions by the much heavier and practically insoluble anions such as phosphomolybdate or phosphotungstate. Approximately six molecules of the dye are required per molecule of $(3H_2O \cdot P_2O_5 \cdot 24MoO_3)$. Only one of the amino nitrogens of a basic dyestuff molecule combines with phosphomolybdate ion at any one time. This accounts for the fact that only a very slight change, if any, is observed in the shade of the basic dyestuff after conversion to its corresponding PMA pigment.

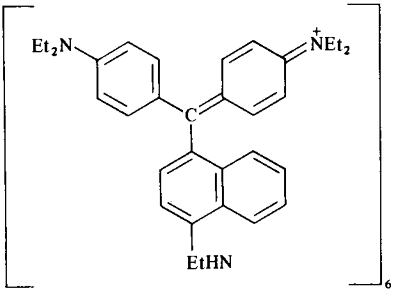
For the manufacture of PMA colors, the basic dyestuff is dissolved in water at 60–70° at a dye concentration of about 1%. The pH of the solution is adjusted to about 3 by means of acetic acid. The complex acid (with a 1:24 ratio of P_2O_5 and MoO_3) solution is prepared from soluble phosphate and molybdate salts by adding a mineral acid to bring the pH within the range 3 to 4. The temperature of the complex solution is maintained at 20° to 30° and then added to the warm dye solution at a proper rate under controlled agitation. Then the mixture is heated for the stabilization of the pigment. A slight excess of complex acid solution may be added to account for any liberated dye during heating.

These organic pigments are noted for their brilliance, strength, and greatly improved stability to heat, light, and water. Generally the PTMA colors are superior to PMA and PTA colors in their stability to sunlight. The principal use of these pigments is in the field of printing inks.



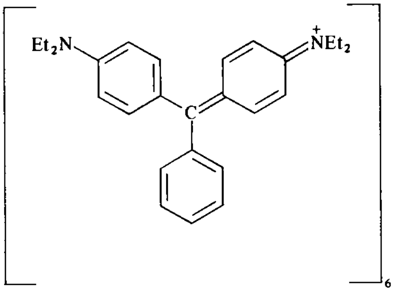
$O_3 \cdot P_2O_5 \cdot 24MoO_3^{6-}$

(CXXXI)



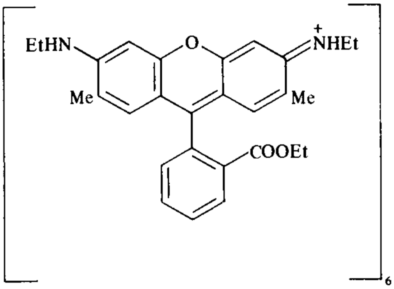
$O_3 \cdot P_2O_5 \cdot 24MoO_3^{6-}$

(CXXXII)



$O_3 \cdot P_2O_5 \cdot 24MoO_3^{6-}$

(CXXXIII)



$O_3 \cdot P_2O_5 \cdot 24MoO_3^{6-}$

(CXXXIV)

In addition, they can be used for tinting white paper, in water colors, in wax crayons, in colored paper, and in enamels for children's toys, since they are practically insoluble in water and are nontoxic. A method was developed to deposit the insoluble lakes of PMA within the fiber, especially vicose rayon, thus giving good fastness to washing and light.[133] The basic dye and the lake-forming acid are mixed in the presence of an alkali phosphate buffer to maintain the pH between 5 and 12.5. This principle of lake formation is made use of in the estimation of micro amounts of phosphates in solutions.[134] A molybdate reagent is added. *n*-Propyl acetate selectively extracts phosphomolybdate complex in nitric acid solution at pH 0.2 to 0.5. Treatment of the extract with acidified dye such as Crystal Violet, Methyl Violet, Malachite Green, or Brilliant Green yields an insoluble phosphomolybdate dye complex, which can be estimated spectrophotometrically in *n*-propyl acetate–acetone solution.

XIII. Manifold Record Systems

Manifold record systems are also referred to as transfer sheet materials. The idea in the development of a pressure-sensitive record system is to use a single material both as a receiving and as a transferring sheet. Such materials can be used in a pile under a sheet. An entry on the top sheet can be reproduced by impact or pressure on all the undersheets without using the conventional carbon papers. The record material is uniformly and profusely coated by two types of substances. One is a finely divided solid inorganic substance and the other a liquid phase consisting of a solution of an organic compound. Direct contact between the two kinds of substances is avoided by encasing the liquid phase in microscopic capsules of gelatine or agar before applying to the paper. The solid inorganic phase consists of electron acceptor or acidic substances such as attapulgite, halloysite, Kaolin, magnesium trisilicate, and zeolite. The liquid organic phase consists of a solution in oily medium (such as chlorinated biphenyl) of electron donor aromatic compounds, which can be converted into more highly polarized conjugated form in contact with acidic substances. Application of pressure ruptures the minute capsules and the two phases react with the production of colored marks at the point of impact.[120,135-137]

[133] Calico Printers Association Ltd., *BP* 699,086.

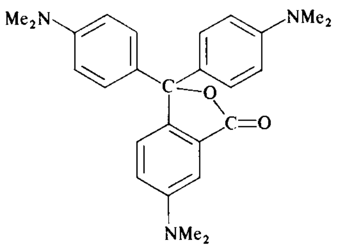
[134] A. K. Babko, Y. F. Shkarovskii, and E. M. Ivashkovich, *Ukr. Khim. Zh.* 33, 951 (1967).

[135] National Cash Register Co., *USP* 2,550,466–2,550,469.

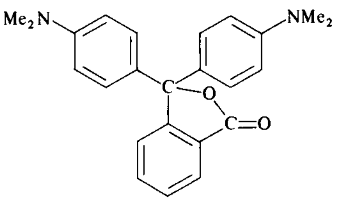
[136] National Cash Register Co., *USP* 2,550,470–2,550,473.

[137] National Cash Register Co., *USP* 2,712,507.

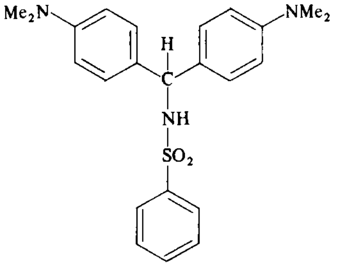
The organic color-forming reactants should have good solubility in nonpolar solvents. They should be colorless in solution and should possess stability to light before impact. The Crystal Violet lactone (CXXXV) and the Malachite Green lactone (CXXXVI) give bluish violet and greenish markings, but these colors gradually fade. Superior colored impressions are obtained by using leuco diphenylmethane and triphenylmethane derivatives. A few such derivatives have already been described in this chapter. Sulfonamide derivatives such as (CXXXVII) and (CXXXVIII) are prepared by the condensation of equimolar amounts of benzenesulfonamide and 3-pyridinesulfonamide, respectively, with Michler's hydrol in the presence of a base.[138] These sulfonamide derivatives, which are similar to (XVI) and (XVII), are useful in colorless transfer sheet materials.



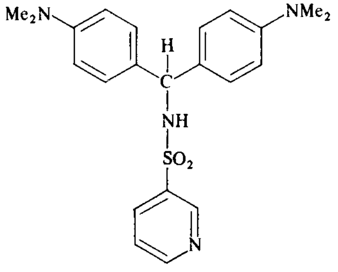
(CXXXV)



(CXXXVI)



(CXXXVII)



(CXXXVIII)

The benzoyl derivative of leuco Methylene Blue (CXV) which is prepared by refluxing benzoyl chloride with the zinc chloride double salt of leuco Methylene Blue in pyridine gives permanent blue markings when used in transfer sheet materials.[137] The 1- and 2-naphthoyl derivatives

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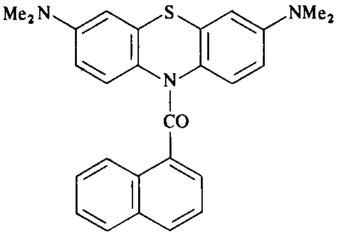
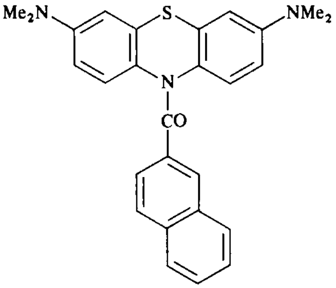
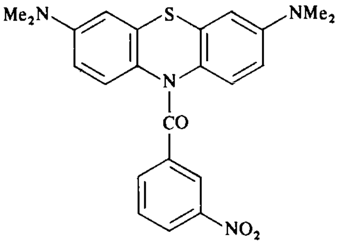
[138] NAC, *USP* 2,948,753.



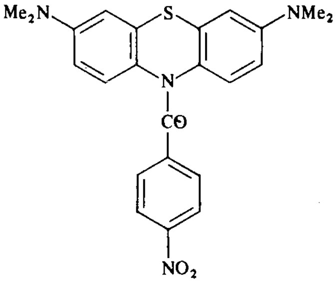
(CXXXIX)



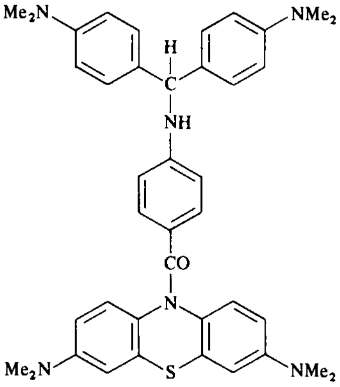
(CXL)



(CXLI)



(CXLII)



(CXLIII)

(CXXXIX) and (CXL)[139] and the nitro derivatives of 10-benzoyl-3,7-bis(dimethylamino)phenothiazine (CXLI) and (CXLII)[140] have better light stability than (CXV). The *p*-nitro derivatives (CXLII) can be reduced to the corresponding *p*-aminobenzoyl derivative and further condensed with Michler's hydrol to give (CXLIII) which is colorless but yields lightfast blue images in contact with acid copy sheets.[34]

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[139] National Cash Register Co., *USP* 2,783,227.

[140] National Cash Register Co., *USP* 2,783,228.

CHAPTER IV

CATIONIC DYES FOR SYNTHETIC FIBERS

Donald R. Baer

JACKSON LABORATORY ORGANIC CHEMICALS DEPARTMENT
E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE

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I. Introduction

The introduction of Orlon Type 42 polyacrylonitrile fiber in 1953[1] by the du Pont Company ushered in a major new era in the history of commercial dyes. This fiber contained acidic dyesites and could be dyed readily with classical basic dyes, which showed a surprisingly high order of light- and wash-fastness when compared with the same dyes on natural fibers. Although the lightfastness of most basic dyes on acrylics was improved over that on silk and acetate, further improvements were still necessary since the durability of acrylic fibers imposed more stringent fastness requirements.

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[1] P. L. Meunier, J. F. Laucius, J. A. Brooks, and R. J. Thomas, *Am. Dyestuff Reptr.* **42**, 470 (1953).

The initial commercial dyes for acrylic fibers consisted of selected and modified polymethine[2] and selected oxazine and triarylmethane types.[3] Within a short time modifications of the above dyes were designed to improve lightfastness still further.[4]

Some of the major uses for acrylics were in the sweater market and in blends with wool where the high bulk and warmth of the fiber were important. These created an even greater demand for dye lightfastness. Dye manufacturers turned their research toward novel dye types in an effort to improve this property. This has led to the development of a new field of "pendant" cationic dyes in which a cationic charge is placed on a molecule in a position which is essentially insulated from the chromophore. In this way most lightfast chromophores can now be adapted for use on acrylic fibers. Size, however, is a limitation since large molecules such as copper phthalocyanine and benzanthrone derivatives will not penetrate the fiber. The second major development has been the commercialization and expansion of a broad new field of diazahemicyanine dyes which offer a combination of brightness and fastness heretofore impossible.

The development of new dyes has been so successful that dyed acrylic fibers are currently considered to have the best combination of lightfastness, brightness, and wash-fastness of any textile fiber, and currently set the standards for the rest of the industry.

The acrylic fiber industry is one of the few cases where the development of improved dyeing technology has greatly influenced the market potential for the fiber. The major markets for polyacrylonitrile fibers did not develop until after 1954 when the cationic-dyeable fibers were introduced. Since 1954 the worldwide production of acrylic and modacrylic fibers[5] has grown from 29 million pounds to an expected production capacity of 2.8 billion pounds in 1970.[6] The major acrylic fibers, their manufacturers, and their trade names are listed in Table I. Also included is the relative saturation value of each fiber for basic dyes, which is indicative of the number of acidic dyesites present.[7]

Most of the acrylic fibers are dyeable with cationic dyes with the exception of a few relatively small volume products such as Orlon Type 44, which is dyeable with acid dyes.

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[2] See Astrazons, Vol. II, p. 1174.

[3] Vol. II, Chapter XXIII–XXV.

[4] R. A. Clarke and L. Bidgood, *Am. Dyestuff Reptr.* **44,** 631 (1955).

[5] Acrylic fibers are defined as those containing 85% or more polyacrylonitrile. Modacrylic fibers are defined as those containing 35–85% polyacrylonitrile.

[6] *Textile Organon* **40,** 98 (1969).

[7] W. Beckman, *J. Soc. Dyers Colourists* **77,** 616 (1961).

TABLE I
MAJOR ACRYLIC FIBERS

Fiber	*Relative saturation value*[1]	*Manufacturer*
Acrilan 16	1.4	Chemstrand, U.S.A.
Acrybel	1.2	Fabelta, Belgium
Courtelle	2.8	Courtaulds, U.K.
Crylor	1.4	Soc. Crylor, France
Dolan	1.5	Süddeutsche Zellwolle, Germany
Dralon	1.4–2.1	Bayer, Germany
Exlan L	1.15	Exlan Ind., Japan
Leacril 16	1.1	Acsa, Italy
Orlon 42	2.1	du Pont, U.S.A.
Orlon 21	5	du Pont, U.S.A.
Redon F	1.4	Phrix Werke, Germany
Tacryl	3.3	Superfosfat, Sweden
Verel	—	Union Carbide, U.S.A.
Vonnel	1.3	Mitsubishi, Japan

[1] Maximum dye uptake of pure dye of mol. wt. ≈400 in percent of fiber weight at equilibrium.

The success of cationic-dyeable acrylic fibers has led to modification of other synthetic fibers to accept cationic dyes, thus hoping to improve brightness. Generally speaking no other acid-modified fibers offer the same combination of fastness and brightness as acrylics. The mere introduction of acidic sites into a polymer does not guarantee any of the above properties. In most cases the lightfastness of cationic dyes is poorer on all other substrates. Shades of fluorescent dyes are generally duller. Wash-fastness is poorer if the fiber is more hydrophilic.

A few limited correlations of structure vs. light fastness of cationic dyes on acrylic fibers have been presented,[7a] as well as a summary of light fastness of cationic dyes on various fibers.[7b]

However, there are several other acid-modified fibers currently on the market in which the major interest is for cross-dyeability in fiber blends and patterns: Dacron Type 64 polyester fiber (du Pont), 66 nylon T-844 or T-824 (du Pont) and Dye 1 (Monsanto). The major dyeing problem with the acid-modified polyesters is lightfastness[8] while on acid-modified 66 nylon the major current problem is inadequate wash-fastness for apparel use.

[7a] R. F. Johnson, O. A. Stamm, and H. Zollinger, "Optische Anregung organischer Systeme," pp. 375–390 (23 references), Verlag Chemie, Weinheim/Bergstr. 1966; [7b] M. Pestemer, *loc. cit.*, pp. 491–497.

[8] S. B. Maerov and H. Kobsa, *Textile Res. J.* **31,** 697 (1961).

TABLE II
CATIONIC DYE LINES

Trade name	*Manufacturer*
Sevron	du Pont
Deorlene	Ciba
Calcozine	American Cyanamid
Basacryl	Badische
Astrazon	Bayer
Genacryl	General Aniline and Film
Maxilon	Geigy
Sandocryl	Sandoz
Nabor	National Aniline
Sumiacryl	Sumitomo
Amacryl	American Aniline
Remacryl	Hoechst
Eastacryl	Eastman

A 2 billion pound market for cationic-dyeable acrylics represents a new annual cationic dye business of over 20 million pounds or an annual world dye market value in excess of $70 million, essentially all based on technology developed since 1954. These dyes are manufactured under a number of different trade names. The major suppliers are listed in Table II.

II. Classification of Cationic Dyes for Synthetic Fibers

Cationic dyes are those in which the positive charge is associated with the chromophore part of the molecule. There is always an accompanying anion which normally has little effect on the dyeing properties. It may, however, play an important role in the solubility characteristics of a dye and the ability to isolate a pure dye. Current cationic dyes can be divided into three distinct classes.[9]

(a) *Pendant Cation (Nonresonating Charge)*. These dyes are structurally similar to the disperse dyes except that a cationic charge has been added, insulated from the chromophore, thus enabling the dye to be absorbed by the acid-modified fibers. They have been especially designed to give high lightfastness. Their shade, strength, and fastness properties are similar to the disperse dyes from which they are derived. Consequently, these extremely lightfast dyes do not offer the extreme brilliance of shade and the strong tinctorial value of the classical triarylmethane and related dyes.

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[9] H. P. Landerl and D. R. Baer, *Am. Dyestuff Reptr.* **54,** 222 (1965).

(b) *Delocalized Positive Charge* (*Resonating Charge*). Cationic dyes carrying a delocalized positive charge are in general the brightest and strongest tinctorially. Examples include modified oxazine, triarylmethane, azacyanine, polymethine, and polyazamethine types.

(c) *Amine Salts* (*Cation Formed by Protonation under Acidic Conditions*). Since most acrylics are dyed under acidic conditions, basic dyes which do not contain a formal positive charge except in the presence of acid may be used to dye acrylic fibers. Under neutral or alkaline conditions these products will behave more like disperse dyes.

A. STRUCTURES OF COMMERCIAL CATIONIC DYES

Since most of the technology of cationic dyes for synthetic fibers has been developed within the past 15 years and continues to be developed, there is considerable competition between dye manufacturers and very little published technical information on specific dye structures. Most of the new cationic dyes are listed in the *Colour Index* with only a generic name. In the following discussion of dye structures an attempt will be made to indicate typical commercial dye structures and technology, but specific commercial dye names will be used only if they appear in the published literature.

III. Pendant Cationic Dyes

Dyes containing a localized positive charge which is not conjugated with the chromophore system are classified as pendant cationic dyes. Usually the cationic function is a substituted quaternary ammonium salt, although examples of sulfonium, hydrazinium, and thiouronium salts are known. The quaternary ammonium salt is preferred since it generally is easy to prepare and is stable over a broad pH range.

Prior to the development of acrylic fibers a limited number of pendant cationic dyes had been prepared. Derivatives of (*m*-aminophenyl)trimethylammonium chloride, such as (I), formed part of the Janus range of colors which were of limited use on rayon, silk–wool unions, and on cotton (aftertreated with fixing agents).[10]

Isothiouronium salts are prepared by heating a chloromethylated dye with tetramethylthiourea. These salts are then applied to cellulosic fibers and insolubilized with heat and an acid acceptor to produce wash-fast dyeings. This chemistry forms the basis of the Alcian X (II) dye line

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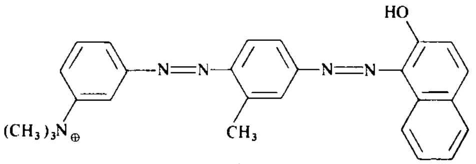
[10] Vol. I, p. 521.

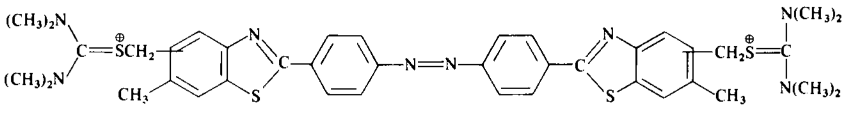
of ICI.[11] More recently ICI has patented monoisothiouronium salts of selected azo compounds as dyes for polyacrylonitrile.[12]

Pendant ammonium dyes were also known as colorants for leather and in fact one currently important red pendant cationic azo dye (III) was first described in the patent literature as a dye for leather.[13]



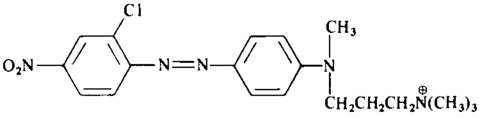
(I)

Janus Red B, Basic Red (CI 26115)



(II)

Alcian Yellow GXS



(III)

Basic Red 18 (CI 11085)

A. Azo Dyes

The cationic group in a pendant azo dye is most conveniently prepared by preforming it into the radical containing the diazonium group or into the coupler with subsequent formation of the dye. Generally speaking, there are more pendant cationic dyes based on a cationic coupling component than on the diazo compound due to the ease of synthesis.

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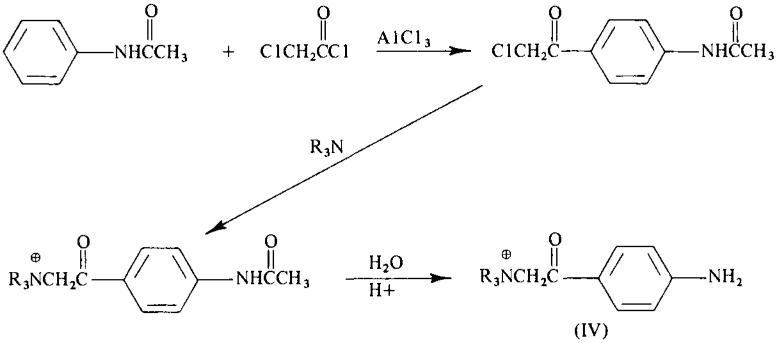
[11] A. Schaeffer, "Chemie Der Farbstoffe and Deren Andwendung," p. 176. Steinkopff, Darmstadt, 1963.

[12] ICI, *BP* 931,118.

[13] FBy, *USP* 2,972,508.

Early evaluation of the Janus-type dyes containing a trimethylammonium group directly on the diazo component showed them to be deficient in lightfastness on acrylic fibers. Boyd[14] developed a new diazo component (IV) and a practical synthesis (Chart 1) leading to lightfast pendant cationic azo dyes in the yellow to red range.

CHART 1



Diazotization and coupling of (IV) to aromatic primary, hindered secondary, or teritiary aromatic amines gives lightfast dyes. Examples of the shades obtained are as follows: → *m*-toluidine, orange; → *o*-chloro-*N*-(2-cyanoethyl)aniline, yellow; → *N,N*-diethylaniline, red. Variations in the R group have little effect on the shade and fastness properties although other physical properties such as dyeing rate and solubility can be affected. Coupling to pyrazolones[15] gives green-yellows (V).

Disazo dyes may be prepared by diazotizing the *m*-toluidine derivative above and coupling to a wide variety of couplers.[16] Coupling of (IV) to Tobias acid, desulfonates the coupler during the dye-forming process, producing the 2-naphthylamine derivative (VI). This scarlet dye has excellent pH stability and is surprisingly lightfast.[17] The 6-(methylsulfamoyl) analog of (VI) is an orange color.[18]

Since almost all acrylics are dyed in the pH range from 3 to 6 it is important that the dyes be shade-stable in this range. The azo dyes containing strongly basic amine groups such as the *p*-dimethylamino group are generally quite prototropic (change in shade with increased acidity). Consequently, most practical dyes in this class use less basic amines

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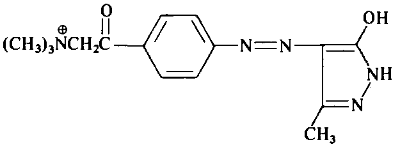
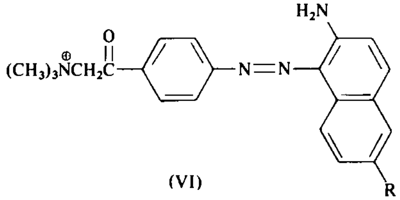
[14] DuP, *USP* 2,821,526.
[15] DuP, *USP* 3,074,926.
[16] DuP, *USP* 3,020,272.
[17] DuP, *USP* 3,074,926.
[18] CIBA, *BP* 1,102,990.

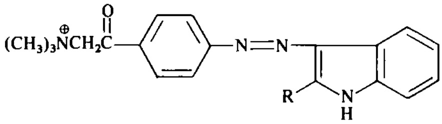
such as (cyanoethyl)- or (hydroxyethyl)anilines or are couplings to active methylene compounds. Unfortunately the less basic the amine the more hypsochromic the shade, and thus the practical shade range for dyes derived from (IV) is green-yellow to scarlet. The greenest yellow types are derived from couplings to 1,3-indandione[19] or 2,4-quinolinediol.[20] Couplings to heterocyclic rings such as 2-methylindole or 2-phenylindole[21] give yellow and orange dyes (VII) having excellent lightfastness and pH stability, e.g., Deorlene Yellow 4RL.



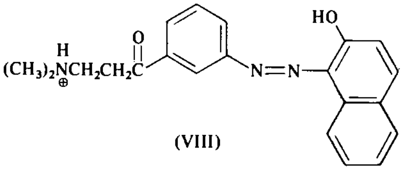
(V)



(VI)



(VII)
$R = CH_3$ yellow
$R = C_6H_5$ orange



(VIII)

An alternative route to cationic diazo components starts with *m*-aminoacetophenone. The CH_3CO– can be treated with formaldehyde and a secondary amine to yield a modified Mannich base with a diazotizable amino group.[22] A typical orange dye is (VIII). This dye type has not achieved the technical importance of the preceding types since the Mannich reaction is reversible, causing problems of dye instability.

Formation of the cationic group in the coupling component can occur in a number of ways such as shown in Chart 2. As in the case of the previous dyes, the R group has little effect on shade and fastness but has a direct influence on dyeing properties. Diazotization of 2-chloro-4-nitroaniline and coupling to a molecule similar to (IX) gives the important brownish red dye,[23] Basic Red 18, CI 11085 (III).

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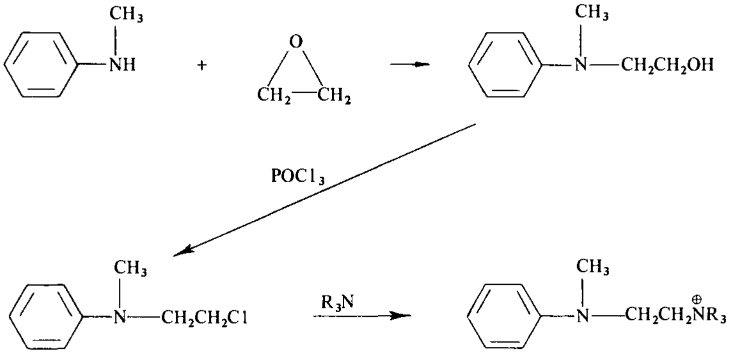
[19] CIBA, *BP* 990,495.
[20] DuP, *USP* 2,965,631.
[21] CIBA, *BP* 902,728.
[22] B, *BP* 857,391.
[23] D. Haigh, *Dyer* **132, 111** (1964).

CHART 2



(IX)

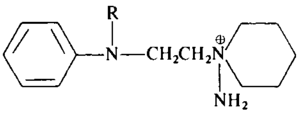
A number of patents deal with alternate cationic groups in the above type couplers. Some examples are (X)–(XIX).[24-32]

With the same diazo, all of these couplers produce similar shades. The major difference is in the stability of the cationic charge at the required temperature and pH required for dyeing.

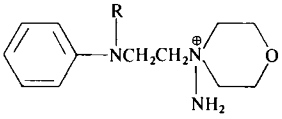
Most of the azo dyes prepared by coupling to a typical "quaternized dialkylaniline" (IX)–(XIX) are dull yellow-orange to red-brown shades. Typically, couplings from aniline give yellows; *p*-nitro- or *p*-cyanoanilines, orange to reds; 2,6-dihalo-4-nitroanilines, brown. Disazo dyes have been prepared[33] but seem to offer little advantage over the monoazo dyes and tend to have slower dyeing rates and produce heavy staining on other fibers.

Heterocyclic diazo components have been used in an attempt to improve brightness of cationic dyes containing quaternized dialkylaniline couplers. Thus, Bayer has patented red dyes[34] from thiadiazoles (XX), and violet dyes from 2-amino-5-nitrothiazole,[35] and du Pont[36] has

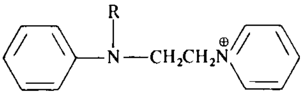
[24] S, *BP* 1,016,371.
[25] YDC, *BP* 1,047,293.
[26] B, *BP* 864,280.
[27] B, *DBP* 1,045,969.
[28] B, *BP* 914,074.
[29] ICI, *BP* 939,268.
[30] S, *BP* 1,004,284; 1,008,636; 1,048,482; *USP* 3,374,221.
[31] S, *BP* 1,072,235.
[32] S, *BP* 931,557.
[33] FBy, *BP* 849,994.
[34] FBy, *BP* 855,153.
[35] FBy, *USP* 2,972,508.
[36] DuP, *USP* 3,033,847.



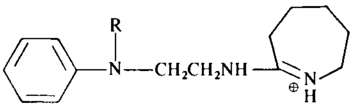
(X)[24]



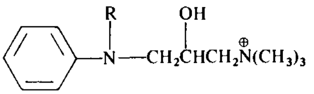
(XI)[24]



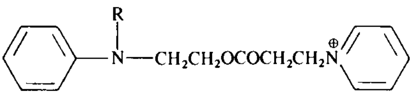
(XII)[25]



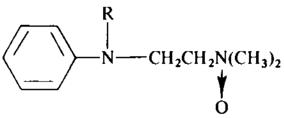
(XIII)[26]



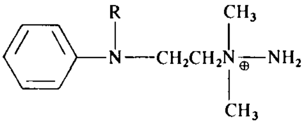
(XIV)[27]



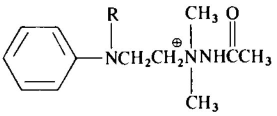
(XV)[28]



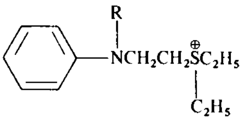
(XVI)[29]



(XVII)[30]



(XVIII)[31]



(XIX)[32]

patented cationic dyes from 2-amino-5-(alkylsulfonyl)thiazoles. Attempts to produce the bright red naphthol shades have led to the synthesis of the naphthalene types of couplers (XXIa),[37] (XXIb).[38] In general the naphthol shade can be prepared with good fastness and improved brightness using the cyanine type dyes, and the above dyes are of little commercial importance.

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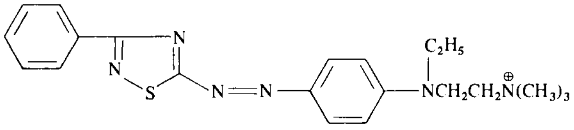
[37] TE, *USP* 3,079,375.

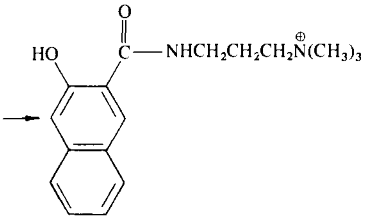
[38] TE, *USP* 3,043,827.

Other routes to cationic couplers for azo dyes include the intermediates (XXII),[39,40] (XXIII),[41] and (XXIV).[42]

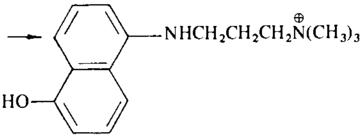
Premetalized monocationic azo dyes can be prepared using the naphthol couplers (XXIa) and (XXIb). Divalent metals such as copper or nickel give dull red to violet shades.[43] Coupling to pyrazolones give yellow shades.[44] These dyes have the expected good lightfastness but cause excessive staining of other fibers, such as wool, in blend fabrics.



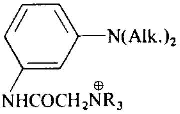
(XX)



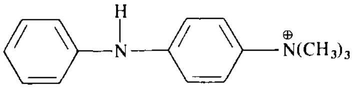
(XXIa)



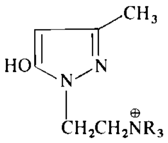
(XXIb)



(XXII)



(XXIII)



(XXIV)

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[39] G, *BP* 935,903.
[40] G, *USP* 3,148,181.
[41] CIBA, *BP* 957,634.
[42] B, *DBP* 1,085,276.
[43] TE, *USP* 3,079,375.
[44] CIBA, *USP* 3,057,845.

B. ANTHRAQUINONE DYES

Early in the development of cationic dyes for acrylic fibers it was recognized that the existing classical blue basic dyes could offer brightness but not the necessary degree of lightfastness required for blends, especially with wool. New dyes had to be developed. It was found that blue anthraquinone disperse dyes would produce pastel shades on Orlon 42 with good lightfastness. Modification of these molecules with a pendant cationic charge generally produced dyes having equal fastness but much better buildup. Good lightfastness in the case of anthraquinone dyes for acetate and polyesters requires hydrogen bonding of the carbonyl group with amino or hydroxy auxochromes in the α-positions. Thus, in lightfast pendant cationic anthraquinones, the group carrying the charge must be placed in the molecule in a manner that will not eliminate the necessary α-hydrogen bonds of the amino or hydroxyl groups. Fume fastness of anthraquinone dyes on acrylics and modacrylics is not a problem since the fiber is not readily permeable to oxides of nitrogen. On the other hand the same dyes on acid-modified polyamides can be seriously affected by oxides of nitrogen or ozone.

The molar extinction coefficient of anthraquinone dyes is only about ½ that of azo dyes and ¼ to ⅛ that of the delocalized cationic dyes. Therefore most commercial pendant cationic anthraquinones are based on well-known anthraquinone intermediates, since specialty intermediates result in dyes with low commercial value-in-use.

Several early types of lightfast blues for acrylics resulted from reaction of a 4-halo-1-aminoanthraquinone with a dialkylaminoalkylamine followed by quaternization[45,46] [(XXV)-(XXVIII)].

Reddish violet dyes (XXIX) are obtained if the quaternary group is part of a 1,2,4-triazole side chain.[47]

Extremely lightfast green-blue dyes (XXX) based on 1,4-diamino-2,3-anthraquinonedicarboximides were developed by du Pont.[48]

Cationic groups may be placed in the 2-position of the anthraquinone nucleus by means of an oxygen or sulfur bridge and still retain good fastness properties. Treatment of 1-amino-2-bromo-4-hydroxyanthraquinone with dialkylamino alcohols in the presence of a base yields lightfast pink shades[49] (XXXI). Somewhat bluer pink shades are obtained by

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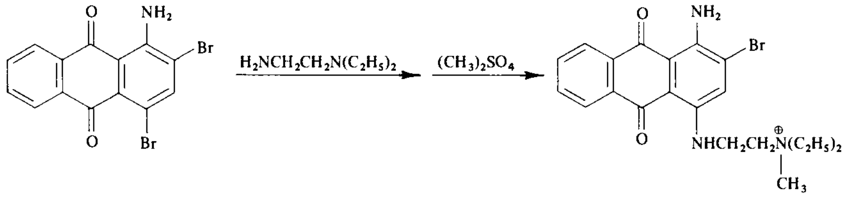
[45] DuP, *USP* 2,716,655.

[46] FBy, *BP* 807,241.

[47] *BP* 1,104,053.

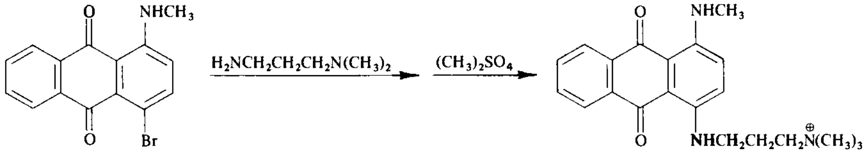
[48] DuP, *USP* 2,701,801; 2,701,802.

[49] DuP, *USP* 2,737,517.



(XXV)

(XXVI)
Red-blue



(XXVII)

(XXVIII)
Green-blue

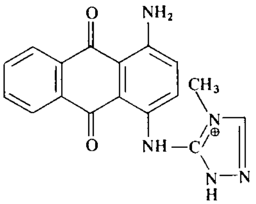
chloromethylating 1-amino-2-phenoxy-4-hydroxyanthraquinones followed by quaternization with an amine,[50] or a hydrazine (XXXII).[51]

Blue dyes may be prepared using similar techniques and having an amino or substituted amino group in the 4-position of the anthraquinone. Commercial blue dyes (XXXIII)[52] and (XXXIV)[53] are known.

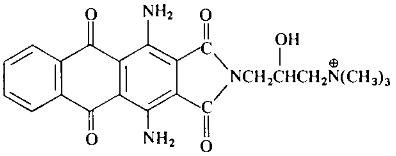
Dyes containing a sulfur bridge are prepared by reaction of dialkylaminoethanethiols with 1-amino-2-anthraquinonesulfonic acids followed by quaternization.[54] Basic Blue 49 is disclosed as having structure (XXXV).[55]

Other methods have been disclosed for forming pendant cationic anthraquinone dyes, such as treatment of a sulfonyl halide with a dialkylaminoalkylamine followed by quaternization,[56] reaction of primary aminoanthraquinones with paraformaldehyde and *N,N*-dimethylaniline followed by quaternization,[57] formation of carboxamides either on the anthraquinone nucleus or on a side chain by converting a carboxylic acid

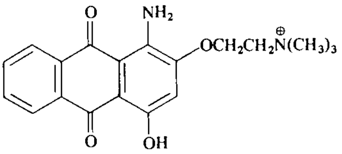
[50] DuP, *USP* 2,837,500.
[51] S, *BP* 1,061,461.
[52] Gy, *USP* 3,355,243.
[53] G, *FP* 1,277,496; *BP* 1,919,221.
[54] G, *DBP* 1,248,834.
[55] Gy, *USP* 3,355,243.
[56] CCC, *USP* 2,938,914.
[57] CFM, *DRP* 1,211,734.



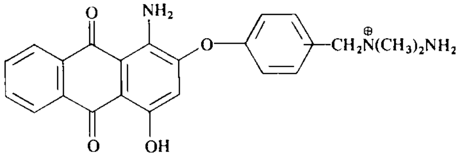
(XXIX)



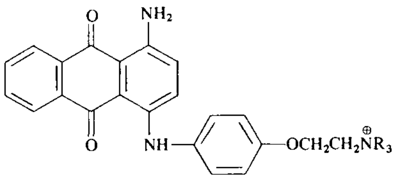
(XXX)



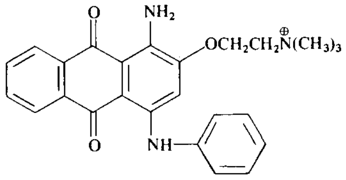
(XXXI)



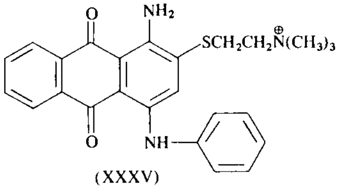
(XXXII)



(XXXIII)



(XXXIV)



(XXXV)
Basic Blue 49

to the carbonyl chloride and then treatment with a dialkylamino alcohol or amine.[58–61]

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[58] TE, *USP* 2,968,661.
[59] NAC, *USP* 3,076,821.
[60] S, *BP* 1,068,084.
[61] B, *BP* 1,039,119.

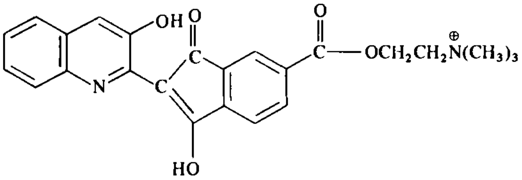
Many variations of the above methods are known in the patent literature. Alicyclic amines may be used to carry the charge and almost any linkage to the chromophore may be used. This technology may also be extended to almost any type of stable chromophore providing the final dye is not too large to penetrate the fiber.

C. Miscellaneous Pendant Dyes

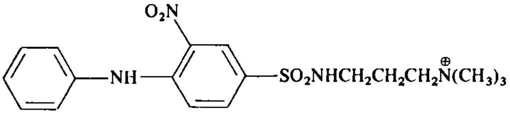
Bright yellow fluorescent methine dyes (XXXVI) have been prepared by condensation of a dialkylaminobenzaldehyde containing a cationic group with an active methylene compound.[62]

Lightfast quinophthalone yellows (XXXVII) have been prepared by condensation of trimellitic anhydride with a hydroxyquinaldine followed by formation of the cationic ester or amide derivatives.[63] Yellow dyes

(XXXVI)



(XXXVII)



(XXXVIII)

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[62] TE, *USP* 3,247,215.

[63] DuP, *USP* 3,023,212.

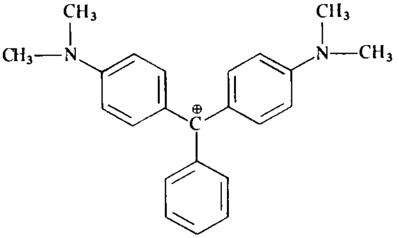
[64] DuP, *USP* 2,834,793; 2,834,794.

having excellent lightfastness on acid-modified polyesters[64] have been obtained from nitrodiphenylamine dyes (XXXVIII).

IV. Delocalized Cationic Dyes

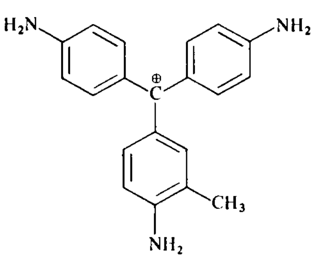
Dyes in which the positive charge in the molecule participates in the chromophoric system are called delocalized (or distributed) dyes. Patents and publications exist on a wide variety of delocalized cationic dyes for synthetic fibers but the most important commercial types are in the triarylmethane, oxazine, cyanine, and azacyanine groups. Most of the other delocalized cationic dyes are either too fugitive to light or do not have the hydrolytic stability required for application to acrylic fibers.[64a]

Since classical basic dyes have such high tinctorial value they are of major importance in deep shades such as blacks. However, most of these must be modified for improved lightfastness, and in doing so tinctorial strength is often reduced. However, there is one major exception where classical triarylmethane dyes are used commercially. Both Malachite Green (XXXIX) and Fuchsin (XL) have less than 5 hours lightfastness as self-shades on Orlon. However, when mixed they produce a black having 20 hours lightfastness, since the dyes have compensating fade characteristics. This combination is the most important black for acid-modified fibers due to its high tinctorial strength and value-in-use. Blacks having further improved fastness properties may be obtained by mixing dyes specifically designed for acrylic fibers, but the cost penalty to the



(XXXIX)

Malachite Green



(XL)

Fuchsin

[64a] A review of novel chromophoric systems, many of which are based on a delocalized cationic charge is found in S. Hünig and H. Quast, "Optische Anregung organischer Systeme," pp. 184–263 (346 references), Verlag Chemie. Weinheim/Bergstr. 1966.

dyer is 3 to 6 times that of the classical mix. Other than the black mixture of (XXXIX) and (XL), and a few selected cyanines, very few of the basic dyes existing before **1954** have achieved prominence on synthetic fibers without chemical modification.

A. DI- AND TRIPHENYLMETHANES

The major commercial representative of the diphenylmethane class is Auramine.[65] Auramine is a tinctorially strong yellow dye which is unfortunately not useful on acrylic fibers since, as an imine, it is readily hydrolyzed in a refluxing dyebath to Michler's ketone and ammonia.[66] No satisfactory means of stabilizing this type of dye has yet been uncovered, so it is not used on synthetics.

Triarylmethanes still form an important group of colors, particularly in the red to green range where maximum color value is desired. However, they have several disadvantages, and research in recent years has aimed at reducing these deficiencies. The problems include poor lightfastness, heavy wool stain in blends, reversion of certain dyes, such as Malachite Green, to the colorless leuco or carbinol form when the fibers are exposed to the high temperatures required for permanent creases or pleats.

Progress in the field of improved triarylmethane dyes for acrylics has been limited by conflicting factors. The strongest dyes are those which are the most symmetrical and which have the most basic amino groups. However, these two aspects reduce the chances for a practical solution to the problem. Reducing the basicity penalizes the most important property of the triarylmethanes, high tinctorial value. Substitution to improve fastness tends to destroy symmetry which also reduces tinctorial value.

J. Wegmann[67] discussed these aspects in relation to constitution and properties of basic dyes on polyacrylonitrile fibers. As a rough approximation, the light stability of a dye molecule decreases with increasing basicity, while the staining of wool increases (Chart 3).

In spite of the fact that (XLI) (Soluble Sky Blue Base[68]) has good lightfastness (and is thus an exception among triarylmethanes), it is not used on acrylic fibers because it is water-insoluble and does not produce level or well-penetrated dyeings.

Dyeing properties can be improved by making the above dyes less

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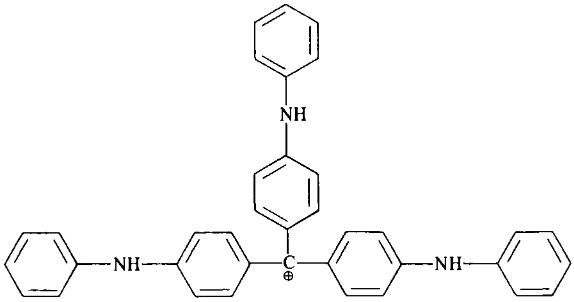
[65] Vol. II, p. 705.

[66] Vol. II, p. 707.

[67] *Melliand Textilber.* **39,** 408 (1958).

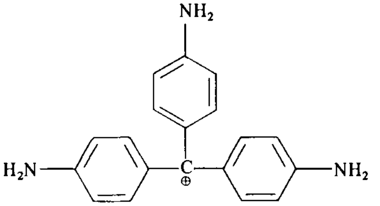
[68] Vol. II, p. 723.

CHART 3



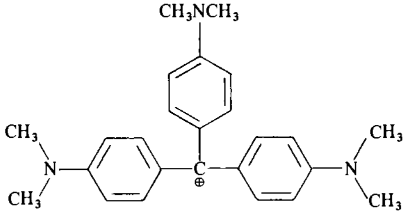
(XLI)

Blue Light 6 Wool stain moderate



(XLII)

Blue-Red Light 5 Wool stain average



(XLIII)

Violet Light 2 Wool stain heavy

symmetrical. Thus treatment of 4,4′,4″-trichlorotriphenylmethane with 4 moles of a substituted aniline at 100°, in an inert solvent, in the presence of a Lewis acid such as aluminum chloride, produces dyes (XLIV) which are lightfast on acrylic fibers.[69]

Bright greenish blue dyes (XLV) showing good pH stability are prepared from *o*-chlorobenzaldehyde and 2 moles of *N*-alkyl-*N*-(2-cyanoethyl)-anilines.[70]

Certain indole derivatives of diphenylmethanes produce lightfast

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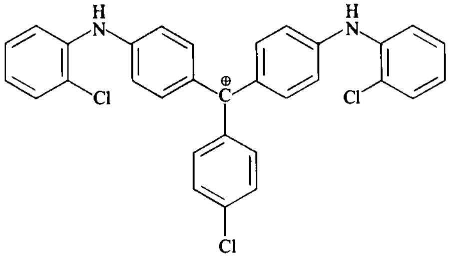
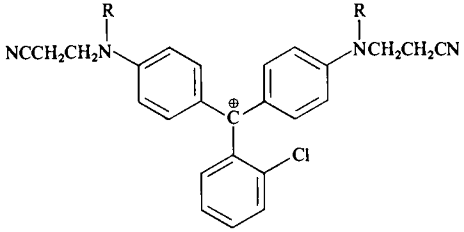
[69] MLB, *BP* 1,000,664; 1,003,684.

[70] DuP, *USP* 3,021,344.



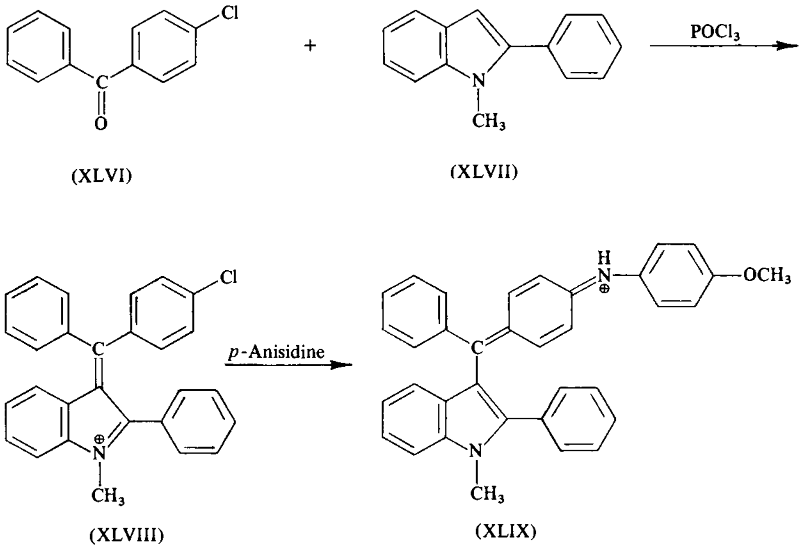
(XLIV)



(XLV)

dyeings on polyacrylonitrile.[71] Dyes with blue-green shades are obtained by reacting 4-chlorobenzophenone with 1-methyl-2-phenylindole and *p*-anisidine (Chart 4). By varying the amine and the benzophenone derivative (XLVI), shades ranging from green to violet can be obtained.

CHART 4



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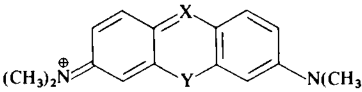
[71] FBy, *BeP* 702,239.

B. AZINES

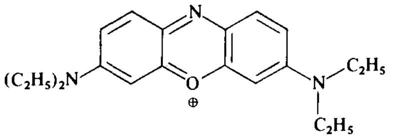
Closely related to the diphenylmethane dyes are the indamine types and the corresponding well-known cyclic derivatives such as acridines, pyrans, azines, oxazines, and thiazines. Wegmann[67] has shown the relationship between shade, and lightfastness in this series. This is summarized in Table III.

TABLE III
SHADE AND FASTNESS OF AZINES AND RELATED STRUCTURES

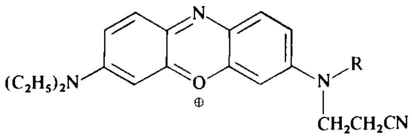


X	*Y*	*Dye type*	*Shade*	*Lightfastness*
—CH=	—H, —H	Diphenylmethane	Blue	Good
—CH=	—N—	Acridine	Orange	Poor
—CH=	—O—	Pyran	Red	Fair
—CH=	—S—	Thiopyran	Violet	Fair
—N=	—H, —H	Indamine	Green	(Unstable)
—N=	—N—	Azine	Violet	Poor
—N=	—O—	Oxazine	Blue	Good
—N=	—S—	Thiazine	Blue-green	Fair

Based on shade and lightfastness, the oxazines are the only major commercially useful dyes in this series. Basic Blue 4, CI 51004 (L) has



(L)



(LI)

been described by Ciba[72] as a useful bright blue on polyacrylonitrile fibers. Improved lightfastness has been obtained as in other basic dyes by use of the 2-cyanoalkyl group in the oxazines (LI).[73]

Basic Blue 3, CI 51005 has been designated as similar to (L) but having an ethoxyl group in the α position peri to the oxazine nitrogen. This is based on the synthetic method which involves nitrosation of

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[72] CIBA, *BP* 751,150.

[73] DuP, *USP* 2,741,605.

N,N-diethyl-*m*-anisidine and then condensation with *m*-diethylaminophenol under acidic conditions. Two almost simultaneous disclosures in the United States and Germany[73a] have shown that ethanol is eliminated in the condensation, and the structure of Basic Blue 4 is identical with that of Basic Blue 3 (L).

Most of the other (classical basic) azine dyes are of little interest on acrylic fibers due to poor light stability. However, diazotization of Safranine T[74] followed by coupling to *N,N*-dialkylanilines[75] gives deep blues (LII) which have excellent lightfastness on both acrylic and polyester fibers. Similarly, violet shades having equal fastness are obtained by couplings to phenols or cresols. Diazotization of diethylsafranine and coupling to phenol gives a dye which produces lightfast charcoal and black shades on acrylic and polyester fibers (LIII).[76] Although the azosafranines have good lightfastness, their utility is limited to 100% synthetic fibers and their blends, due to the fact that in the presence of wool, or strong acids, the dye is decomposed to the red shade of the safranine. This lack of stability is general in cationic azo dyes in which an azo group is part of the resonance conjugation system (see diazahemicyanines).

Quaternary salts of 5,12-diphenylfluorindine (LIV) formed by treatment with dimethyl sulfate are reported to produce fast blue dyeings.[77]

Rhodamine 3B[78] and related products, produce strong brilliant fluorescent pink and red shades with rather unusual properties (LV). Lightfastness on the acrylics is poor (5 hours), but light pink shades can be obtained with 20 hours fastness on acid-modified polyesters. Contrary to the general rules of lightfastness, increasing the dye concentration on the fiber reduces the lightfastness in this case.

C. CYANINE DYES AND THEIR DERIVATIVES

The cyanine dyes have long been known and used in the photographic industry in the role of photosensitizers. The chemistry and nomenclature of these dyes has been discussed previously.[79] It was surprising when it was found that selected cyanines had good to outstanding fastness on polyacrylonitrile fibers while producing bright, tinctorially strong shades.

[73a] M. S. Moores, W. J. Balon, and C. W. Maynard, Jr., *J. Heterocyclic Chem.* **6**, 755 (1969). H. Psaar and H. Heitzer, *Chem. Ber.* **102**, 3603 (1969).

[74] Vol. II, p. 766.

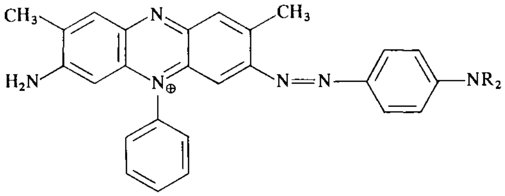
[75] DuP, *USP* 3,121,711.

[76] DuP, *USP* 3,068,056.

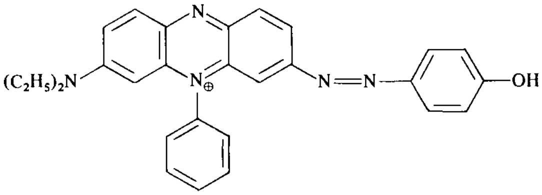
[77] CFM, *DRP* 1,250,783.

[78] Vol. II, p. 751.

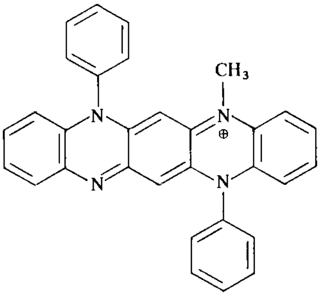
[79] Vol. II, p. 1146.



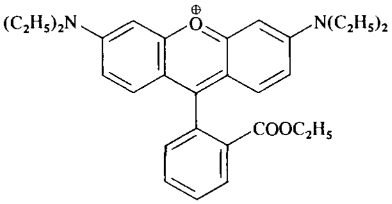
(LII)



(LIII)



(LIV)



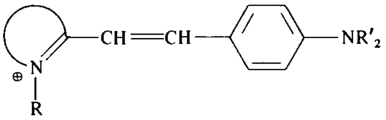
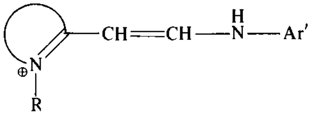
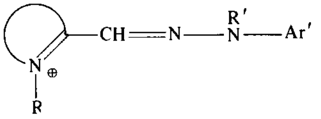
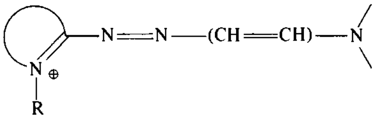
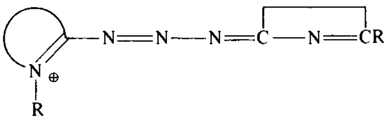
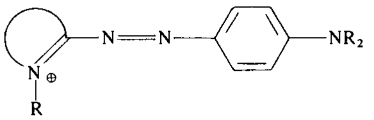
(LV)

However, many of the cyanine classes do not offer adequate photostability or hydrolytic stability for application to synthetic fibers at or near the boil.

The wide variation in cyanine dye properties has stimulated much research in the last 15 years, which has led to many important developments in bright lightfast dyes and in new technology for synthesis of these dyes.

The following discussion will be concerned mainly with the modifications of cyanine dye chemistry which have produced new commercial dyes. The most important classes of cyanine dyes for commercial use on synthetic fibers are shown in Chart 5.

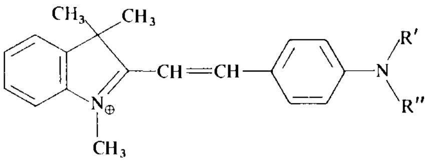
CHART 5

Class	General structure	Major shades
Hemicyanine (styryl)		Red
Azacarbocyanine		Green - yellow
Diazacarbocyanine		Yellow-orange
Diazacarbocyanine		Yellow
Triazacarbocyanine		Yellow
Diazahemicyanine (diazastyryl)		Red to blue

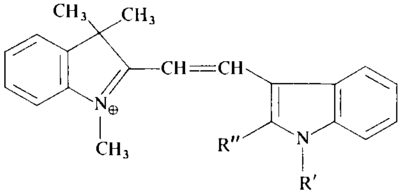
1. *Hemicyanines* (*Styryl Dyes*)

Among the products first used for acrylic fibers were Astrazon Red FG (CI Basic Red 13) (LVI; R′ = CH_3 and R″ = $-CH_2CH_2Cl$) and CI Basic Violet 16 (Genacryl Red 4B, "Sevron" Brilliant Red 2B) (LVI; R′ = R″ = C_2H_5). Shades can be varied scarlet to blue-red by substituting the R groups on the aniline ring, and several variations are found in most lines of cationic dyes for synthetics. In general the more basic the amine the bluer the shade and the poorer the lightfastness. When $R' = R'' = -CH_2CH_2CN$, there result brilliant reddish orange shades on acrylic fibers and scarlet shades having good lightfastness on polyester fibers.[80] In general, dyes of this type produce more bathochromic shades on polyester fibers than on acrylics.

Brilliant orange dyes (LVII) are prepared by condensing Fischer's aldehyde (1,3,3-trimethyl-Δ-2,α-indolineacetaldehyde) (LIX; see Chart 6) with substituted indoles.[81]



(LVI)



(LVII)

$R' = H$, $R'' = CH_3$
CI Basic Orange 21
$R' = CH_3$, $R'' = C_6H_5$
CI Basic Orange 22

Two methods are used to prepare these dyes. Selection of the method depends on the ease of isolation of the pure dyes and the availability of starting materials. An example (LXII) of a golden yellow[82] produced by either the pyrazolone aldehyde (LX) or the pyrazolone (LXI), as shown in Chart 6.

2. *Carbocyanines*

These products, which have a trimethine bridge between the ring systems, have not achieved much technical success on acrylic fibers due to poor lightfastness. The best known example is Basic Red 12 (CI 48070, Astrophloxine Pink FF) which is prepared by the reaction of Fischer's aldehyde (LIX) with Fischer's base (LVIII) in acetic acid.

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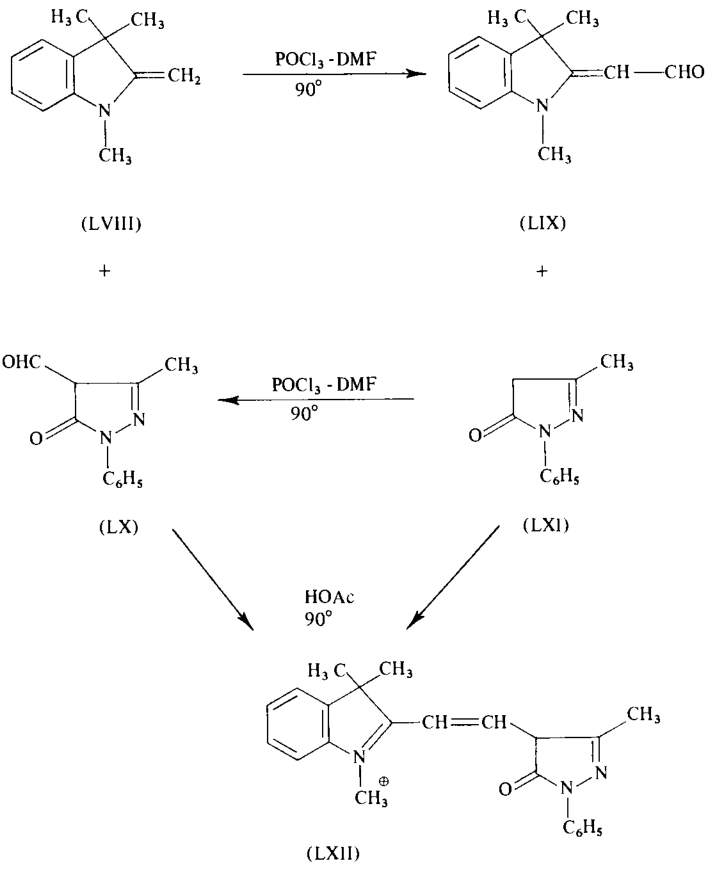
[80] DuP, *USP* 3,379,723.
[81] FBy, *DRP* 1,044,022.
[82] FBy, *BP* 895,240.

CHART 6

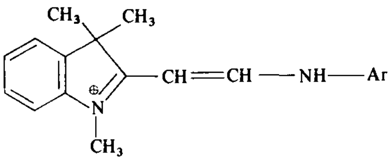


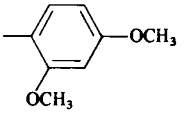
3. *Azacarbocyanines*

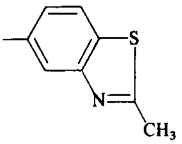
Replacement of a carbon atom in a carbocyanine with nitrogen has the effect of shortening the conjugation system. Thus most of the dyes in this series are yellow. The earliest dyes for synthetics in this series were those made by condensing Fischer's base with primary aromatic amines. These products produce bright green-yellow to yellow shades having remarkably high lightfastness, >80 hours on acrylic fibers.

Commercial dyes are exemplified by Basic Yellow 11, CI 48055; (LXIII) and Basic Yellow 12, CI 48065 (LXIV). When the aromatic amine is *N*-alkylated as part of a ring system (LXV), the shade is little changed and the condensation is more difficult.[83]

[83] B, *BP* 809,392.



(LXIII) Ar =


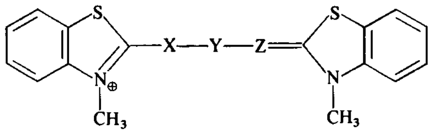
(LXIV) AR =


Voltz[84] has reviewed the dyeing properties of azacyanines and compared them with the parent cyanine in the symmetrical benzothiazole series and has made various comparisons of shade and fastness (Table IV).

As can be seen from Table IV, on acrylic fibers the triazatrimethine cyanines and the unsymmetrical diazatrimethine cyanines offer the best combination of lightfastness and dyebath stability of the azacyanine dyes.

Stable triazatrimethines are prepared by alkylation of linear triazene groups (diazoamino compounds) connecting an aromatic ring with a heterocyclic radical containing nitrogen. Thus diazotization of a *p*-substituted aniline coupling to 2-aminobenzothiazole in glacial acetic acid

TABLE IV
AZACYANINE DYES



—X—Y—Z	λ_{max}[1]	Lightfastness on Orlon	Dyebath pH stability
—N=N—N=	483	V. good	Stable 4–7
—N=N—CH=	479	V. good	Stable 4–8
—N=CH—CH=	466	Poor	Stable to acids
—N=CH—N=	412[2]	—	Unstable
—CH=CH—CH=	522	Poor	Good

[1] In methanol.
[2] In 1,2-dichloroethane.

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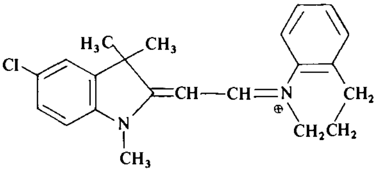
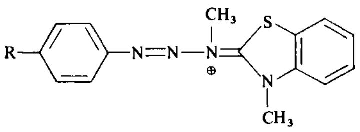
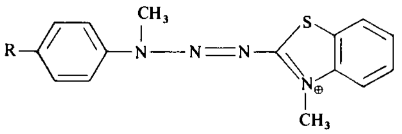
[84] J. Voltz, *Angew. Chem. Intern. Ed. Engl.* I, 532 (1963).

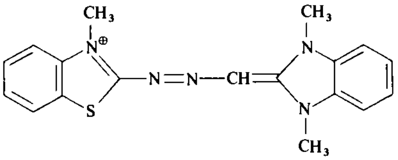
followed by dimethylation of the isolated triazene, produces a pure yellow shade having excellent lightfastness.[85] The structure of the yellow dye is probably a mixture of both isomers (LXVI) and (LXVII), the relative amounts of each being a function of the electronic nature of R and the amount of steric hindrance.

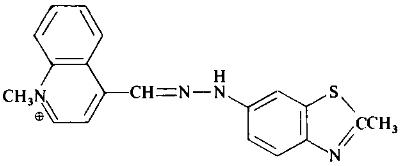
Unsymmetrical diazatrimethine cyanines are prepared by coupling a heterocyclic hydrazine to an active methylene heterocycle by oxidative coupling techniques.[86,87] In this manner the yellow chromophores (LXVIII) and (LXIX) are obtained.


(LXV)


(LXVI)


(LXVII)


(LXVIII)


(LXIX)

Diazatrimethine cyanines can be further alkylated on the chain nitrogen. They are generally less stable to light and alkaline pH than the unsubstituted dyes. The alkylated diazatrimethine yellow and orange cationic dyes may also be prepared by coupling a diazonium salt to an

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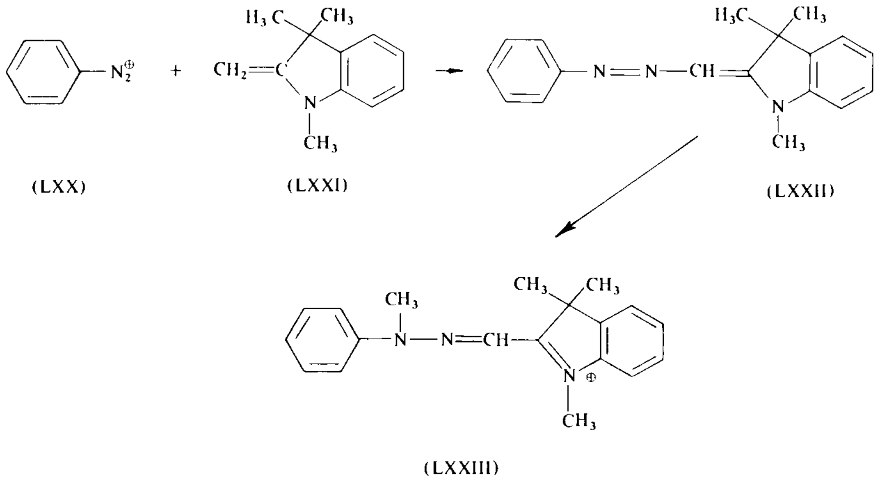
[85] Gy, *USP* 3,055,881.
[86] B, *FP* 1,270,744.
[87] FBy, *DBP* 1,150,476.

active methylene on a heterocyclic ring followed by quaternization[88] [(LXX)-(LXXIII)]. Dyes such as (LXXIII) show strong golden shades having excellent lightfastness.



4. *Diazahemicyanines* (*Diazastyryl Dyes*)

One of the most important advances in the field of cationic dyes for synthetic fibers was the almost simultaneous, discovery in Germany, Switzerland, and the United States of the value of diazahemicyanines on acrylic fibers for producing deep shades having excellent lightfastness and brightness.

Diazahemicyanines had been known previously,[89] but synthetic procedures were difficult and products were obtained in poor yield. Normal diazotization can be applied to heterocyclic amines only in selected cases. Heterocyclic amino compounds such as 2-aminopyridine are difficult to diazotize, requiring strong acid conditions which protonate the hetero atom, making diazotization difficult or the diazonium salt very unstable, and resulting in poor yield.

a. Oxidative Coupling. Hünig discovered that nitrogen heterocyclic hydrazones could be coupled with an aromatic coupling component in the presence of a mild oxidizing agent such as sodium or potassium ferri-

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[88] FBy, *USP* 3,345,355.

[89] A. I. Kiprianov and G. M. Oksengendler, *T. G. Shevchenko' Kiev State Univ., Chem. Collective* Vol. **5**, 27 (1949); R. H. Glauret, F. G. Mann, and A. J. Tetlow, *J. Chem. Soc.* p. 3742 (1953).

cyanide, cupric salts, mercuric salts, ferric chloride, lead dioxide, hydrogen peroxide, ferrous salts, lead tetraacetate, or other similar compounds. The reaction medium is generally water plus an organic solvent, such as dimethylformamide, methanol, or glycol ethers.

This chemistry is discussed in detail in a series of 29 papers published between 1957 and 1968.[90-117] For a general treatment of the chemistry of oxidative coupling, the references 92, 109, 112, and 116b are recommended.

As a rule all aromatic amines, phenols, or active methylene compounds which undergo a standard azo coupling reaction will form azo dyes with hydrazones under oxidizing conditions. Due to the presence of the oxidizing agent certain easily oxidizable couplers do not couple as they are more easily oxidized than the hydrazone. Coupling pH conditions also are similar to classical rules. Amines require weakly acidic conditions (pH 2 to 5) and phenols and enols require mildly alkaline conditions (pH 9). Strongly basic media are to be avoided since the hydrazones

[90] S. Hünig and K. H. Fritsch, [I] *Ann.* **609,** 143 (1957).

[91] S. Hünig and H. Balli, [II] *Ann.* **609,** 160 (1957).

[92] S. Hünig and K. H. Fritsch, [III] *Ann.* **609,** 172 (1957).

[93] S. Hünig, [IV] *Angew. Chem.* **70,** 215 (1958).

[94] S. Hünig and G. Köbrich, [V] *Ann.* **617,** 181 (1958).

[95] S. Hünig and G. Köbrich, [VI] *Ann.* **617,** 203 (1958).

[96] S. Hünig and G. Köbrich, [VII] *Ann.* **617,** 216 (1958).

[97] S. Hünig, R. D. Rauschenbach, and A. Schütz, [VIII] *Ann.* **623,** 191 (1959).

[98] S. Hünig and H. Werner, [IX] *Ann.* **628,** 46 (1959).

[99] S. Hünig and H. Balli, [X] *Ann.* **628,** 56 (1959).

[100] S. Hünig and H. Nöther, [XI] *Ann.* **628,** 69 (1959).

[101] S. Hünig, H. Balli, [XII] H. Nöther, and H. Geiger, *Ann.* **628,** 75 (1959).

[102] S. Hünig and H. Nöther, [XIII] *Ann.* **628,** 84 (1960).

[103] S. Hünig and H. Herrmann, [XIV] *Ann.* **636,** 21 (1960).

[104] S. Hünig and K. H. Oette, [XV] *Ann.* **640,** 98 (1961).

[105] S. Hünig and K. H. Oette, [XVI] *Ann.* **641,** 94 (1961).

[106] S. Hünig and K. H. Oette, [XVII] *Ann.* **641,** 104 (1961).

[107] S. Hünig and W. Lampe, [XVIII] *Ann.* **647,** 66 (1961).

[108] S. Hünig and W. Lampe, [XIX] *Ann.* **647,** 77 (1961).

[109] S. Hünig, *Palette,* [XX] Sandoz A. G. Basel (1961).

[110] S. Hünig and F. Müller, [XXI] *Ann.* **651,** 73 (1962).

[111] S. Hünig and F. Müller [XXII] *Ann.* **651,** 89 (1962).

[112] S. Hünig, [XXIII] *Angew. Chem.* **74,** 818 (1962).

[113] S. Hünig, F. Brühne, and E. Breither, [XXIV] *Ann.* **667,** 72 (1963).

[114] S. Hünig and F. Brühne, [XXV] *Ann.* **667,** 86 (1963).

[115] S. Hünig, H. Geiger, G. Kaupp, and W. Kniese, [XXVI] *Ann.* **697,** 116 (1966).

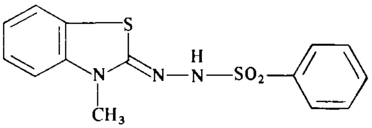
[116] S. Hünig and G. Kaupp, [XXVII] *Ann.* **700,** 65 (1966).

[116a] S. Hünig and G. Kaupp, [XXVIII] *Tetrahedron* **23,** 1411 (1967).

[116b] S. Hünig, [XXIX] *Angew. Chem. Intern. Ed. Engl.* **7,** 335 (1968).

[117] B, *USP* 2,832,764.

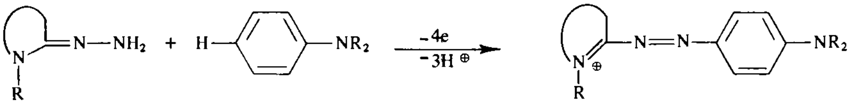
decompose at high pH. When strongly alkaline conditions are required the *N*-sulfonylhydrazones can be used (LXXIV).[97,118]

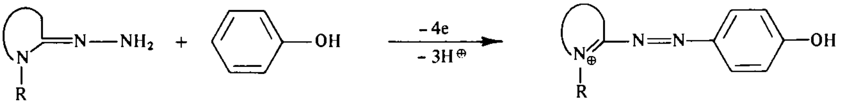


(LXXIV)

Zollinger, in discussing the mechanism of oxidative coupling,[119] compared it with classical electrophilic substitution of the diazo coupling reaction with the essential difference being in the mode of formation of the electrophilic component. A parallel is the formation of indamine and indophenol dyes by the reaction of phenylenediamines with aromatic amines and phenols.

The fundamental reaction involved in oxidative coupling is a four-electron oxidation according to Eqs. (1) and (2).





b. Properties of Diazahemicyanine Dyes. Hünig's technology would have been largely an academic curiosity had not the products shown unusual shades and fastness properties on synthetic fibers. As was discussed under the hemicyanine dyes, in order to obtain more bathochromic shades it is necessary to increase the basicity of the aromatic amino nitrogen and when this occurred lightfastness decreased significantly. However, replacement of the –CH=CH– grouping in the hemicyanine dyes with –N=N– not only causes a bathochromic shift of about 100 mμ but also produces increased lightfastness. In the pyridine series shades go from yellow-orange (LXXV) to blue-red (LXXVI).

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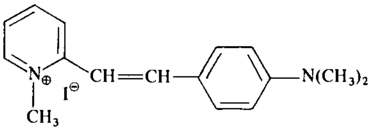
[118] B, *BP* 871,426.

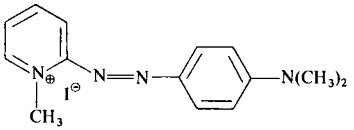
[119] H. Zollinger, "Azo and Diazo Chemistry," p. 243ff. Wiley (Interscience), New York, 1961.

In the benzothiazole series shades go from the red hemicyanine dyes (LXXVII) to the bright, lightfast, blue-violet diazahemicyanine (LXXVIII).[120]



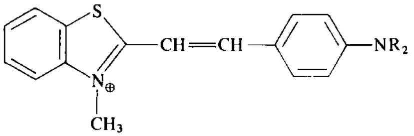
(LXXV)

λ_{max} (DMF) 456 mμ



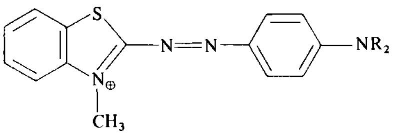
(LXXVI)

λ_{max} (DMF) 560 mμ



(LXXVII)

λ_{max} (CH_3OH) 519 mμ; red



(LXXVIII)

λ_{max} (CH_3OH) 592 mμ; blue-violet

Insertion of an arylene ring between the hetero ring and the azo system results in a significant hypsochromic shift in absorption, the shade changing from blue-violet to yellow (LXXIX).

A much smaller shade shift is seen when the conjugation is spread through a quinoline ring vs. a pyridine ring. Thus compound (LXXX) is a maroon and (LXXXI) is a violet.[121]

A number of commercial dyes have been developed from this chemistry. As examples, Basacryl Blue and Maxilon Blue (CI Basic Blue 41) are examples of 6-methoxy-2-aminobenzothiazole derivatives (LXXXII).[122] Maxilon Red BL (CI Basic Red 22) is an example of a 1,2,4-triazolium dye (LXXXIII), and Calcozine Acrylic Violet 3R (CI Basic Violet 18) (LXXXIV) and Calcozine Acrylic Red 3G (CI Basic Red 30) (LXXXV) are examples of pyridinium dyes.

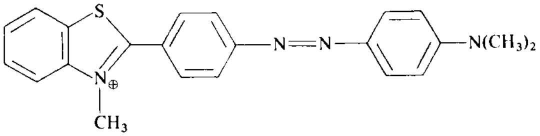
As in the hemicyanine class, increasing the basicity of the coupling component deepens the shade. Baumann and Dehnert[123] showed this for the imidazole series (Table V).

[120] J. Voltz, *Chimia* (*Aarau*) **15,** 168 (1961).

[121] CCC, *USP* 2,893,816.

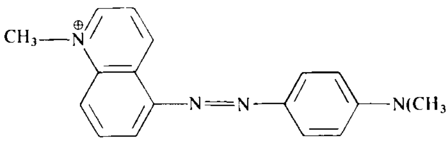
[122] CCC, *USP* 2,893,816.

[123] H. Baumann and J. Dehnert, *Chimia* (*Aarau*) **15,** 163 (1961).

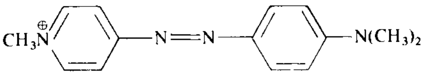


(LXXIX)

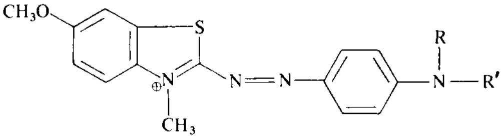
Yellow



(LXXX)



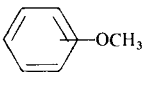
(LXXXI)



(LXXXII)

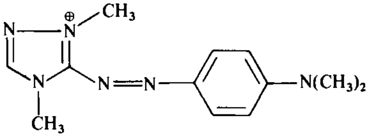
R = R′ = CH_3

R = CH_3, R′ =



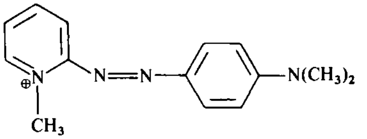
The same deepening of shade with increasing basicity of the coupling component holds true for the benzothiazole series (LXXXII) where there is a shade shift from the red-violet 563 mμ where R = R′ = H to the blue 616 mμ where R = CH_3, R′ = C_6H_5.[121]

Since the diazahemicyanine dyes can be formed from a large variety of heterocycles to produce shades which almost cover the complete visible spectrum, a number of different diazahemicyanine structures are



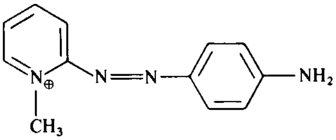
(LXXXIII)

Red



(LXXXIV)

Violet



(LXXXV)

Red

given in Table VI.[124-130] This table shows how shades vary not only with the hetero ring and its substituents, but also with the nature of the coupling component. The structures also are indicative of the extensive research which has been carried on in this area.

c. Other Routes to Diazahemicyanine Dyes. In addition to the important advance by Hünig and co-workers on a practical synthesis of these dyes, a number of other routes have been developed during further investigations of this chromophore system.

i. Diazotization and coupling followed by quaternization. This method can be used with success if the amine to be diazotized is separated from the hetero nitrogen by at least one vinyl group as in certain heterocycles, or where the hetero atom is not strongly basic. Thus 4-aminopyridines or quinolines, 2-aminothiazoles or benzothiazoles can be diazotized directly. Careful control of pH, time, and temperature must be maintained.

ii. Condensation of amine with aromatic nitroso compounds. Geigy chemists[131] produced a variety of heterocyclic dyes by this method

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[124] *RP* 129,768.

[125] CCC, *USP* 3,132,133.

[126] HCC, *USP* 3,132,132.

[127] Gy, *USP* 2,883,373.

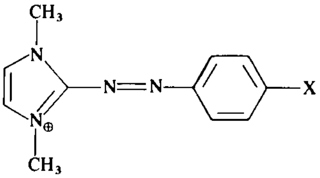
[128] CN, *USP* 3,374,220.

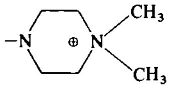
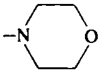
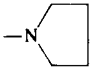
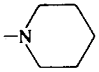
[129] B, *FP* 1,235,357; *DBP* 1,163,775.

[130] DuP, *USP* 3,192,195; *BP* 896,681.

[131] Gy, *USP* 2,864,813.

TABLE V



X	λ_{max}	$\epsilon_{max} \times 10^{-3}$
H	357	21.9
Cl	368	25.4
	482	–
	504	37
$-N(CH_3)_2$	522	48.2
	527	46.0
	531	45.0

[(CI)–(CIV)]. A dry toluene solution of 2-aminopyridine is treated with sodium amide to produce the sodio salt (CI). Freshly prepared *p*-nitroso-*N,N*-dimethylaniline (CII) is added and the reaction mass is refluxed for 3 hours, then evaporated to dryness. The dye (CIII) is extracted with hot

TABLE VI

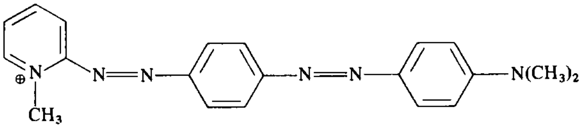
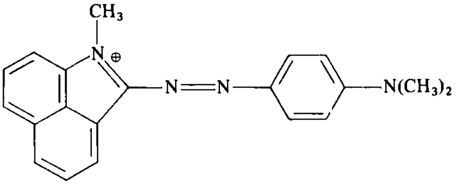
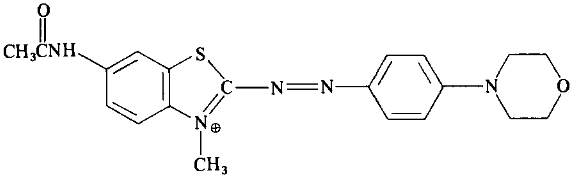
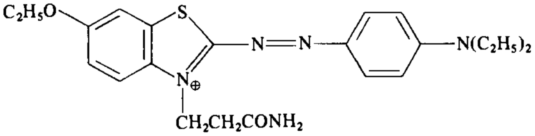
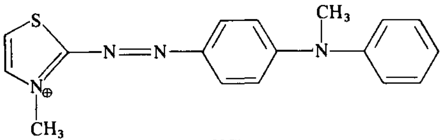
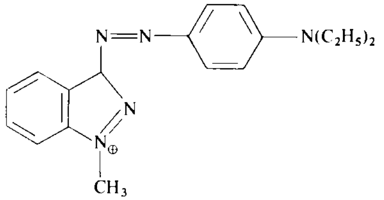
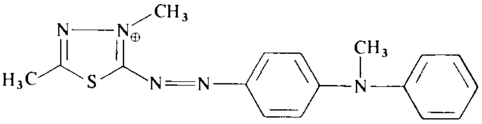
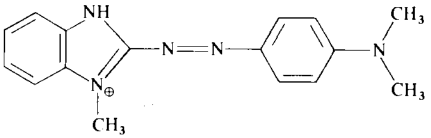
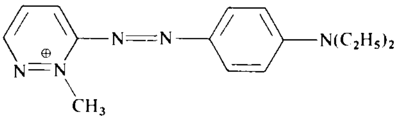
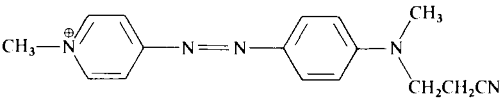
 (LXXXVI)	Deep blue
 (LXXXVII)	Blue[124]
 (LXXXVIII)	Blue[125]
 (LXXXIX)	Blue[126]
 (XC)	Reddish blue[127]

TABLE VI (*Continued*)

 (XCI)	Red-blue[127]
 (XCII)	Violet[127]
 (XCIII)	Violet[127]
 (XCIV)	Violet[128]
 (XCV)	Bordeaux[125]

acetic acid and crystallized. The dry dye is alkylated to produce the cationic dye (CIV).

iii. Condensation of active halogen compounds with hydrazines followed by oxidation.[132] 2-Bromopyridine (CV) may be condensed with

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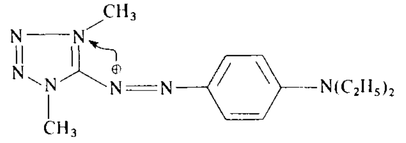
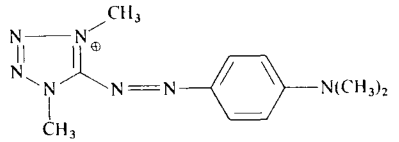
[132] CCC, *USP* 2,893,816.

TABLE VI (*Continued*)



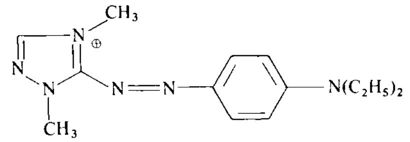
(XCVI)

Red[127]



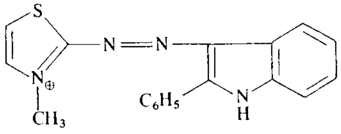
(XCVII)

Red[127]



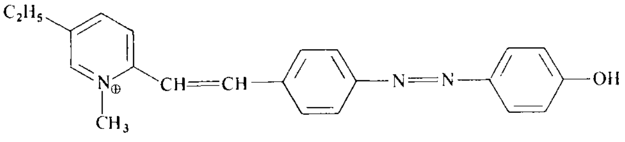
(XCVIII)

Red[127]



(XCIX)

Red[129]

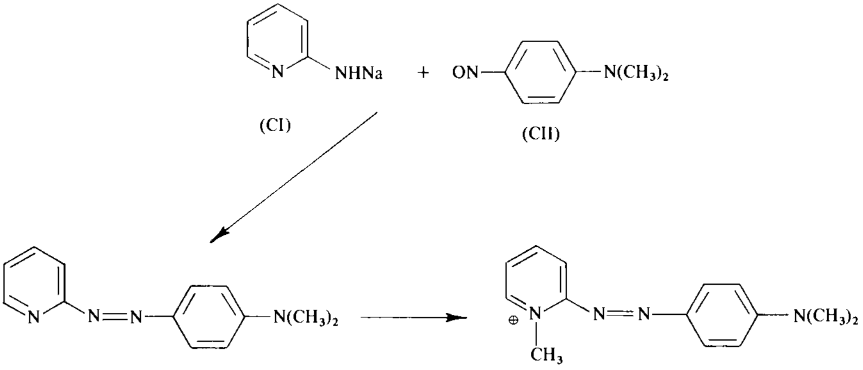


(C)

Yellow[130]

p-nitrophenylhydrazine (CVI), the hydrazo (CVII) oxidized, and the nitro group reduced and alkylated to yield the dye (CVIII) [(CVI)–(CVIII)]. This method is of little practical interest due to the limited availability of the starting materials and the large number of reaction steps.

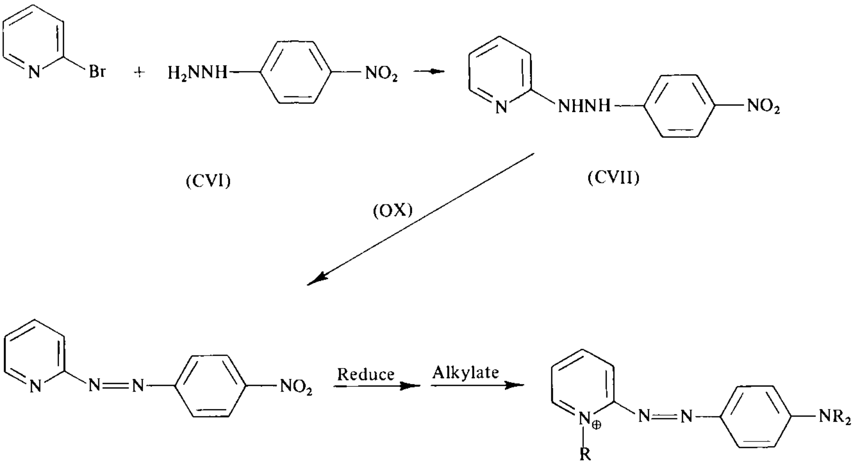
iv. Quaternization with acrylamides. Most of the synthetic methods require quaternization of the hetero nitrogen as a step in the synthesis. Standard alkylating agents used are dialkyl sulfates, alkyl halides, alkyl



(CI) (CII)

(CIII) (CIV)

toluenesulfonates, etc. Suzuki and co-workers[126,133] have found that azo dyes formed by coupling diazotized 2-aminothiazoles or 2-aminobenzothiazoles to various *N*,*N*-dialkylanilines or 2-phenylindoles can be heated



(CVI) (CVII)

(CVIII)

with acrylamide in glacial acetic acid at 95° in the presence of a mineral acid to cause a facile alkylation to occur. The resulting cationic dye has a 2-carbamoylethyl side chain (CIX).

v. Formation of diazahemicyanines from N-oxide dyes. Unlike 2-

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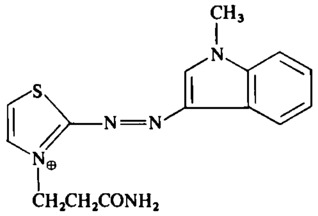
[133] HCC, *USP* 3,136,751.



(CIX)

aminopyridine, which cannot be diazotized, 2-aminopyridine-1-oxide is readily diazotized under classical conditions (Chart 7). The *N*-oxide (CX) may then be methylated to form the *N*-alkoxy quaternary dye (CXI) which has properties similar to those of the *N*-alkyl product (CXIV). Brody[134] has shown that the *N*-alkoxy compound (CXI) may be demethoxylated by refluxing in alcoholic ammonium hydroxide. The resultant dye base (CXIII) can then be re-alkylated under normal conditions to give the diazahemicyanine dye. Liss[135] has shown that the diazahemicyanine dye (CXV) may be obtained directly from the *N*-oxide, depending on the conditions of quaternization. Alkylation with dimethyl sulfate in toluene gave the expected *N*-methoxy derivative (CXII). Use of an excess of methyl iodide in refluxing chloroform gave unexpectedly the *N*-methyl derivative (CXV). At room temperature the *O*-methyl product was formed (CXII) with the same reagent. It was shown that the alkylation with methyl iodide is reversible and the demethylation is caused by oxidation of the iodide by the *N*-oxide to form the base (CXIII) which is readily alkylated with the excess methyl iodide to form the triiodide salt (CXV).

The physical properties of the *N*-oxide derivatives are given in Table VII.

vi. Displacement of active halogen or alkoxyl on preformed diazahemicyanine dyes. Many weakly basic amines or those with oxidizable groups do not couple well under the oxidative conditions of the Hünig reaction. An alternative route to this type of dye, found by Baumann and Dehnert,[136] involves displacement of an activated halogen atom or alkoxy group on the preformed diazahemicyanine. Thus the reddish yellow dye (CXVI) is heated with 4-aminoacetanilide and sodium acetate at 50° until the yellow color disappears and a claret dye (CXVII) is formed.

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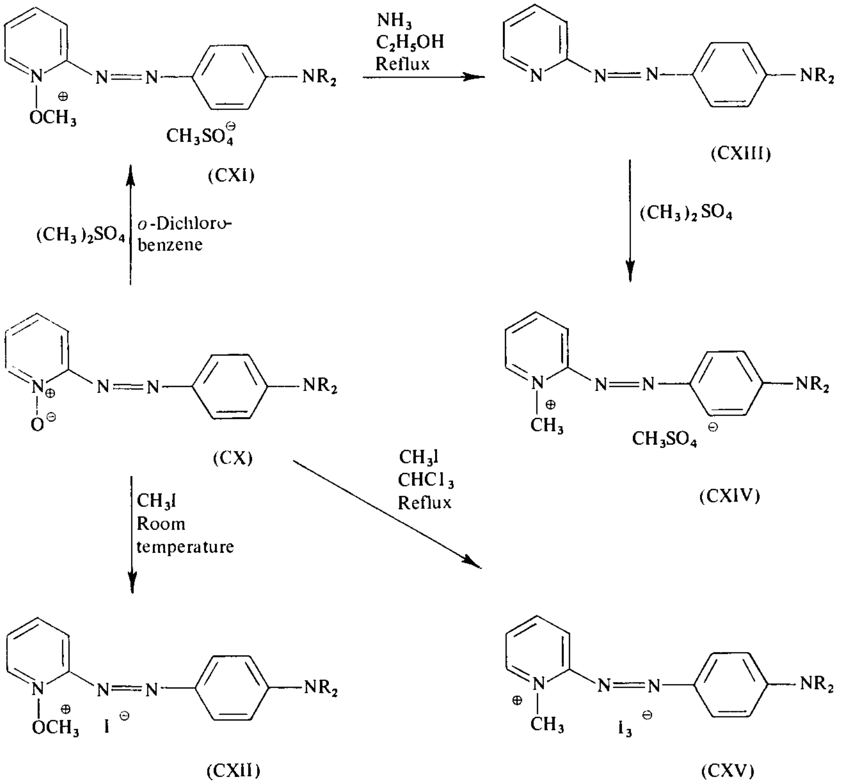
[134] CCC, *USP* 3,118,871.

[135] T. A. Liss, *J. Org. Chem.* **32**, 1146 (1967).

[136] B, *USP* 3,102,878.

CHART 7

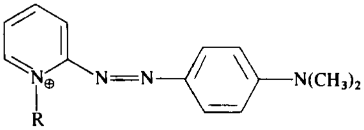


This method is broadly adaptable to production of a wide variety of derivatives (CXVI–CXVII).

d. Dyeing Properties of the Diazahemicyanine Dyes. The many structural variations possible in the diazahemicyanine dyes offer a wide range of shades having good fastness properties. Being relatively small molecules and having high color intensity, they generally dye at a somewhat lower temperature and transfer more readily than do the larger, more bulky triarylmethane or pendant cationic dyes. For this reason they are very important on the modacrylic fibers where dyeing is done at temperatures in the region of 80–90°.

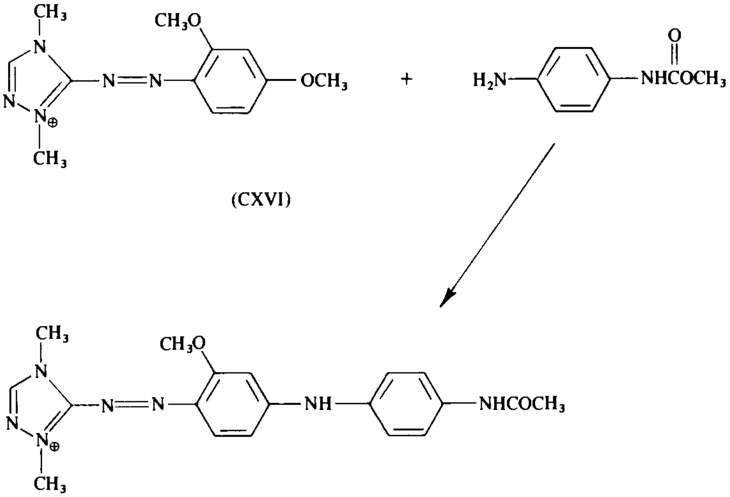
Like the azosafranines (see Section IV,B) the diazahemicyanine dyes are decomposed by wool or strong acids. This apparent shortcoming, however, becomes an advantage in dyeing wool blends with the diazahemicyanine dyes. In the dyeing process for the important wool blends with acrylic or acid-modified polyesters, much of the cationic dye is

TABLE VII



R	$\lambda_{max}(CH_3OH)(m\mu)$	$\epsilon_{max} \times 10^{-3}$
–	432 (ethanol)	29.5
—O	495	32.5
—OCH_3 (iodide)	563	72.9
—CH_3 (iodide)	555	58.7

absorbed by the wool in the initial phases of dyeing. As the dyeing proceeds the dye only gradually desorbs from the wool and moves to the synthetic fiber. With triarylmethane, oxazine, or hemicyanine types, the wool usually retains much of the dye due to low transfer and to some residual affinity of the dye for wool. This results in poor fastness of the blend to light and washing. The diazahemicyanine dyes, on the other hand, decompose to colorless products on prolonged dyeing, in the



(CXVI)

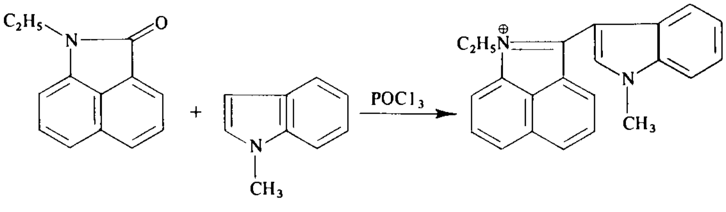
(CXVII)

presence of wool. Optimum contrast and fastness on the blend is then obtained when the wool is subsequently dyed with typical acid or premetalized colors.

D. Naphthostyril Dyes

Another approach to lightfast, deep-shade cationic dyes for synthetic fibers is the naphthostyril (*peri*-naphthazolone or 8-amino-1-naphthoic lactam) dyes discovered by Bayer.[137] Intense red to green-blue shades have been obtained having good lightfastness on acrylic fibers and the dyes are claimed to have minimum wool staining character. These dyes may be prepared by a number of routes typical of those described previously for hemicyanine dyes.

Red shades are formed by heating *N*-ethylnaphthostyril (CXVIII) with 1-methylindole (CXIX) at 120° in the presence of $POCl_3$ according to CXVIII–CXX to produce the dye (CXX). With *N*-methyl-*N*-phenyl-*p*-phenetidine, a red-violet is obtained (Basic Violet 20). Blue dyes (CXXII) are obtained by condensing the quaternized naphtholactam (CXXI) with dialkylaminobenzaldehydes in the presence of acetic acid and acetic anhydride at 100° according to CXXI–CXXII.[138] Compound (CXXIV), the 1,2-dimethylbenz[*c*,*d*]indolium cation, is prepared from *N*-methylnaphthostyril (CXXIII) via a Grignard reaction, followed by elimination of water on hydrolysis [CXXIII–CXXIV].



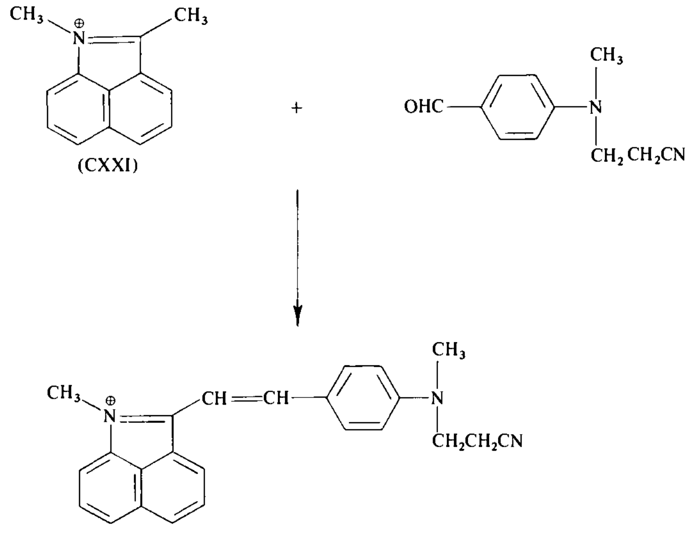
(CXVIII) (CXIX) (CXX)

E. Miscellaneous Delocalized Cationic Dyes

A number of classes of cationic dyes have been investigated for use on synthetic fibers. Few show the combination of fastness properties, economics, and shade that would allow them to compete on a commercial basis with the previously discussed types. In many cases it is possible to

[137] FBy, *BP* 973,259; 987,828; 1,058,508; 1,064,605.

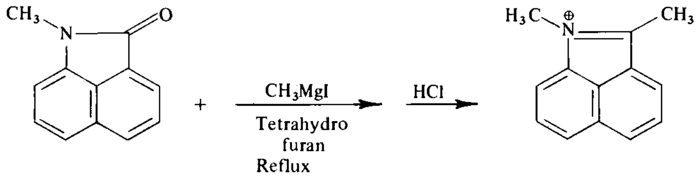
[138] FBy, *USP* 3,362,953; *BP* 1,024,486; 1,055,832; 1,064,584; 1,071,381.



(CXXII)
Green-blue

alkylate heterocyclic nitrogen atoms on a colored molecule and thereby produce a dye having good affinity for acid-modified fibers. Some of the specific types described in the literature are discussed in this section.

Häusermann and Voltz[139] have uncovered a group of extremely brilliant fluorescent flavine shade dyes in the benzimidazolium derivatives



(CXXIII) (CXXIV)

of dialkylaminocoumarins. Dyes such as (CXXV) produce intensely fluorescent green-yellow shades which can be used alone or in mixtures. Lightfastness is only marginal but is adequate for fashion styling shades. Quaternization of a ring-closed naphthoylbenzimidazole [11-methozy-7*H*-benzimidazo(2,1-*a*)benz[*de*]isoquinolin-7-one] (RRI 5818)[140] is also reported to give bright green-yellow compounds (CXXVI).

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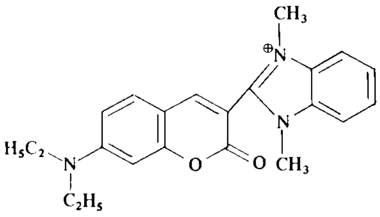
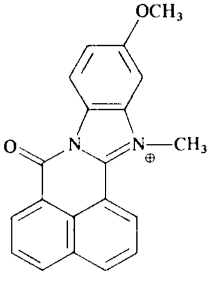
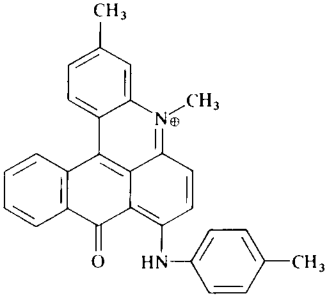
[139] Gy, *USP* 3,014,041.
[140] CN, *FP* 1,440,053.

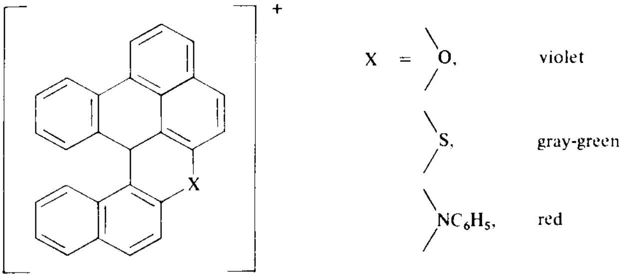




(CXXVI)



(CXXVII)



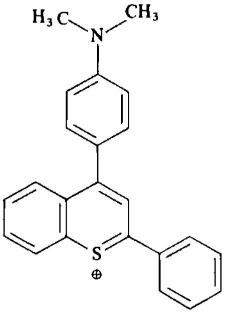
(CXXVIII)

The above polycyclic derivatives have been used as dyes for polyacrylonitrile. One of the few self-shade polycyclic greens is the quaternary coeramidonine (CXXVII),[140a] which is a mixture of isomers plus some of the bis-cationic products. Strong colors of the novel polycyclic series (CXXVIII) have been patented by Hoechst.[141] Shades from yellow to blue having good fastness properties have been obtained by variations of the hetero atom from oxygen to sulfur to nitrogen.

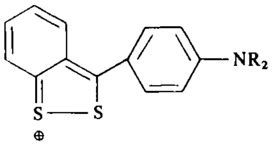
[140a] FBy, *USP* 3,107,247.
[141] MLB, *DBP* 1,098,910.

The use of hetero atoms other than nitrogen is less common, due either to synthesis difficulties or to instability of the final dye under the hydrolytic conditions of the boiling dyebath required for deep shades on synthetic fibers.

BASF has described sulfonium dyes with deep blue to green shades having good fastness in the thioflavonium class.[142] Compound (CXXIX) is prepared by heating equal parts of *N*,*N*-dimethylaniline and 1-thioflavone at 90° with $POCl_3$ and zinc chloride. The dye is precipitated by drowning on ice.[143]

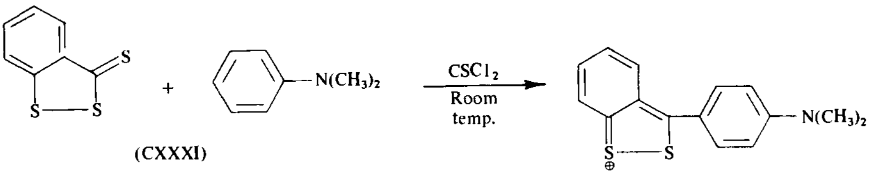


(CXXIX)



(CXXX)

1,2-Benzodithiolium dyes (CXXX) have been patented by American Cyanamid.[144] They are prepared by condensing a 1,2-benzodithiole-3-thione (CXXXI) with a tertiary aniline in the presence of thiophosgene, to produce bright blue dyes (CXXXII).



(CXXXI)

(CXXXII)
Bright blue

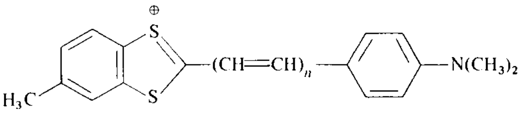
A group of bright dyes [e.g., (CXXXIII)] containing the 1,2-benzdi-

---

[142] B, *BP* 693,143.
[143] *BP* 1,048,926.
[144] CCC, *USP* 3,141,891.

thiolium group has been patented by Ciba.[145] These are prepared by condensation of 1,2-dithiols with substituted aromatic carboxylic acids in the presence of phosphorus oxychloride. Many variations in structure are possible.

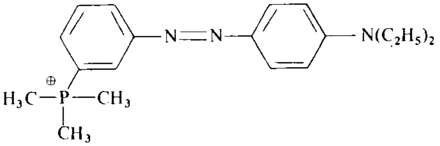
A limited amount of work has been reported on phosphonium dyes. ICI[146] has patented derivatives of diazotized (*m*-aminophenyl) trimethylphosphonium chloride. Coupling *N*,N-diethylaniline gives the orange dye (CXXXIV), reported to have good light- and wash-fastness on polyacrylonitrile.



(CXXXIII)

n = 0, carmine

n = 1, blue



(CXXXIV)

V. Amine Salts

This category of cationic dye contains no formal charge under neutral or alkaline conditions. In the presence of the acidic dyeing conditions required for synthetic fibers the molecule assumes a positive charge and acts like a cationic dye. Classical examples of amine dyes are chrysoidine (CXXXV) and Acridine Orange (CXXXVI).

Amine dyes differ in their dyeing characteristics from conventional cationic dyes in that they assume a more disperse dye character due to the fact that Eq. (13) is an equilibrium reaction under normal dyebath conditions. This results in a high degree of levelness of the dyeings. On the other hand, the disperse dye character provides affinity for a num-

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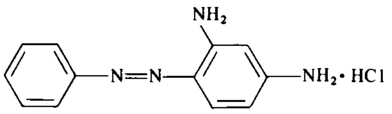
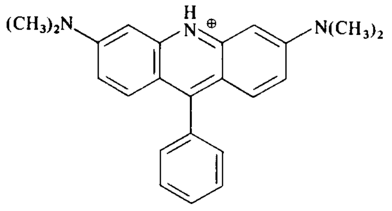
[145] CIBA, *BP* 903,994.

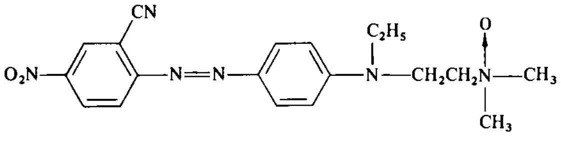
[146] ICI, *BP* 926,998.



(CXXXV)



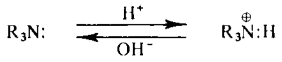
(CXXXVI)



(CXXXVII)

ber of other fibers, resulting in considerable staining of wool, nylon, polyesters, etc., when used in blends with the acid-modified fibers.

A wide variety of amine dyes have been prepared for use on synthetics. The most important technically are the pendant aminoalkyl disperse dyes which are used to provide high lightfastness and multifiber affinity (see Section III).



$$R_3N: \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} R_3\overset{\oplus}{N}:H$$

A unique group of amine dyes are the *N*-oxides. Although they possess no formal cationic charge, the *N*-oxide under acidic dyebath conditions acts like an amine dye.[147] The amine oxide dyes are prepared by the action of oxidizing agents such as hydrogen peroxide, peracids or per-salts (persulfate, perborate, etc.) in a solvent medium at moderate temperatures. Compound (CXXXVII) produces red shades on polyacrylonitrile in the presence of acetic acid. That the amine oxide is indeed acting as a cationic dye is demonstrated by the following experiment. The dyesites in the fiber are "blocked" or saturated by treatment of the fiber with an excess of a colorless cationic agent. This "blocked"

[147] S, *USP* 3,119,809.

fiber can still be dyed with disperse dyes but not with cationic dyes. The amine oxide dyes do not dye "blocked" fiber and thus behave like conventional cationic or amine dyes.

VI. Polycationic Dyes

Numerous references appear in the literature on bis-cationic dyes for synthetic fibers. These can be prepared by a number of methods, examples of which follow: (a) pendant coupler/delocalized diazonium group (CXXXVIII),[148] (b) bis-pendant group (CXXXIX) and (c) bis-delocalized charge (CXL).[149]

The polycationic dyes have not achieved much commercial success for use on synthetic fibers. They produce level shades but are generally slow-dyeing, exhaust poorly, and have limited buildup. This is because most acid-modified synthetic fibers derive their desirable physical properties from the fact that they are hydrophobic in nature. Introduction of acidic dyesites increases the hydrophilic nature of the polymer and makes it more susceptible to hydrolysis and chemical degradation. Indeed the excellent wash-fastness of cationic dyes on synthetics is due to the fact that the hydrophobic fiber requires higher temperatures to dye than are encountered in normal washing cycles.

It is possible to modify cellulose to accept cationic dyes by grafting acidic sites on the polymer. Deep shades are readily obtained in aqueous dyeings but in the presence of soaps and detergents the dye is readily removed even at low temperatures.

Thus the number of dyesites in synthetic polymers is maintained at as low a value as possible to achieve optimum fiber properties and dye fastness. The number of sites is generally just adequate to produce deep black shades. Polycationics which occupy more than one site are thus inherently limited in their overall utility and tend to block other dyes.

VII. Trends in Cationic Dyes for Synthetic Fibers

Since 1953 cationic dyes have taken their place among the more important classes of dyes for textile fibers. The outlook for the future is bright. Included among the cationic dyes are the strongest and brightest colors known for textile use. The discovery that outstanding lightfastness is possible on certain acrylic fibers dispels the theory that these dyes have poor durability to light. The synthetic organic chemist, by discover-

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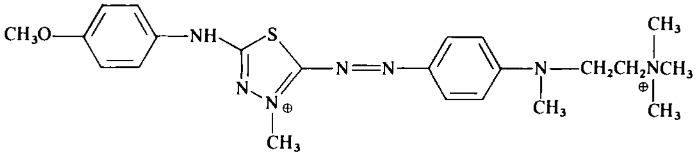
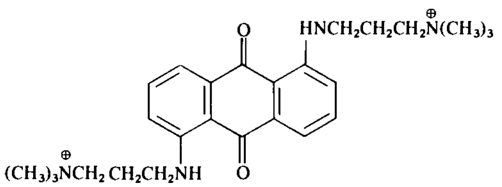
[148] B, *USP* 3,086,003.

[149] B, *BP* 884,885.

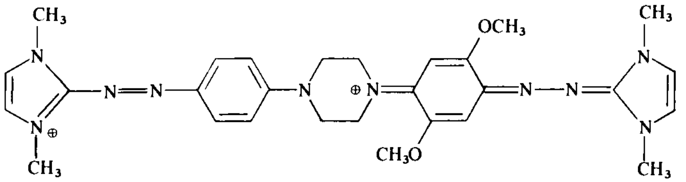


(CXXXVIII)

Green-blue



(CXXXIX)



(CXL)

λ_{max} 535

ing new reactions and new dye classes during the past 15 years, has shown that significant improvements in brightness and lightfastness can be achieved by chemical modification of the dye molecules. There is no doubt that this trend will continue over the next 15 years. As the use of color grows, and consumers are no longer afraid of poor fastness in bright shades, so will the cationic dye market grow.

Trends in the textile and carpet industries toward styling and multicolor dyeings will open up a large new vista for cationic dyes. Due to the fickleness of the consumer in his color demands, coloration is becoming increasingly important in the later stages of textile processing. Yarn dyeings will be largely replaced by piece dyeing. The use of synthetic fibers which are receptive to various classes of dyes, such as an acid-modified fiber woven in with a basic-modified fiber, is making it possible to dye multicolor shades in one dyebath by means of basic and acid dyes. Here the basic dyes become prominent because their brilliance is needed to produce maximum contrast.

Blends of various textile fibers are playing an increasing role in today's market, since the weaver is able to combine the best aspects of each fiber to obtain desirable anesthetic properties as well as optimum physical properties in the finished garments. Here also piece or continuous dyeing is important in high-production runs. Important requirements are brightness and minimum staining of the other fibers in the blend. Cationic dyes by nature are eager to color almost any substrate which can develop a negative potential. Any staining is undesirable because it reduces contrast as well as reducing the overall light- and wet-fastness of the blends. Here the organic chemist and textile chemist must devote much future work to developing new dyes and dyeing methods which will enable rapid coloration of fiber blends with a minimum effect on the overall blend properties. The progress in the past 15 years in cationic dyes has been great, but there is much to be done.[150]

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[150] For a review in Russian of the subject of "Cationic Dyes for Polyacrylonitrile Fibers," see N. V. Ufimtsev and L. V. Arinich [*Zh. Vses. Khim. Obshchestva im. D. I. Mendeleeva* **11,** No. 1, 21 (1966); *Chem. Abstr.* **64,** 16047i (1966)], 68 references.

CHAPTER V

CYANINE DYES

G. E. Ficken

RESEARCH LABORATORIES, ILFORD LIMITED, ILFORD, ESSEX, ENGLAND

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I. Introduction

The last two decades have seen no abatement of interest in the cyanine dyes, an interest which arises not from their use as textile dyes, which remains negligible, but from their unrivalled ability to impart light-sensitivity to a silver halide in a region of the spectrum to which it is not normally sensitive.[1,2]

Since 1950 very many variations have been carried out on the fundamental cyanine structure (I). Much of this work, appearing in the patent literature, represents a somewhat haphazard attempt to obtain spectral sensitizers of superior performance. In addition, however, there is a considerable body of published work describing systematic variations in the cyanine structure, and the effect of these variations on the properties, photographic and otherwise, of the resulting dyes. The contribution to this work of the Russian chemists is particularly impressive.

Although the true cyanines have two nitrogen-heterocyclic rings joined by a conjugated chain of carbon atoms as in formula (I), it is customary

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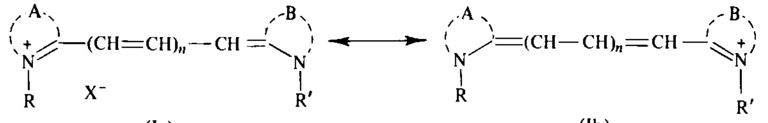
[1] *CSD II,* Chapter XXXVIII.

[2] C. E. K. Mees and T. H. James, "The Theory of the Photographic Process." Macmillan, New York, 1966 (particularly Brooker, Chapter 11, and West and Carroll, Chapter 12).


(Ia) (Ib)

$$X{-}(CR)_n{-}X'$$

(II)

to consider in the context of cyanine dye chemistry a number of related structural types, e.g., dyes with noncyclic end groups (such as the hemicyanines and styryl dyes), and the merocyanines.[1] A recent paper by Dähne has shown that all of these diverse types can be accommodated within a generalized polymethine formula (II), in which n is an odd positive integer, and in which $(n + 3)$ π-electrons are distributed over the polymethine chain and the terminal atoms X and X′. This formulation, moreover, serves to bring out interesting analogies, not only with other dyes such as those of the azine and triphenylmethane types, but also with certain simpler molecules which would not normally be considered in relation to the cyanines.[3]

II. Synthetic Methods and Reaction Mechanisms

A. GENERAL

By the time Volume II of the present work was written, various methods of synthesis for cyanines and related dyes were well established (see, for instance the review by Hamer,[4] or for more detail the book by the same author[5] which reviews the literature, mainly from the preparative point of view, up to 1959). Indeed, such methods sufficed for the synthesis of the majority of the dyes to be described in later sections of this chapter. The present section will therefore deal only with the more interesting variants of these older methods, together with studies designed to elucidate reaction mechanisms; a few newer methods will also be considered.

Most of the synthetic methods used in cyanine dye chemistry involve reaction of a 2-(or 4-)methyl heterocyclic quaternary salt (III) with some other reagent in the presence of a basic condensing agent. Brooker

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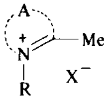
[3] S. Dähne, *Z. Chem.* **5**, 441 (1965).

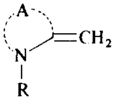
[4] F. M. Hamer, *Quart. Rev.* (*London*) **4**, 327 (1950).

[5] F. M. Hamer, *in* "Cyanine Dyes and Related Compounds" (A. Weissberger, ed.), Wiley (Interscience), New York, 1964.

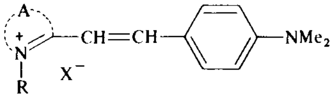
et al.[6] have discussed qualitatively the relationship between the basicity of heterocyclic nuclei and the reactivity of their quaternary salts in dye preparations, in terms of the ease of formation of the corresponding methylene base (IV). Mastagli *et al.*[7] have subsequently placed this reactivity on a more quantitative basis by studying the kinetics of the reaction of various quaternary salts with *p*-dimethylaminobenzaldehyde to give the styryl dyes (V).



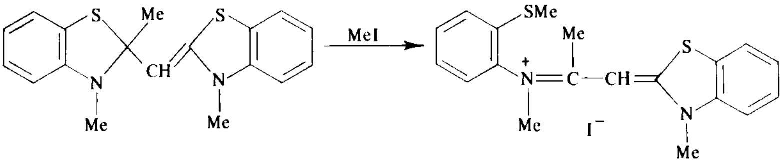
(III)



(IV)



(V)



(VI) (VII)

Apart from the well-known Fischer's base and related indoline bases, the so-called methylene bases (IV) cannot generally be isolated in a monomeric form. Consideration of the physical and chemical properties of the methylene base from a 2,3-dimethylbenzothiazolium salt has led Larivé and Dennilauler[8] to the conclusion that it is in fact an unsymmetrical dimer of structure (VI). This formulation thus accounts easily for the formation of the hemicyanine dye (VII) by the action of methyl iodide; similar products are obtained by the action of acyl halides and cyanogen bromide.[9] Other reactions of the methylene bases from benzo-

---

[6] L. G. S. Brooker, S. G. Dent, D. W. Heseltine, and E. VanLare, *J. Am. Chem. Soc.* **75**, 4335 (1953).

[7] P. Mastagli, H. Larivé, and P. Étevenon, *Compt. Rend.* **252**, 3782 (1961).

[8] H. Larivé and R. J. Dennilauler, *Chimia* (*Aarau*) **15**, 115 (1961).

[9] F. S. Babichev, *Zh. Obshch. Khim.* **20**, 1904 (1950); *CA* **45**, 2934 (1951); F. S. Babichev and L. I. Kravchenko, *Ukr. Khim. Zh.* **16**, 199 (1950); *CA* **46**, 5051 (1952); F. S. Babichev and A. I. Kiprianov, *Zh. Obshch. Khim.* **34**, 2759 (1964); *CA* **61**, 14657 (1964); cf. V. Denes and M. Farcasan, *Zh. Obshch. Khim.* **32**, 199 and 654 (1962); *CA* **57**, 12466 (1962); **58**, 1446 (1963); V. Denes, M. Farcasan, and G. Ciurdaru, *Chem. Ber.* **97**, 1246 (1964).

thiazole and quinoline quaternary salts have been described by Metzger *et al.*,[10,11] with particular reference to reactions leading to cyanines.

B. METHINECYANINES

1. *The Isocyanine Synthesis*

Although the reaction of a quinoline quaternary salt (VIII) with a quinaldine quaternary salt (IX) in the presence of a strong base to give isocyanine was described as long ago as 1883, the mechanism of the reaction has only recently been established. Metzger *et al.* have shown that the mechanism proposed previously[12] is untenable, and that the first stage of the reaction is the formation of the mixed anhydro base dimer (X); this can be isolated, and its structure has been rigorously established, particularly by NMR spectroscopy.[11] Further reaction with another molecule of (VIII) then gives isocyanine (Ethyl Red) (XI) and the dihydroquinoline (XII). The quinolinium salt (VIII) is in fact not specific for this latter stage; a wide variety of known hydride acceptors will also convert (X) into (XI), e.g., Malachite Green, Methylene Blue, quinones.[10a,13]

Oxidation of a similar type of intermediate is presumably involved in the preparation of the isocyanine (XIII; R = Me) by oxidation of 1,2-dimethylquinolinium iodide by silver nitrate; in the presence of iodine, the dye (XIII; R = $-CO_2H$) was formed.[14]

2. *Other Methods Involving Reactive Methyl Groups*

The usual method of preparation of a methinecyanine (XV) involves the elimination of YH between two quaternary salts: one has a reactive methyl group (III), the other some other reactive group Y (XIV). The most flexible of these methods is probably that in which Y is an alkylthio group, but there has been a tendency to find alternatives, obviously because of the unpleasant nature of the mercaptan evolved.

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[10] J. Metzger, H. Larivé, R. J. Dennilauler, R. Baralle, and C. Gaurat, *Bull. Soc. Chim. France* pp. 2857, 2868, 2879, 2888 (1964); pp. 30, 40, 57 (1967).

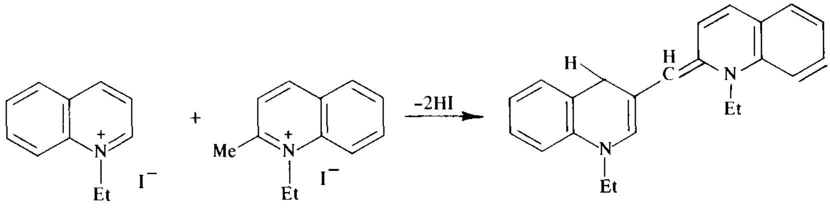
[10a] J. Metzger *et al.*,[10] p. 57 (1967).

[11] J. Metzger, H. Larivé, É.-J. Vincent, and R. Dennilauler, *Bull. Soc. Chim. France* p. 46 (1967).

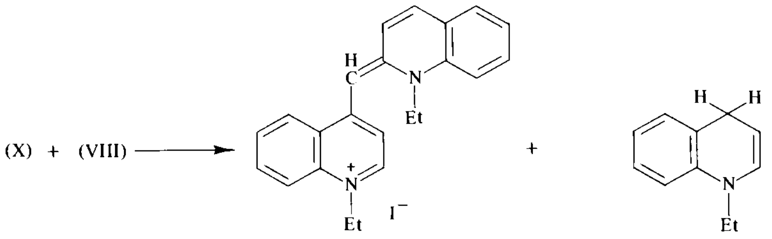
[12] Cf. *CSD II*, p. 1148.

[13] J. Metzger, H. Larivé, R. Dennilauler, R. Baralle, and C. Gaurat, *Compt. Rend. 36th Congr. Intern. Chim. Ind., Brussels, 1966* Vol. 3; see *Ind. Chim. Belge* **32**, Spec. No., 96 (1967).

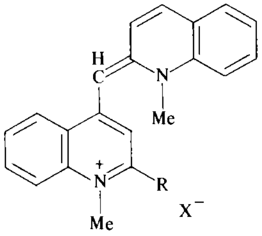
[14] J. B. Adams, J. Cymerman-Craig, C. Ralph, and D. Willis, *Australian J. Chem.* **8**, 392 (1955).



(VIII) (IX) (X)



(XI) (XII)



(XIII)

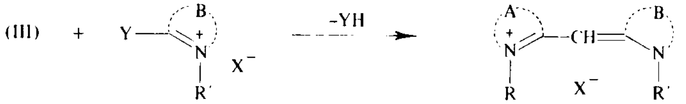
Thus, interest has revived in the use of chloro quaternary salts (XIV; Y = Cl).[15] Also, 2-methoxy or phenoxy salts have been used (XIV; Y = –OMe or –OPh)[16]; the 4-phenoxyquinolinium salt (XVI) will condense with itself to give isocyanine (XVII).[17] Probably the most useful of the newer methods, however, involves the use of a quaternary salt with a methylsulfonyl ($-SO_2Me$) or sulfonic ester ($-SO_3R$) sub-

---

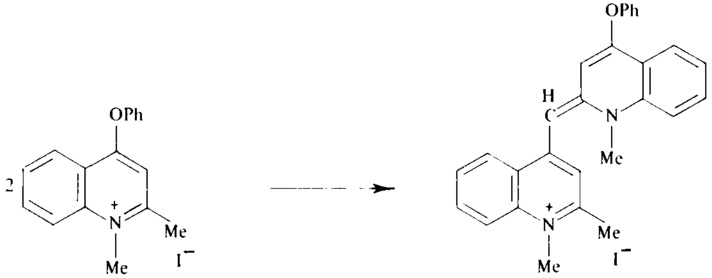
[15] H. Larivé, R. J. Dennilauler, and Eastman Kodak, *USP* 3,149,105; N. N. Sveshnikov and N. A. Damir, *Dokl. Akad. Nauk SSSR* **164,** 1077 (1965); *CA* **64,** 3470 (1966).

[16] P. D. Collet and Kodak-Pathé, *FP* 1,242,962.

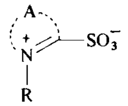
[17] M. Katayanagi, *J. Pharm. Soc. Japan* **66,** 61 (1946); **68,** 133 (1948); *CA* **45,** 6638 (1951); **47,** 7503 (1953).



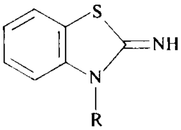
(XIV) (XV)



(XVI) (XVII)



(XVIII)



(XIX)

stituent,[18] or of a zwitterionic salt (XVIII).[19] A related method uses a 2-imino-3-alkylbenzothiazoline (XIX), ammonia being evolved.[20]

The cyanobenzothiazoline (XX), prepared by reaction of a 2,3-dimethylbenzothiazolium salt with cyanide, behaves in most respects like the quaternary salt: it reacts with an alkylthio quaternary salt to give a monomethinecyanine, and with ethyl orthoformate to give the symmetrical trimethinecyanine.[21] The benzoselenazoline analog behaves similarly.[22]

3. *Miscellaneous Methods*

Reaction of an alkylthio quaternary salt with acetic anhydride gave a symmetrical methinecyanine; use of propionic or phenylacetic an-

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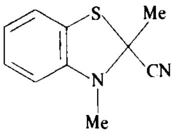
[18] H. Larivé, P. D. Collet, and Eastman Kodak, *USP* 2,708,669; 2,798,066.

[19] H. Larivé, P. Collet, and R. Dennilauler, *Bull. Soc. Chim. France* p. 1443 (1956).

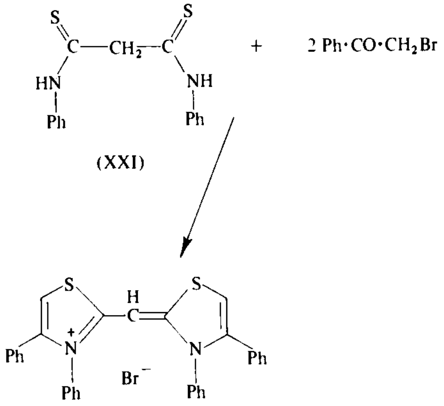
[20] G. M. Oksengendler, *Zh. Obshch. Khim.* **23**, 135 (1953); *CA* **48**, 672 (1954).

[21] H. Wahl and J. J. Vorsanger, *Bull. Soc. Chim. France* p. 3359 (1965).

[22] J. Bourson, *Bull. Soc. Chim. France* p. 4028 (1966).



(XX)



(XXI)

(XXII)

hydrides likewise yielded dyes with the methine group substituted by Me or Ph.[23]

A symmetrical thiazole methinecyanine (XXII) has been synthesized by a method which forms the heterocyclic rings in the final stage, *viz.*, reaction of the dithiomalonanilide (XXI) with phenacyl bromide.[24]

C. TRIMETHINECYANINES

1. *The Ortho Ester Synthesis*

This reaction, being the most useful synthetic method for symmetrical trimethinecyanines, with or without a meso substituent,[5,25] has received a certain amount of attention recently. The method involves heating a methyl quaternary salt (III) with an ortho ester, generally in pyridine, and evidently involves at least one intermediate stage. By the use of triethylamine and a phenol as condensing agent in place of pyridine, Larivé and Dennilauler have shown that the first product is in fact a methylene base, which then reacts with the ortho ester to give an alkoxyalkenyl derivative (XXIII).[26] Such compounds can be isolated and characterized, and in a subsequent stage two molecules combine with the elimination of ethyl acetate (if ethyl orthoacetate was used in the reac-

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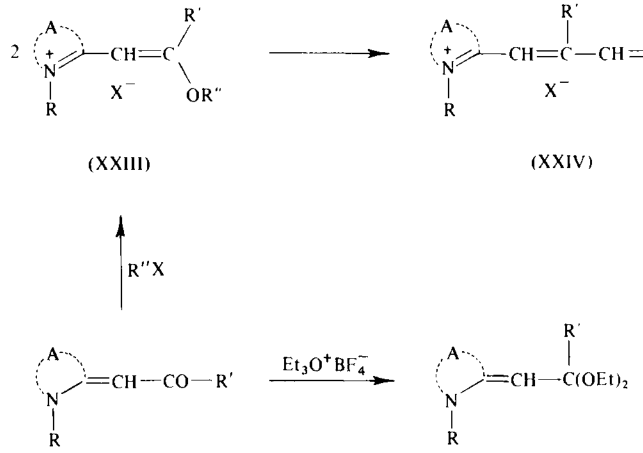
[23] J. M. Nys, T. H. Ghys, and Gevaert Photo-Producten, *BP* 811,156.

[24] A. D. Grabenko, L. N. Kulaeva, and P. Pelkis, *Khim. Geterotsikl. Soedin,* p. 364 (1966); *CA* **65**, 12190 (1966).

[25] *CSD II,* pp. 1157, 1159.

[26] H. Larivé and R. Dennilauler, *Compt. Rend. 31st Congr. Intern. Chim. Ind., Liege, 1958;* see *Ind. Chim. Belge* Suppl. 2, 499 (1959).

tion) to yield the dye (XXIV; $R' = Me$).[27] Use of this reaction medium (a phenol + triethylamine) appears to be definitely advantageous in some cases, particularly with benzoxazolium salts for which the use of pyridine frequently gives rather low yields.[28] Apart from this, and the use of nitrobenzene in the preparation of benzimidazole dyes,[29] there is no evidence that any of the other varied condensing agents suggested periodically have any advantage over pyridine.[30]



(XXIII) (XXIV)

(XXV) (XXVI)

Other methods are available for the preparation of intermediates of type (XXIII). If the quaternary salt (III) is heated with excess of the ortho ester alone or in acetic anhydride, then little dye is formed and (XXIII) is obtained in good yield; the acylmethylene compound (XXV) may, however, be formed as a by-product.[31,32] Alternatively this type of intermediate (XXV)[33] may be heated with a quaternizing agent (e.g.,

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[27] H. Larivé, R. Dennilauler, and R. Baralle, *Chimia (Aarau)* **19,** 238 (1965).

[28] H. Larivé, E. M. Geiger, and Eastman Kodak, *USP* 2,921,067.

[29] A. van Dormael and M. J. Libeer, *Sci. Ind. Phot.* [2] **20,** 451 (1949).

[30] Cf. F. M. Hamer,[5] p. 94.

[31] I. I. Levkoev, M. V. Deichmeister, and N. N. Sveshnikov, *Dokl. Akad. Nauk SSSR* **129,** 331 (1959); *CA* **54,** 7691 (1960).

[32] G. Bach, *Veroeffentl. Wiss. Photolab. AGFA* **9,** 94 (1961).

[33] For methods of preparation of compounds (XXV), and their use in the synthesis of cyanines, see F. M. Hamer,[5] pp. 154–157; see also N. N. Sveshnikov, I. I. Levkoev, N. I. Shirokova, and N. A. Damir, *Dokl. Akad. Nauk SSSR* **148,** 1091 (1963); *CA* **59,** 6551 (1963).

dimethyl sulfate) to give (XXIII).[34] The alkoxy group is reactive and can be used to synthesize unsymmetrical trimethinecyanines, merocyanines, etc.[32,35] Reaction of an intermediate (XXV) with triethyloxonium fluoroborate gave a product of type (XXVI) which could be used likewise to prepare unsymmetrical trimethinecyanines.[36]

2. *From a 2-Methyl Quaternary Salt and a Base*

In this reaction, discovered by Brooker and White,[37] a 2-methylbenzothiazole quaternary salt yields a *meso*-methyl-substituted-trimethinecyanine when heated with pyridine and preferably triethylamine. The occurrence of this reaction has on occasion led to false conclusions; for instance, a dye obtained from a 2-methylbenzothiazole quaternary salt and methyl orthocarbonate, and originally thought to be a *meso*-methoxy dye, has now been shown to be in fact the *meso*-methyl dye, evidently formed by the Brooker and White reaction.[38]

That the *meso*-methyl group is derived from the 2-methyl group of the quaternary salt has been confirmed by the use of a salt labeled with ^{14}C in the methyl group.[39] The detailed mechanism has been clarified by Metzger *et al.*; the first-formed anhydro base (VI) reacts with a further molecule of the quaternary salt (XXVII) to give (XXVIII).[39a] This product then undergoes the normal reaction of an anilinovinyl quaternary salt, reacting with a further molecule of methyl quaternary salt to give the dye (XXIX).[27,39b] The same authors have also discussed the mechanism of the formation of a trimethinecyanine, together with a monomethinecyanine, by reaction together of two benzothiazole quaternary salts, one with a 2- methyl substituent, the other unsubstituted.[40]

3. *Other Syntheses Using 2-Methyl Quaternary Salts*

Other reagents which are said to condense with quaternary salts carrying reactive methyl groups include the following: formamide (oxonols

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[34] N. N. Sveshnikov, I. I. Levkoev, A. F. Vompe, and B. S. Portnaya, *Dokl. Akad. Nauk SSSR* **88,** 281 (1953); *CA* **48,** 2685 (1954).

[35] G. Bach, *EGP* 9727; G. E. Ficken and D. J. Fry, *BP* 1,012,825.

[36] H. Yamaguchi, *Yakugaku Zasshi* **86,** 918 (1966); *CA* **66,** 76911 (1967).

[37] L. G. S. Brooker and F. L. White, *J. Am. Chem. Soc.* **57,** 547 (1935).

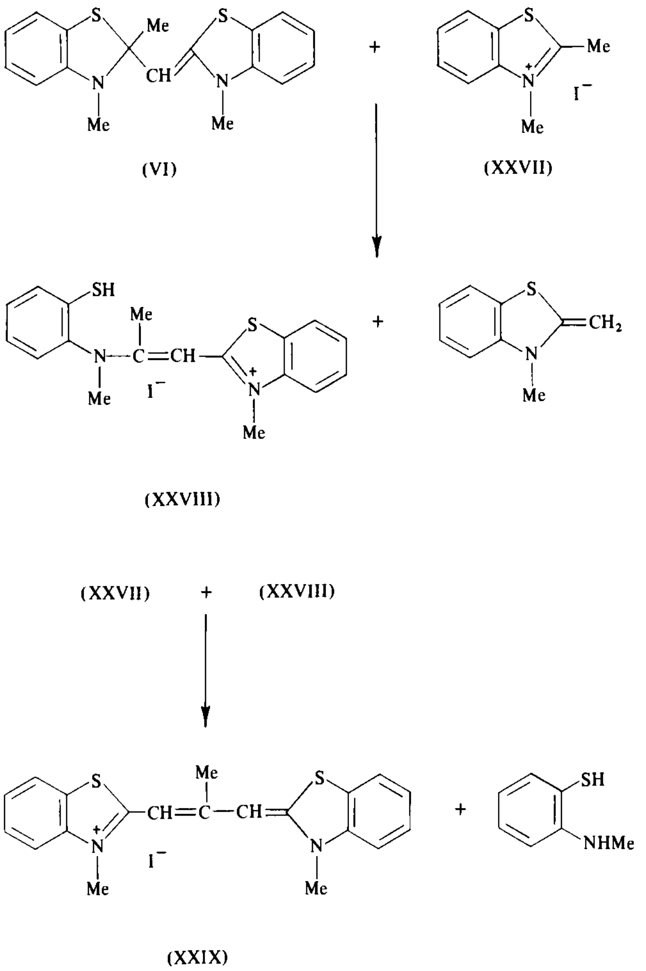
[38] I. K. Ushenko and M. F. Serdyuk, *Ukr. Khim. Zh.* **16,** 446 (1950); *CA* **49,** 1013 (1955); cf. F. M. Hamer,[5] pp. 150–152.

[39] K. Taki and Y. Hishiki, *Kagaku Kenkyusho Hokoku* **33,** 350 (1957); *CA* **52,** 16334 (1958); *Rika Gaku Kenkyusho Hokoku* **35,** 269 (1959); *CA* **54,** 20211 (1960).

[39a] J. Metzger *et al.,*[10] p. 2868 (1964).

[39b] J. Metzger *et al.,*[10] p. 2888 (1964).

[40] W. H. Mills, *J. Chem. Soc.* **121,** 455 (1922).



and merocyanines may also be prepared),[41] dialkoxyalkyl esters [$(RO)_2$-CHOCOR′],[42] ethoxymethylenemalonic esters,[43] dialkoxyamines, e.g., $(EtO)_2CHNMe_2$[44] *O*-ethylisoacetanilide [PhN=C(OEt)Me][45] and the

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[41] S. Hünig, *Ann. Chem.* **574**, 99, 106, 112 (1951).

[42] S. G. Dent, L. G. S. Brooker, and Eastman Kodak, *USP* 2,537,880; *USP* 2,533,206 describes the similar preparation of methineoxonols.

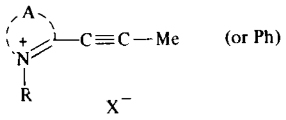
[43] N. N. Sveshnikov and N. S. Stokovskaya, *Zh. Vses. Khim. Obshchestva im. D. I. Mendeleeva* **7**, 111 (1962); *CA* **57**, 12669 (1962).

[44] H. Meerwein, W. Florian, N. Schön, and G. Stopp, *Ann. Chem.* **641**, 1 (1961).

[45] Fuji Photo Film Co., *JP* 2626 (1964); *CA* **61**, 3244 (1964).

compound $(Me_2N{=}CHCl)^+Cl^-$.[46] In some cases intermediate products could be isolated, and hence unsymmetrical dyes.

Kiprianov and Dyadyusha have prepared ethynyl quaternary salts of the pyridine and quinoline series (XXX); these react readily with 2-methyl quaternary salts to give *meso*-methyl or phenyl trimethinecyanines.[47] A benzimidazole intermediate of the same type has also been used to prepare trimethinecyanines and merocyanines[48]; apart from a trinuclear dye of the type described in Section VII,A,2, these are the first recorded examples of chain-substituted benzimidazole dyes. Chain-substituted trimethinecyanines with two benzimidazole rings remain unknown, however.



(XXX)

Reaction of methyl quaternary salts with *s*-triazine is said to give trimethinecyanines in surprisingly high yield.[49]

4. *Other Methods*

An ingenious method of building the two heterocyclic rings onto an existing carbon chain involves reaction of *β*-chloroglutaryl chloride with an *o*-substituted aniline of type (XXXI); when Y = O, S, or NR, symmetrical benzoxazole, benzothiazole, and benzimidazole dyes are formed (XXXII).[50]

Ogata and Noguchi have described the cleavage of a trimethinecyanine chain by a quaternary salt, by heating at high temperature, to give a different dye, e.g., (XXXIII) → (XXXIV); by heating trimethinecyanines with ketomethylene compounds merocyanines were formed.[51]

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[46] CIBA, *BP* 954,240.

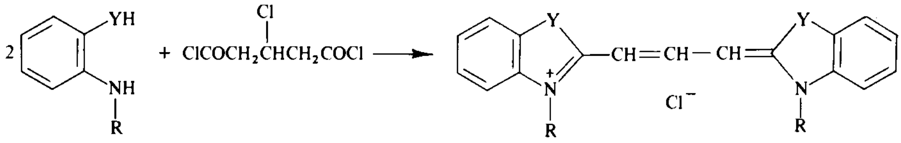
[47] A. I. Kiprianov and G. G. Dyadyusha, *Zh. Obshch. Khim.* **29,** 1708 (1959); **30,** 3647, 3654 (1960); *CA* **54,** 8817 (1960); **55,** 22833 (1961).

[48] P. D. Collet, M. A. Compere, and Eastman Kodak, *BP* 1,093,938; 1,093,940.

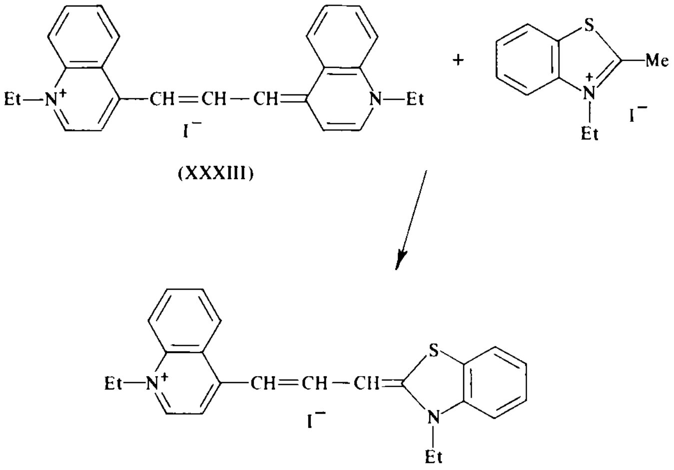
[49] A. Kreutzberger, *Arch. Pharm.* **299,** 897, 984 (1966).

[50] O. Neunhoeffer and VEB Filmfabrik Agfa Wolfen, *DBP* 1,055,155.

[51] T. Ogata and M. Noguchi, *J. Sci. Res. Inst.* (*Tokyo*) **45,** 154 (1951); cf. J. Metzger *et al.*[39b] and H. Zenno, *J. Pharm. Soc. Japan* **74,** 1236 (1954); *CA* **49,** 14736 (1955).



(XXXI) (XXXII)



(XXXIII)

(XXXIV)

D. PENTAMETHINECYANINES

A convenient method for the preparation of symmetrical pentamethinecyanines involves reaction of a methyl quaternary salt (III) with a malonaldehyde acetal (XXXV; R″ = H) (now available commercially) to give (XXXVI; R″ = H)[52]; β-alkyl-substituted dyes (XXXVI; R″ = alkyl) are prepared similarly.[53]

An alternative method involves reaction of a 2-aminopyrimidine (XXXVII) or a pyrimidine quaternary salt with the methyl quaternary salt.[54] The oxonol (XXXVIII; $n = 1$) has been prepared by a similar reaction from 2-thiobarbituric acid.[55]

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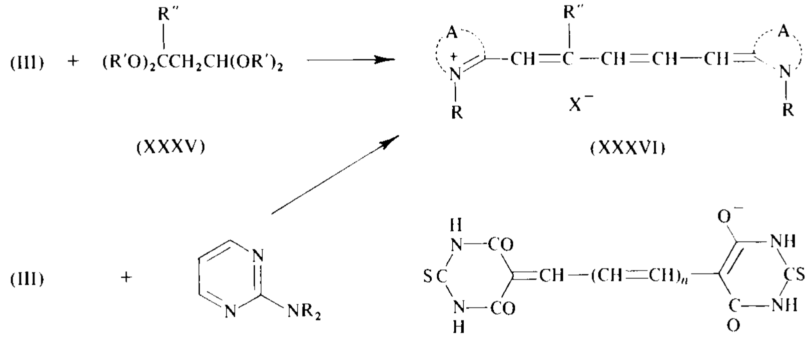
[52] S. Kimura, S. Homma, S. Kobayashi, and Fuji Photo Film Co., *JP* 6437 (1956); *CA* **52,** 5180 (1958).

[53] A. V. Kazymov and E. P. Shchelkina, *RP* 192,018; *CA* **68,** 50983 (1968).

[54] D. J. Fry, J. D. Kendall, A. J. Morgan, and Ilford, *BP* 859,452; 870,633.

[55] R. G. Shepherd, *J. Chem. Soc.* p. 4410 (1964).



(XXXV) (XXXVI) (XXXVII) (XXXVIII)

Whereas reaction of a methyl quaternary salt with pyridine and 2-chlorobenzoxazole was known to give a heptamethinecyanine (ring-opening of the pyridine providing the five central methine links), a similar reaction involving 2-chloro-3,3-dimethyl-3*H*-indole unexpectedly gave a pentamethinecyanine; the 2-, 3-, and 4-carbons of the pyridine ring here provided the $\beta\gamma\beta'$-methine links.[56] A similar result is obtained when thiobarbituric acid is reacted with a suitably quaternized pyridine or with a glutaconaldehyde derivative; Shepherd has shown, however, that the pentamethineoxonol (XXXVIII; $n = 2$) is first formed, decomposing on mild heating to the trimethineoxonol (XXXVIII; $n = 1$)[55] (see also Gehauf[57] and Section VIII,D).

Hirsch and Förster have described the preparation of the compound ($Me_2N{=}CH{-}CH{=}CH{-}SMe)^+$ ClO_4^-, and its use in the synthesis of symmetrical and unsymmetrical pentamethincyanines.[57a]

III. Substituents in the Common Heterocyclic Nuclei

The chapter on cyanine dyes in Volume II[1] devoted separate sections to dyes derived from the following heterocycles: quinoline, benzoxazole, benzothiazole (also including simple thiazoles and the naphthothiazoles), benzoselenazole, and indole. A few other ring systems received only the briefest mention. Since then the above-named rings, together with the important addition of benzimidazole, have remained the most frequently

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[56] G. E. Ficken and J. D. Kendall, *J. Chem. Soc.* p. 3988 (1959).

[57] B. Gehauf, *USP* 2,769,001.

[57a] B. Hirsch and E. Förster, *Chimia (Aarau)* **20**, 126 (1966).

used in cyanine dye chemistry. This section is therefore devoted to a discussion of the quite considerable amount of work which has been devoted to varying the substituents in these commonest heterocyclic rings.

A. Thiazoles and Oxazoles

Two dyes possessing a 4,5-diphenylthiazole nucleus were described in Volume II, and aryl groups have remained the commonest type of substituent in thiazole cyanines. A series of papers by Sych *et al.*[58] has described the preparation of dyes of this type, mostly with phenyl or more complicated aryl and heterocyclic substituents (naphthyl, acenaphthyl, styryl, thienyl, etc.); the light absorption was discussed in terms of the electronic and steric effects of the substituents. Sych and Kiprianov[59] have shown that, although a 5-phenyl group is coplanar with the thiazole ring, a 4-phenyl group is not, due to steric hindrance with the adjacent *N*-alkyl group. Other aryl-substituted thiazole dyes have been described by Rout *et al.*[60] and others,[61] and the following substituents have also been introduced: amino and acetamido,[62] hydroxymethyl,[63] aryloxy and arylthio,[64] azulenyl,[65] furyl,[66] 2-benzothiazolyl,[67] and phthalimidomethyl.[68]

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[58] E. D. Sych, *Ukr. Khim. Zh.* **22,** 80, 217 (1956); **24,** 79, 89 (1958); **25,** 344, 767 (1959); **27,** 83 (1961); *CA* **50,** 16751 (1956); **51,** 372 (1957); **52,** 18377 (1958); **54,** 5619, 13143 (1960); **55,** 22831 (1961); E. D. Sych and E. D. Smaznaya-Il'ina, *Zh. Obshch. Khim.* **32,** 984 (1962); **33,** 74 (1963); *CA* **58,** 6953, 14151 (1963); *Ukr. Khim. Zh.* **28,** 1087 (1962); *CA* **59,** 11698 (1963); E. D. Sych and L. P. Umanskaya, *Zh. Obshch. Khim.* **34,** 2068 (1964); *CA* **61,** 10805 (1964).

[59] E. D. Sych and A. I. Kiprianov, *Zh. Obshch. Khim.* **31,** 3926 (1961); *CA* **57,** 9834 (1962).

[60] B. K. Patnaik and M. K. Rout, *J. Sci. Ind. Res.* **16B,** 253 (1957); *J. Indian Chem. Soc.* **34,** 543 (1957); **35,** 511 (1958); B. Das and M. K. Rout, *ibid.* p. 505; **36,** 640 (1959); B. K. Sabata, B. K. Patnaik, and M. K. Rout, *J. Sci. Ind. Res.* **20B,** 121 (1961).

[61] B. S. Portnaya, I. I. Levkoev, and N. S. Spasokukotskii, *Dokl. Akad. Nauk SSSR* **75,** 231 (1950); *CA* **45,** 6626 (1951); W. Franke, F. Bauriedel, and Adox Fotowerke, *DBP* 1,237,895.

[62] G. De Stevens, R. H. Sprague, and Sperry Rand, *USP* 2,892,834; Ferrania, *BP* 1,103,334.

[63] V. M. Zubarovskii and R. N. Moskaleva, *Zh. Obshch. Khim.* **32,** 570 (1962); *CA* **58,** 2525 (1963).

[64] E. B. Knott, *J. Chem. Soc.* p. 4099 (1952).

[65] J. Brunken and E. J. Poppe, *Chem. Ber.* **93,** 2572 (1960).

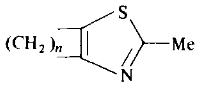
[66] E. B. Middleton and DuP, *USP* 2,524,674.

[67] V. M. Zubarovskii, *Zh. Obshch. Khim.* **29,** 2018 (1959); *CA* **54,** 8792 (1960).

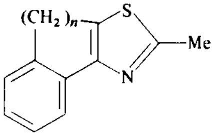
[68] N. Bregant, *Arhiv Kem.* **23,** 192 (1952); *CA* **48,** 6889 (1954).

Some cyanines and merocyanines with aryl-substituted oxazole rings have also been described.[69]

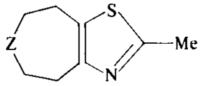
A batch of patents from the Sperry Rand Corp. described the preparation of a number of thiazole bases with various rings fused in the 4,5-position, and of derived cyanines.[70] The bases included those of type (XXXIX), optionally with alkyl or spirocycloalkyl substitution in the carbocyclic rings; a related oxazole base; analogs of (XXXIX; $n = 4$) with an oxygen or sulfur atom replacing one of the $-CH_2-$ groups; and the tricyclic bases (XL; $n = 1$ or 2); the light absorption of some of the dyes has been discussed.[71] Dyes from (XXXIX; $n = 5$) have also been described by Bassignana and Gandino,[72] and from bases (XL; $n = 1$ and 2) and two isomeric bases by Sych *et al.*[73] Yokoo and Morosawa have prepared dyes from (XLI; $\text{Z} = \rangle\text{NCO}_2\text{Et}$ or $\rangle\text{N}^+\text{Me}_2$), originally assigned an isomeric structure.[74]



(XXXIX)
$n = 3\text{–}5$



(XL)



(XLI)

Some dyes have been prepared from Δ^2-thiazoline bases containing one

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[69] T. Takahashi and K. Satake, *J. Pharm. Soc. Japan* **71,** 905 (1951); *CA* **46,** 7915 (1952); R. A. Jeffreys, *J. Chem. Soc.* p. 4823 (1952); p. 3396 (1957); J. Götze, E. Böckly, K. Lohmer, and AGFA, *DBP* 1,131,991; E. D. Sych and Zh. N. Belaya, *Zh. Obshch. Khim.* **33,** 1507 (1963); *CA* **60,** 695 (1964), E. D. Sych, Zh. N. Belaya, and G. G. Dyadyusha, *Ukr. Khim. Zh.* **30,** 1065 (1964); *CA* **62,** 9268 (1965); E. D. Sych, Zh. N. Belaya, L. P. Umanskaya, and E. D. Smaznaya-Il'ina, *Ukr. Khim. Zh.* **32,** 274 (1966); *CA* **65,** 2379 (1966).

[70] G. De Stevens and Sperry Rand, *USP* 2,882,160; 2,892,835–6; 2,905,666; 2,916,487–8; G. De Stevens, R. H. Sprague, and Sperry Rand, *USP* 2,892,837; 2,912,434; 2,937,181; I. A. Prager, R. H. Sprague, and Sperry Rand, *USP* 2,886,565, R. H. Sprague and Sperry Rand, *USP* 2,892,838; 2,899,430; 2,912,433.

[71] R. H. Sprague, *J. Am. Chem. Soc.* **79,** 2275 (1957); R. H. Sprague and G. De Stevens, *ibid.* **81,** 3095 (1959).

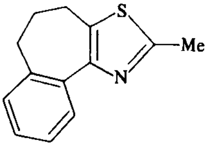
[72] P. Bassignana and M. Gandino, *Compt. Rend. 31st Congr. Intern. Chim. Ind., Liege, 1958;* see *Ind. Chim. Belge.* Suppl. 2, 518 (1959).

[73] E. D. Sych and L. P. Umanskaya, *Ukr. Khim. Zh.* **28,** 714 (1962); *CA* **58,** 6951 (1963); E. D. Sych, L. P. Umanskaya, and E. K. Perkovskaya, *Ukr. Khim. Zh.* **33,** 68 (1967); *CA* **66,** 96203 (1967).

[74] S. Morosawa, *Bull. Chem. Soc. Japan* **33,** 1118 (1960); *CA* **55,** 27364 (1961); A. Yokoo and S. Morosawa, *Bull. Chem. Soc. Japan* **36,** 599 (1963); **40,** 1954 (1967); *CA* **60,** 9386 (1964); **68;** 21873 (1968).

or two aryl substituents in the 4- or 5-positions[75,76]; unlike thiazole dyes, phenyl substitution in thiazoline dyes leads to reduced sensitizing action.[76] Hydroxymethyl groups have been introduced into the 4-position in thiazoline and oxazoline cyanines.[77]

Yamane *et al.* have used the novel tricyclic base (XLIa) to prepare cyanines.[77a]



(XLI)

B. BENZOXAZOLES

Introduction of a 5-phenyl group into the benzoxazole nucleus gave rise to cyanines with useful sensitizing properties,[78] so that subsequent work has tended to concentrate on the introduction of other bulky groups in the 5-position. Thus benzoxazole (and benzothiazole) dyes have been prepared with 1-naphthyl, 2-thienyl, and 2-furyl substituents,[79] and the unusual substituent (XLII) has also been used.[80]

Vinton and Firestine claim that trimethinecyanines with 5-carboxy-substituted benzoxazole rings are useful sensitizers with a reduced tendency to leave a stain after photographic processing.[81] The 5,6-methylenedioxy group ($-OCH_2O-$) has been introduced into benzoxazole dyes.[82]

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[75] T. G. Gnevysheva and I. I. Levkoev, *Dokl. Akad. Nauk SSSR* **146,** 1081 (1962); *CA* **58,** 3529 (1963); T. G. Gnevysheva, E. B. Lifshits, I. I. Levkoev, and Z. P. Sytnik, *Kinotekhn., Nauchn.-Tekhn. Sb.* p. 19 (1963); *CA* **62,** 16417 (1965).

[76] T. G. Gnevysheva, E. B. Lifshits, I. I. Levkoev, and Z. P. Sytnik, *Kinotekhn., Nauchn.-Tekhn. Sb.* p. 37 (1963); *CA* **61,** 13454 (1964).

[77] J. Nys and M. J. Libeer, *Bull. Soc. Chim. Belges* **65,** 377, 403 (1956).

[77a] K. Yamane, M. Banno, S. Koichi, and T. Mori, *Nippon Kagaku Zasshi* **89,** 787 (1968); *CA* **70,** 58899 (1969).

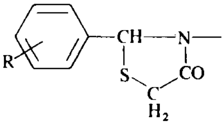
[78] Cf. *CSD II,* p. 1166.

[79] G. Bach and VEB Filmfabrik Agfa Wolfen, *DBP* 1,063,028, J. Götze and Agfa, *BP* 874,011; M. A. Al'perovich and L. T. Bogolyubskaya, *Zh. Obshch. Khim.* **34,** 645 (1964); *CA* **60,** 14639 (1964); M. A. Al'perovich, M. K. Grechko, and L. T. Bogolyubskaya, *Zh. Nauchn. i Prikl. Fotogr. i Kinematogr.* **9,** 90 (1964); *CA* **61,** 1423 (1964).

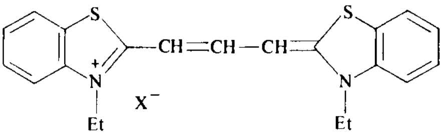
[80] Ferrania SpA, *BP* 1,104,952.

[81] J. C. Firestine and DuP, *USP* 2,609,371; W. H. Vinton and DuP, *USP* 2,647,053; W. H. Vinton, J. C. Firestine, and DuP, *USP* 2,647,054.

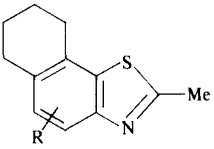
[82] L. Basaglia and B. Mariani, *Chim. Ind. (Milan)* **46,** 633 (1964); *CA* **61,** 12119 (1964).



(XLII)



(XLIII)



(XLIV)

C. BENZOTHIAZOLES AND RELATED HETEROCYCLES

In order to illustrate the wide variety of substituents which have been introduced into the benzothiazole ring in cyanine dyes, the wavelength (in nm) of maximum absorption of the symmetrical dyes (XLIII) is given in columns 2 and 3 of Table I; these columns refer, respectively, to the substituents R of column 1 in the 5- and 6-positions of the benzothiazole ring. In order to make the Table as complete as possible, a few references to older work are included. The figures in parentheses refer to dyes similar to (XLIII), but with N-substituents other than ethyl.

The data will not be discussed in detail, but the general comment can be made that any significant effect of a substituent on the light absorption, relative to the unsubstituted dye, will always be bathochromic. Moreover, this effect tends to be appreciably greater for 6-substitution compared to 5-substitution.

The following information supplements that given in the Table.

1. *Halogen Substituents*

Natanson has discussed the absorption and sensitization spectra of the four 5,5′-dihalogeno-*meso*-ethyl trimethinecyanines.[83]

2. *Alkyl and Alkoxy Substituents*

Levkoev *et al.* have prepared trimethinecyanines from all six dimethyl- and four of the dimethoxybenzothiazoles.[84] Dyes have also been prepared

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[83] S. V. Natanson, *Dokl. Akad. Nauk SSSR* **106,** 497 (1956); *CA* **50,** 13607 (1956).

[84] I. I. Levkoev, A. F. Vompe, N. N. Sveshnikov, and N. S. Barvyn, *Zh. Obshch. Khim.* **22,** 879 (1952); *CA* **46,** 10985 (1952); I. I. Levkoev, Z. P. Sytnik, S. V. Natanson, V. V. Durmashkina, T. V. Krasnova, and R. S. Shuser, *Zh. Obshch. Khim.* **24,** 2034 (1954); *CA* **49,** 4427 (1955).

with 5,6-dihydroxy or diacetoxy substitution,[85] with the substituents $-OCH_2CH_2CONH_2$ and $-OCH_2CH_2CN$,[86] and from the tetrahydronaphthothiazole (XLIV) with methoxy and other substituents.[87] Various alkoxy- and acyloxybenzoselenazoles have been claimed as sensitizers.[88]

3. *Sulfo Substituents*

Libeer and Depoorter have recently shown that chlorosulfonation of 2-methylbenzothiazole gives a mixture of all four possible chlorosulfonyl derivatives, with the 6-isomer preponderant. From the pure isomers, prepared from the aminobenzothiazoles, the corresponding acids and sulfonamides were prepared, and hence four series of cyanines.[89]

4. *Amino and Nitro Substituents*

The Russian workers have discussed the light absorption of benzothiazole trimethinecyanines with a 5-(or 6-)nitro or amino substituent and some other substituent at the adjacent 6-(or 5-)position.[90] A chlorine atom has little effect, but a larger group such as methyl or methoxy partly annuls the bathochromic effect of an $-NMe_2$ group (but not of $-NH_2$). This effect, due to steric hindrance to coplanarity of the $-NMe_2$ group and the benzene ring, is even greater with the bulky $-CMe_3$ group adjacent to $-NMe_2$. Similar effects are observed with the nitro-substituted dyes.

5. *Unsaturated Substituents*

Among the 5- and 6-styrylbenzothiazole dyes, those with a *trans*-styryl group were more effective sensitizers than the *cis*-isomers.[91] In addition to the styryl-substituted dyes included in the Table, other dyes

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[85] A. I. Kiprianov and G. M. Golubushina, *Ukr. Khim. Zh.* **29,** 1173 (1963); *CA* **60,** 5668 (1964).

[86] C. B. Roth, L. Horwitz, H. Levine, and G, *USP* 3,062,815; L. Horwitz, C. B. Roth, and G, *USP* 3,080,363.

[87] M. A. Al'perovich, Z. I. Miroshnichenko, and I. K. Ushenko, *Zh. Obshch. Khim.* **29,** 989 (1959); *CA* **54,** 1494 (1960).

[88] Ferrania SpA, *FP* 1,480,882.

[89] M. J. Libeer and H. Depoorter, *Compt. Rend. 36th Congr. Intern. Chim. Ind., Brussels, 1966* Vol. 3; see *Ind. Chim. Belge* **32,** Spec. No., 66 (1967).

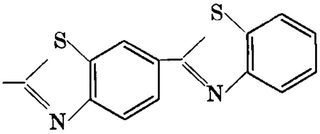
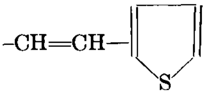
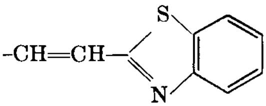
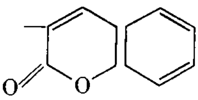
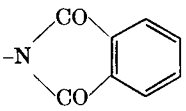
[90] A. I. Kiprianov and I. K. Ushenko, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* p. 492 (1950); *CA* **45,** 3265 (1951); A. I. Kiprianov and I. N. Zhmurova, *Dokl. Akad. Nauk SSSR* **85,** 789 (1952); *CA* **47,** 9979 (1953); *Zh. Obshch. Khim.* **23,** 493, 874 (1953); *CA* **48,** 3963 (1954); I. I. Levkoev and N. N. Sveshnikov, *Dokl. Akad. Nauk SSSR* **85,** 805 (1952); *CA* **47,** 9980 (1953); E. D. Sych, *Ukr. Khim. Zh.* **18,** 148, 159 (1952); *CA* **48,** 13683 (1954); I. I. Levkoev, N. N. Sveshnikov, N. S. Barvyn, and T. V. Krasnova, *Zh. Obshch. Khim.* **30,** 291 (1960); *CA* **54,** 22575 (1960).

[91] M. A. Al'perovich, M. K. Grechko, and Yu. A. Naumov, *Zh. Nauchn. i Prikl. Fotogr. i Kinematogr.* **8,** 410 (1963); *CA* **60,** 8816 (1964).

TABLE I
ABSORPTION MAXIMA OF BENZOTHIAZOLE AND BENZIMIDAZOLE DYES[a]

Substituent	Benzothiazole dyes (XLIII)		Benzimidazole dyes	
	5-Substituted	6-Substituted	Trimethinecyanines (LXVII)	Merocyanines (LXVIII)
H	557[1]		495[1]	512.5[2]
F	561[1,3]	558[4]	498[1,5]	515[6,7]
Cl	561[1]	560[8]	504[1]	—
Br	562[1]	560[8]	504[1]	—[9]
I	—	571[10]	506[1]	—
Me	565[11]	563[11]	490[12]	—
Et	565[13]	563[13]	—	—
-CMe_3	565[14]	565[14]	—	—
-CH_2CH_2OH	568[15]	567[16]	—	—
-$C(OH)Me_2$	(567)[17,18]	(576)[17,18]	(524)[18,19]	(525)[18,19]
-CHO	—	—	(521)[19,20]	(525)[19,20]
Ac	561[21]	580[21]	(525)[9,18,19]	(524)[9,18,19]
-CO_2H	556[22,23]	572[22,24]	536[25]	—
-CO_2R	555[23,26]	572[24,27]	515[27,28]	—
-CONHEt	—	—	—[9]	—[9]
-CN	—	571[24]	514[29,30]	518[29]
Ph	567[31]	574[31]	515[32]	—
p-$C_6H_4NO_2$	570[33]	581[33]	—	—
Bz	—	—	524[34,35]	(527)[19,34]
-OEt	576[36]	575[10,36]	498[12]	—
-OPh	—	569[36]	—	—
-$CH{=}CMe_2$	—	579[37]	—	—
-$CH{=}CHCO_2H$	571[37]	591[37]	(537)[19,20]	(527)[19,20]
-$CH{=}CHCN$	570[38]	594[38]	—	—
-$CH{=}CH{-}Ph$ (*trans*)	578[31,39]	595[31,39,40]	—	—
(*cis*)	574[39]	579[39]	—	—
-$CH{=}CPh_2$	—	600[37]	—	—
p-$CH{=}CHC_6H_4NO_2$	576[22,41]	601[22,41]	—	—
p-$CH{=}CHC_6H_4NH_2$	589[22]	609[22]	—	—
-$(CH{=}CH)_2Me$	—	589[41]	—	—
-$(CH{=}CH)_2Ph$	592[41]	611[41]	—	—
-$C{\equiv}CPh$	574[42]	592[42]	—	—
-NO_2	560[22]	585[22,24,43]	—[19,44]	—
-NH_2	596[45]	597[10,46]	—	—
-NMe_2	608[47]	612[10,43,47]	—	—
-NHAc	577[45]	581[10,46]	—	—
-$NHSO_2Me$	—	572[46,48]	—	—
-$NHCSNHCH_2CH{=}CH_2$	—	578[49]	—	—
-$NHC(SEt){=}NCH_2CH{=}CH_2$	—	586[49]	—	—
-$N{=}NPh$	(580)[17,50]	(610)[17,50]	—	—

TABLE I (*Continued*)

	Benzothiazole dyes (XLIII)		Benzimidazole dyes	
Substituent	5-Substituted	6-Substituted	Trimethinecyanines (LXVII)	Merocyanines (LXVIII)
p-N=NC$_6$H$_4$NMe$_2$	$(597)^{17,50}$	$(635)^{17,50}$	—	—
-SO$_2$NHEt	—	—	$510^{51,52}$	520^{51}
-SO$_2$NHPh	—	570^{24}	$(513)^{19,52}$	—
-CF$_3$	$557^{3,53}$	561^{53}	507^{54}	515^{55}
-OCF$_3$	561^{56}	560^{56}	502^{7}	518^{7}
-SCF$_3$	560^{57}	$565^{57,58}$	511^{7}	520^{7}
-SOCF$_3$	—	—	$516^{7,55}$	520^{55}
-SO$_2$CF$_3$	556^{22}	575^{53}	522^{54}	524^{7}
-SO$_2$CH$_2$SO$_2$CF$_3$	—	—	517^{59}	—
-CH=CHCF$_3$	—	582^{60}	520^{60}	$(524)^{19,60}$
-CF=CFCF$_3$	—	579^{60}	520^{60}	$(525)^{19,60}$
Thiazolyl	$(573)^{17,21,61}$	$(586)^{17,21,61}$	$(533)^{19,62,63}$	$(529)^{19,62,63}$
2-Benzoxazolyl	—	—	531^{64}	528^{64}
2-Benzothiazolyl	571^{65}	593^{65}	534^{66}	530^{66}
	—	$(602)^{17,67}$	—	—
	584^{31}	606^{40}	—	—
	—	—	$(551)^{19,63}$	$(538)^{19,63}$
	570^{31}	582^{31}	—	—
	568^{45}	568^{45}	—	—
Ferrocenyl	592^{68}	608^{68}	—	—

[a] Key to references:

[1] U. Mazzucato and N. Mongiat, *Ric. Sci., Rend.* [2] **A3,** 317 (1963); *CA* **59,** 11695 (1963). [2] L. G. S. Brooker, G. H. Keyes, R. H. Sprague, R. H. VanDyke, E. VanLare, G. VanZandt, F. L. White, H. W. J. Cressman, and S. G. Dent, *J. Am. Chem. Soc.* **73,** 5332 (1951). [3] A. I. Kiprianov and L. M. Yagupol'skii, *Zh. Obshch. Khim.* **22,** 2209 (1952); *CA* **47,** 4769 (1953). [4] A. I. Kiprianov and L. M. Yagupol'skii, *Zh. Obshch. Khim.* **20,** 2111 (1950); *CA* **45,** 3268 (1951). [5] Other values are 502 nm (Depoorter *et al.*[6]) or 504 nm (Yagupol'skii *et al.*[7]). [6] H. Depoorter, M. J. Libeer, G. G. van Mierlo, J. M. Nys, and Gevaert Photo-Producten, *BP* 955,964; 981,452. [7] L. M. Yagupol'skii, G. I. Klyushnik, and V. I. Troitskaya, *Zh. Obshch. Khim.* **34,** 307 (1964); *CA* **60,** 13352 (1964). The following are also described: 5,6-F$_2$, -CF$_2$OCF$_2$-, -OCF$_2$O-, and -CF$_3$, Cl substitution. [8] B. Beilenson and F. M. Hamer, *J. Chem. Soc.* p. 1225 (1936). [9] L. G. S. Brooker, E. J. VanLare, and Eastman Kodak, *USP* 2,778,823. [10] A. I. Kiprianov, I. K. Ushenko, and E. D. Sych, *Zh. Obshch. Khim.* **15,** 200 (1945); *CA* **40,** 2307 (1946). [11] I. I. Levkoev, N. N. Sveshnikov, E. Z. Kulik, and T. V. Krasnova, *Zh. Obshch. Khim.* **27,** 3097 (1957); *CA* **52,** 9091 (1958). The 4- and 7-methyl dyes are also described. [12] IG, *BP* 505,979. [13] I. I. Levkoev, N. N. Sveshnikov, N. K. Gipp, V. V. Durmashkina, and N. S. Barvyn, *Tr. Vses. Nauchn.-Issled. Kinofotoinst.* No. 40, 5 (1960); *CA* **58,** 14153 (1963). The isopropyl analogs have similar spectra. [14] I. N. Zhmurova and Zh. M. Ivanova, *Ukr. Khim. Zh.* **21,** 504 (1955); *CA* **50,** 707 (1956). [15] V. M. Zubarovskii, T. M. Verbovskaya, and A. I. Kiprianov, *Zh. Obshch. Khim.* **31,** 3056 (1961); *CA* **56,** 15495 (1962). [16] V. M. Zubarovskii and M. P. Bachurina, *Zh. Obshch. Khim.* **34,** 3797 (1964); *CA* **62,** 10561 (1965). [17] *N*-Methyl dyes. [18] V. M. Zubarovskii and G. P. Khodot, *Zh. Organ. Khim.* **1,** 2232 (1965); *CA* **64,** 17755 (1966). [19] 3-Ethyl-1-phenyl dyes. [20] V. M. Zubarovskii, R. N. Moskaleva, and M. P. Bachurina, *Khim. Geterotsikl. Soedin.* p. 571 (1965); *CA* **64,** 3732 (1966). [21] V. M. Zubarovskii and G. P. Khodot, *Zh. Obshch. Khim.* **32,** 1574 (1962); *CA* **58,** 6951 (1963). [22] E. D. Sych and Zh. N. Belaya, *Ukr. Khim. Zh.* **28,** 362 (1962); *CA* **57,** 11343 (1962). [23] J. C. Firestine and DuP, *USP* 2,647,050; W. H. Vinton, J. C. Firestine, and DuP, 2,647,051; E. L. Martin and DuP, *USP* 2,647,052. [24] A. I. Kiprianov and I. K. Ushenko, *Zh. Obshch. Khim.* **15,** 207 (1945); *CA* **40,** 2309 (1946). [25] H. Depoorter, M. J. Libeer, G. G. van Mierlo, J. M. Nys, and Gevaert Photo-Producten, *BP* 981,453. [26] R = Me. [27] R = Et. [28] H. Depoorter, M. J. Libeer, G. G. van Mierlo, J. M. Nys, and Gevaert Photo-Producten, *BP* 981,451. [29] H. Depoorter, M. J. Libeer, G. G. van Mierlo, J. M. Nys, and Gevaert Photo-Producten, *BP* 955,962. [30] Cyano-substituted dyes have also been described by G. Bach and VEB Filmfabrik Agfa Wolfen, *DBP* 1,121,925; 5,6-dicyanobenzimidazole dyes by M. J. Libeer, H. Depoorter, and Gevaert Photo-Producten, *BP* 1,092,063. [31] M. A. Al'perovich, I. K. Ushenko, and L. N. Tyurina, *Zh. Obshch. Khim.* **28,** 2538 (1958); *CA* **53,** 3194 (1959). [32] H. Depoorter, M. J. Libeer, G. G. van Mierlo, J. M. Nys, and Gevaert Photo Producten, *BeP* 600,862. [33] I. K. Ushenko, *Zh. Obshch. Khim.* **31,** 2861 (1961); *CA* **56,** 14434 (1962); also *p*-acetamido-, methoxy-, methylthio-, and hydroxyphenyl substituted dyes. [34] A. V. Stetsenko and L. I. Filileeva, *Ukr. Khim. Zh.* **32,** 853 (1966); *CA* **66,** 38863 (1967). [35] M. J. Libeer, H. Depoorter, and Gevaert Photo-Producten, *BP* 1,062,950. [36] I. I. Levkoev, V. G. Zhiryakov, N. N. Sveshnikov, and N. S. Barvyn, *Sb. Statei Obshch. Khim., Akad. Nauk SSSR* **2,** 1263 (1953); *CA* **49,** 5444 (1955). Other alkoxy, etc., substituents are included. [37] I. K. Ushenko, F. Z. Rodova, and V. I. Korystov, *Zh. Obshch. Khim.* **32,** 3650 (1962); *CA* **58,** 9258 (1963); cf. I. K. Ushenko, *Nauchn. Zap., Donetskii Inst. Sov. Torgovli* p. 153 (1962); *CA* **62,** 7902 (1965). [38] I. K. Ushenko, *Zh. Obshch. Khim.* **30,** 2650 (1960); *CA* **55,** 11852 (1961). [39] M. A. Al'pero-

vich, Yu. A. Naumov, and I. K. Ushenko, *Zh. Obshch. Khim.* **31,** 1344 (1961); *CA* **55,** 22830 (1961). [40] I. K. Ushenko and S. E. Gornostaeva, *Zh. Obshch. Khim.* **28,** 1668 (1958); *CA* **53,** 1309 (1959). [41] M. A. Al'perovich, I. K. Ushenko, and L. N. Tyurina, *Zh. Obshch. Khim.* **29,** 3376 (1959); *CA* **54,** 13913 (1960). [42] I. K. Ushenko, *Zh. Obshch. Khim.* **31,** 2854 (1961); *CA* **56,** 13048 (1962). 6-Phenylethynylquinoline dyes are also described. [43] Merocyanines from 6-nitro- and diethylaminobenzothiazoles have been described by Z. P. Sytnik and L. D. Zhilina, *Zh. Obshch. Khim.* **27,** 215 (1957); *CA* **51,** 12885 (1957). [44] O. Neunhoeffer and A. Keiler, *Chem. Ber.* **91,** 122 (1958). [45] I. K. Ushenko and L. I. Chovnik, *Zh. Obshch. Khim.* **30,** 2658 (1960); *CA* **55,** 11851 (1961). [46] I. I. Levkoev, S. A. Kheifets, and N. S. Barvyn, *Zh. Obshch. Khim.* **21,** 1340 (1951); *CA* **45,** 10107 (1951). [47] A. I. Kiprianov and K. D. Sich, *Zap. Inst. Khim., Akad. Nauk Ukr. RSR* **8,** 103 (1946); *CA* **49,** 2436 (1955); I. I. Levkoev and B. S. Portnaya, *Zh. Obshch. Khim.* **21,** 2050 (1951); *CA* **46,** 2935 (1952). [48] H. Depoorter, M. J. Libeer, and Gevaert Photo-Producten (*BP* 1,080,080) describe dyes with this and similar groups in the 4- and 7-positions. [49] N. F. Turitsyna and I. I. Levkoev, *Zh. Obshch. Khim.* **22,** 309 (1952); *CA* **46,** 10984 (1952). [50] A. I. Kiprianov and I. P. Fedorova, *Zh. Obshch. Khim.* **28,** 1023 (1958), *CA* **52,** 16337 (1958). Various other *p*-phenylazo-substituted dyes are also described. [51] H. Depoorter, M. J. Libeer, G. G. van Mierlo, J. M. Nys, and Gevaert Photo Producten, *BP* 975,504; 986,571. [52] Ferrania SpA, *ItalianP* 663,182; *CA* **64,** 11356 (1966). [53] L. M. Yagupol'skii and V. P. Nazaretyan, *Ukr. Khim. Zh.* **33,** 617 (1967); *CA* **67,** 91670 (1967). [54] L. M. Yagupol'skii and V. I. Troitskaya, *Zh. Obshch. Khim.* **29,** 2409 (1959); *CA* **54,** 11000 (1960). [55] L. M. Yagupol'skii, V. I. Troitskaya, B. E. Gruz, and N. V. Kondratenko, *Zh. Obshch. Khim.* **35,** 1644 (1965); *CA* **64,** 3731 (1966). Dyes were also prepared from benzimidazoles linked by a $-CF_2CF_2-$ group. [56] L. M. Yagupol'skii and V. I. Troitskaya, *Zh. Obshch. Khim.* **27,** 518 (1957); *CA* **51,** 15517 (1957). [57] L. M. Yagupol'skii and M. S. Marenets, *Zh. Obshch. Khim.* **25,** 1771 (1955); *CA* **50,** 5635 (1956). [58] L. M. Yagupol'skii and A. I. Kiprianov, *Zh. Obshch. Khim.* **22,** 2216 (1952); *CA* **47,** 4771 (1953). [59] L. M. Yagupol'skii and N. V. Kondratenko, *Zh. Obshch. Khim.* **33,** 920 (1963); *CA* **59,** 11689 (1963). [60] L. M. Yagupol'skii, N. V. Kondratenko, and Yu. A. Fialkov, *Zh. Obshch. Khim.* **36,** 828 (1966); *CA* **65,** 15547 (1966). [61] 4-Thiazolyl. [62] 2-Thiazolyl. [63] V. M. Zubarovskii and M. P. Bachurina, *Khim. Geterotsikl. Soedin.* p. 209 (1967); *CA* **67,** 116849 (1967). [64] V. M. Zubarovskii, R. N. Moskaleva, and M. P. Bachurina, *Ukr. Khim. Zh.* **30,** 80 (1964); *CA* **60,** 13354 (1964). [65] I. K. Ushenko and K. D. Zhikhareva, *Zh. Obshch. Khim.* **32,** 3656 (1962); *CA* **58,** 9259 (1963). [66] V. M. Zubarovskii, R. N. Moskaleva, and M. P. Bachurina, *Zh. Obshch. Khim.* **32,** 1581 (1962); *CA* **58,** 6952 (1963). [67] A. I. Kiprianov and I. L. Mushkalo, *Zh. Obshch. Khim.* **32,** 4040 (1962); *CA* **58,** 13931 (1963). [68] I. K. Ushenko, K. D. Zhikareva, and F. Z. Rodova, *Zh. Obshch. Khim.* **33,** 798 (1963); *CA* **59,** 10268 (1963).

with similar substitution have been prepared in the monomethinecyanine, merocyanine, and trinuclear series.[92]

Dyes with phenylazo substituents show a single intense band strongly

[92] M. A. Al'perovich, I. K. Ushenko, L. N. Tyurina, and M. K. Grechko, *Zh. Obshch. Khim.* **29,** 3606 (1959); *CA* **54,** 17375 (1960); I. K. Ushenko and S. E. Gornostaeva, *Zh. Obshch. Khim.* **29,** 3807 (1959); *CA* **54,** 17375 (1960); L. N. Tyurina, M. A. Al'perovich, and I. K. Ushenko, *Zh. Obshch. Khim.* **32,** 70 (1962); *CA* **57,** 12663 (1962). For styryl-substituted quinoline dyes, see M. A. Al'perovich and I. K. Ushenko, *Zh. Obshch. Khim.* **29,** 3384 (1959); *CA* **54,** 13915 (1960).

shifted bathochromically compared to the unsubstituted dye (Table I), from which it was concluded that the azo groups and the trimethine chain form a single chromophore.

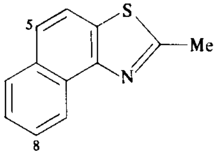
Benzothiazole and quinoline dyes with a methacrylamido substituent (–$NHCOCMe{=}CH_2$) are polymerizable.[93]

6. *Fluorine-Containing Substituents*

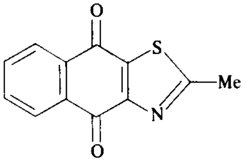
Other trifluoromethylbenzothiazole dyes have been claimed by Mariani.[94] Dyes have also been prepared with 6-acetamido-5-trifluoromethoxy and with 5,6-OCF_2O substitution.[95]

7. *Naphthothiazoles and Related Bases*

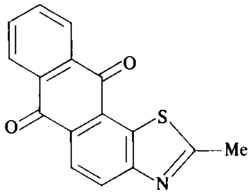
Tiselskii has prepared a number of dyes from naphtho[1,2*d*]thiazole (XLV) with groups such as –OH, –OMe, and –NMe_2 in the 5- and 8-position; substituents in the former position have the greater effect on light absorption.[96]



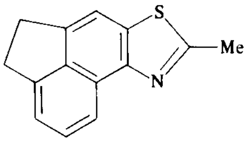
(XLV)



(XLVI)
579 nm



(XLVII)
640 nm (Me)



(XLVIII)
600 nm (Me)

Although the naphthoquinonothiazole (XLVI) was too feebly basic

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[93] DuP, *BP* 903,268.

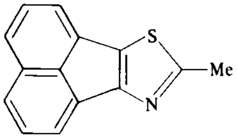
[94] B. Mariani and Ferrania SpA, *BP* 972,001.

[95] L. M. Yagupol'skii, *Zh. Obshch. Khim.* **29,** 1312 (1959); *CA* **54,** 9953 (1960); L. M. Yagupol'skii and V. I. Troitskaya, *Zh. Obshch. Khim.* **31,** 628 (1961); *CA* **55,** 22830 (1961).

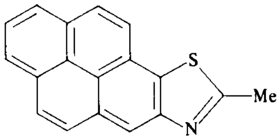
[96] A. P. Tisel'skii, *Ukr. Khim. Zh.* **24,** 648, 749 (1958); *CA* **53,** 12279, 20039 (1959); *Vestn. Kharkovsk. Politekhn. Inst.* **6,** 13, (1966); *CA* **67,** 55149 (1967).

to be quaternized, Kiprianov and Stetsenko were able to prepare a quaternary salt from 2-ethylamino-3-mercaptonaphthoquinone, and hence dyes were prepared; the anthraquinonothiazole (XLVII) was also used to prepare dyes.[97,98]

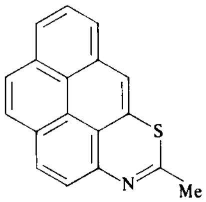
Other thiazoles with more complicated fused carbocyclic ring systems include (XLVIII) and two isomers (the dyes are all bathochromic compared to the corresponding naphthothiazole dyes),[99] the acenaphthenothiazole (XLIX),[100] the pyrenothiazole (L), and its thiazine isomer (LI),[101] and the interesting azulenothiazole (LII).[102]



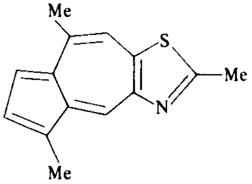
(XLIX)
670 nm



(L)
600 nm (Me)



(LI)
565 nm (Me)



(LII)
630 nm (Me)

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[97] A. I. Kiprianov and A. V. Stetsenko *Ukr. Khim. Zh.* **19,** 508, 517 (1953); *CA* **49,** 8262, 8263 (1955).

[98] Except where otherwise indicated, absorption maxima refer to the symmetrical trimethinecyanines with *N*-ethyl substituents.

[99] A. V. Stetsenko and A. D. Kurbatova, *Ukr. Khim. Zh.* **24,** 354 (1958); *CA* **52,** 21113 (1958); A. V. Stetsenko, *Ukr. Khim. Zh.* **25,** 623 (1959); *CA* **54,** 10328 (1960); A. V. Stetsenko and L. I. Kravets, *Ukr. Khim. Zh.* **30,** 75 (1964); *CA* **60,** 13350 (1964).

[100] E. D. Sych, A. A. Shulezhko, and A. I. Kiprianov, *Ukr. Khim. Zh.* **28,** 213 (1962); *CA* **57,** 4795 (1962).

[101] O. Neunhoeffer and W. Weigel, *Ann. Chem.* **647,** 101, 108 (1961).

[102] G. Fischer and E. J. Poppe, *Veroeffentl. Wiss. Photolab. Wolfen* **10,** 123 (1965).

8. *Thiazoles with Additional Heterocyclic Rings*

A few thiazole bases with a fused-on partially reduced heterocyclic ring have already been discussed in Section III,A. Among bases more closely related to benzothiazole which have been used to prepare cyanines are the thieno[2,3*d*]thiazole (LIII) and its [3,2*d*] isomer,[103] their benzo derivatives,[104] and the base (LIV).[105] Bases (LV)[106] and (LVI)[107] have also been used.

Fridman has prepared a number of dyes from benzothiazoles with another heterocyclic ring of the type triazole, thiadiazole, imidazole, etc., fused in the 6,7-position[108]; similar benzoxazole bases have also been used.[109]

Some interest has been displayed in bases containing two thiazole rings, and which are therefore in theory capable of being quaternized on one or both nitrogen atoms. The simplest has two such rings fused directly together, the quaternary salt being unequivocally of structure (LVII) from the method of preparation. Only the methylthio group was consequently reactive, and monomethinecyanines and merocyanines were prepared; the light absorption of the dyes was bathochromically shifted in relation to the corresponding benzothiazole dyes.[110]

The first benzobis(thiazole) to be used for the preparation of cyanines was base (LVIII); both nitrogen atoms could be quaternized, and hence trinuclear dyes (bis-mono- or trimethinecyanines) could be prepared by

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[103] V. G. Zhiryakov, *Zh. Obshch. Khim.* **34,** 2034 (1964); *CA* **61,** 14814 (1964); V. G. Zhiryakov, P. I. Abramenko, and G. F. Kurepina, *RP* 168,991; *CA* **63,** 1923 (1965).

[104] Z. I. Miroshnichenko and M. A. Al'perovich, *Zh. Obshch. Khim.* **34,** 241, 247 (1964); *CA* **60,** 14639, 14640 (1964); *Zh. Organ. Khim.* **1,** 289 (1965); *CA* **63,** 3079 (1965).

[105] V. G. Zhiryakov, P. I. Abramenko, and G. F. Kurepina, *RP* 177,279; *CA* **64,** 14328 (1966).

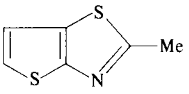
[106] Z. I. Moskalenko and M. A. Al'perovich, *Khim. Geterotsikl. Soedin,* p. 492 (1967); *CA* **68,** 14063 (1968).

[107] G. P. Shumelyak, M. A. Al'perovich, and R. V. Timofeeva, *RP* 179,617; *CA* **65,** 4008 (1966).

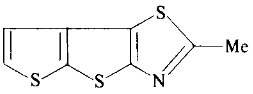
[108] S. G. Fridman, *Zh. Obshch. Khim.* **31,** 1096 (1961); **32,** 1461 (1962); **33,** 207 (1963); **35,** 1364 (1965); *CA* **55,** 24728 (1961); **58,** 1564, 14155 (1963); **64,** 3730 (1966); S. G. Fridman and D. K. Golub, *Khim. Geterotsikl. Soedin.* p. 713 (1965); *CA* **64,** 14315 (1966); cf. L. W. Berlin, H. Hamal, and FH, *USP* 3,058,978; I. P. Fedorova and G. F. Mironova, *Zh. Obshch. Khim.* **32,** 1893 (1962); *CA* **58,** 4535 (1963).

[109] E. Animali, D. Dal Monte, and E. Sandri, *Boll. Sci. Fac. Chim. Ind. Bologna* **22,** 48 (1964); *CA* **62,** 1766 (1965).

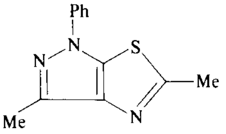
[110] G. P. Shumelyak and M. A. Al'perovich, *Zh. Obshch. Khim.* **34,** 251 (1964); *CA* **60,** 13352 (1964).



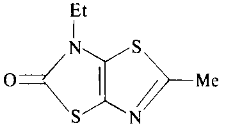
(LIII)
594 nm



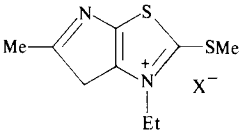
(LIV)



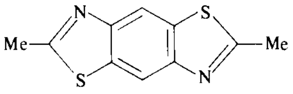
(LV)
558 nm



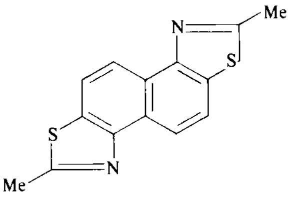
(LVI)



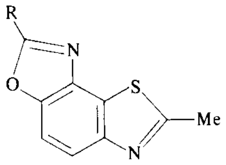
(LVII)



(LVIII)



(LIX)



(LX)
564 nm (R=H)

reaction at both methyl groups.[111,111a] All but one of the other four possible isomers of (LVIII) have also been prepared and used for the synthesis of cyanines (the remaining isomer, with a 1,2,3,4-SNNS substitution pattern in the benzene ring, would presumably be incapable of double quaternization due to severe steric hindrance).[112] Kiprianov has

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[111] Gevaert Photo-Producten, *BP* 632,641.

[111a] A. I. Kiprianov, A. V. Stetsenko, and E. D. Sych, *Ukr. Khim. Zh.* **22,** 760 (1956); *CA* **51,** 8725 (1957); W. Ried and R. Bender, *Chem. Ber.* **91,** 2798 (1958); G. Grandolini and A. Fravolini, *Gazz. Chim. Ital.* **92,** 1334 (1962); *CA* **58,** 14153 (1963).

[112] C. Finzi and G. Grandolini, *Gazz. Chim. Ital.* **89,** 2543 (1959); *CA* **55,** 5468 (1961); U. Chiodoni and B. Mariani, *Ann. Chim.* (*Rome*) **53,** 741 (1963); *CA* **59,** 14136 (1963).

discussed the light absorption of the isomeric bis-trimethinecyanines from three of these bases in terms of the angle included between the two chromophoric systems in each dye.[113] Dyes have also been prepared from the naphthobis(thiazole) (LIX).[114]

Of the six possible thiazolobenzoxazole ring systems, e.g., (LX; R = H or Me), four have been used for the preparation of cyanines. Monoquaternization took place invariably at the more basic thiazole nitrogen atom, so that dye formation occurred only at the methyl group in this ring.[115]

Three of the four thiazolopyridines, viz., (LXI) and the 5- and 7-aza analogs,[116] and a benzo derivative of each of these bases[117] have been used to prepare cyanines. Quaternization apparently occurred in every case at the thiazole nitrogen atom, but Rillaers and Depoorter have recently prepared isomeric quaternary salts of (LXII)[118]; both contained a reactive methyl group, corresponding to the two methylene bases (LXIII) and (LXIV), so that two series of dyes could be obtained, (see the diazaindenes, Section III,E).

Dyes have been prepared from various thiazoloquinolines by Di Modica and Barni.[119] In bases (LXV) and (LXVI; R or R′ = Me) quaternization occurs on the pyridine nitrogen atom, and the methyl group in that ring is activated; it is therefore surprising that in (LXVI; R = R′ = H) quaternization should occur in the thiazole ring.

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[113] A. I. Kiprianov, *Compt. Rend. 36th Congr. Intern. Chim. Ind., Brussels, 1966* Vol. 3; see *Ind. Chim. Belge* **32,** Spec. No., 100 (1967).

[114] A. V. Stetsenko and V. I. Ivanova, *Ukr. Khim. Zh.* **22,** 772 (1956); *CA* **51,** 8726 (1957).

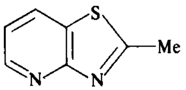
[115] L. Horwitz and G. *USP* 2,876,231; S. G. Fridman and D. K. Golub, *Zh. Obshch. Khim.* **31,** 3394 (1961); **34,** 280 (1964); *CA* **57,** 7413 (1962); **60,** 13353 (1964); P. Bassignana, C. Cogrossi, and M. Gandino, *Ann. Chim.* (*Rome*) **53,** 747 (1963); *CA* **59,** 14135 (1963).

[116] T. Takahashi and T. Goto, *Yakugaku Zasshi* **66,** 2 (1946); *CA* **45,** 8531 (1951); T. Takahashi and K. Sato, *Yakugaku Zasshi* **76,** 195 (1956); *CA* **50,** 13915 (1956); S. G. Fridman and A. I. Kiprianov, *Ukr. Khim. Zh.* **22,** 767 (1956); *CA* **51,** 8725 (1957).

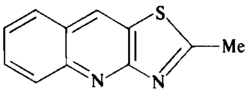
[117] G. Di Modica and E. Barni, *Gazz. Chim. Ital.* **93,** 679 (1963); *CA* **60,** 694 (1964); M. Gandino and Ferrania SpA, *FP* 1,421.863.

[118] G. Rillaers and H. Depoorter, *Compt. Rend. 36th Congr. Intern. Chim. Ind., Brussels, 1966* Vol. 3; see *Ind. Chim. Belge* **32,** Spec. No.. 61 (1967).

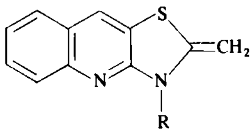
[119] G. Di Modica, E. Barni, and G. Nasimi, *Gazz. Chim. Ital.* **94,** 314 (1964); *CA* **61,** 7143 (1964); G. Di Modica and E. Barni, *Ann. Chim.* (*Rome*) **54,** 530 (1964); *CA* **61,** 16195 (1964); *Boll. Sci. Fac. Chim. Ind. Bologna* **22,** 56 (1964); *CA* **62,** 4140 (1965); E. Barni, *Boll. Sci. Fac. Chim. Ind. Bologna* **25,** 81 (1967); *CA* **68,** 3887 (1968).



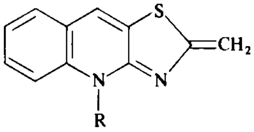
(LXI)



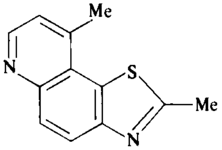
(LXII)
696 nm



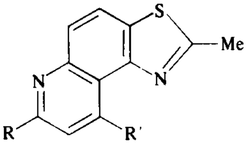
(LXIII)



(LXIV)



(LXV)



(LXVI)

The following novel substituents have been introduced into the 5- and 6-positions of benzothiazole cyanines: vinyl[119a] (various substituted vinyl groups had been used previously; see Table 1), azido ($-N_3$),[119b] formyl,[119c] and the rhodanine substituent (LVIa).[119c] Phenoxy- and phenylthio substituents have been used in the 5-position in benzothiazole and benzoselenazole dyes.[119d]

The interaction between the two chromophores in benzothiazole cyanines with a *p*-dimethylaminophenylazo substituent has been studied further by Kiprianov and Lazukina.[119e]

Novel benzothiazole bases, with an additional fused heterocyclic ring, include (LXVIb),[119f] (LXVIc),[119g] and (LXVId),[119h] and some isomeric bases.

Kiprianov has maintained his interest in dyes from the various benzo-

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[119a] V. M. Zubarovskii and G. P. Khodot, *Khim. Geterotsikl. Soedin.* p. 1003 (1968); *CA* **70,** 107500 (1969).

[119b] I. A. Ol'shevskaya, V. Ya. Pochinok, and L. F. Abramenko, *Khim. Geterotsikl. Soedin.* p. 898 (1968); *CA* **71,** 13064 (1969).

[119c] V. M. Zubarovskii and G. P. Khodot, *Zh. Obshch. Khim.* **34,** 3801 (1964); *CA* **69,** 68246 (1968).

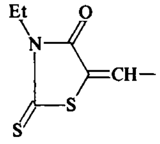
[119d] D. J. Fry, R. W. Burrows, G. E. Ficken, and Ilford, *BP* 1,153,166.

[119e] A. I. Kiprianov and A. L. Lazukina, *Zh. Organ. Khim.* **4,** 1483 (1968); *CA* **70,** 79135 (1969).

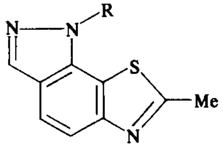
[119f] S. G. Fridman and D. K. Golub, *Khim. Geterotsikl. Soedin.* p. 481 (1967); *CA* **68,** 88182 (1968).

[119g] V. A. Gladkaya and Yu. S. Rozum, *Ukr. Khim. Zh.* **33,** 1287 (1967); *CA* **69,** 3701 (1968).

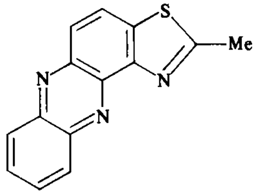
[119h] G. Grandolini, A. Fravolini, and I. Montanini, *Gazz. Chim. Ital.* **96,** 941 (1966); *CA* **69,** 3702 (1968).



(LXVIa)



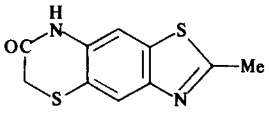
(LXVIb)



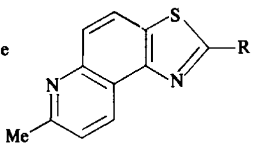
(LXVIc)

bisthiazoles.[119i,119j] In particular, the compound previously thought to be (LXVId) has now been shown to be the isomeric benzo[1,2-*d*:4,3-*d'*]bisthiazole; an unequivocal synthesis of (LXVId) has been devised.[119i]

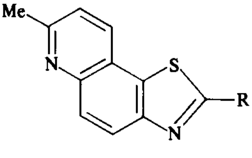
Barni *et al.* have used NMR spectroscopy to examine the quaternization of bases of type (LXVIe) and (LXVIf), and have prepared cyanines from



(LXVId)



(LXVIe)



(LXVIf)

the resulting quaternary salts. Whereas the former react with methyl iodide exclusively on the quinoline nitrogen atom, bases of type (LXVIf) may, depending on the nature of R, react partially at the thiazole nitrogen.[119k]

D. Benzimidazoles

One of the most noteworthy features of cyanine dye chemistry in the past two decades has been the awakening of interest in dyes possessing

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[119i] A. I. Kiprianov and F. A. Mikhailenko, *Khim. Geterotsikl. Soedin.* p. 270 (1967); *CA* **68,** 68919 (1968).

[119j] A. I. Kiprianov, T. M. Verbovskaya, and I. L. Mushkalo, *Zh. Organ. Khim.* **3,** 2036 (1967); A. I. Kiprianov, I. L. Mushkalo, and F. A. Mikhailenko, *ibid.* 2041: A. I. Kiprianov and I. L. Mushkalo, *ibid.* **4,** 2222 (1968); A. I. Kiprianov and L. A. Lazukina, *Ukr. Khim. Zh.* **34,** 795 (1968); *CA* **69,** 52919, 52920 (1968); **71,** 4497 (1969); **70,** 12645 (1969); cf. P. Lochon, P. Meheux, and J. Neel, *Bull. Soc. Chim. Fr.* p. 1093 (1968).

[119k] E. Barni, G. Di Modica, and A. Gasco, *Boll. Sci. Fac. Chim. Ind. Bologna* **25,** 87 (1967); E. Barni, A. Gasco, G. Di Modica, and F. Delle Monache, *ibid.* **25,** 107 (1967); *CA* **68,** 60516, 78183 (1968).

a benzimidazole nucleus. The first true cyanine with this nucleus was not prepared until as late as **1933**,[120] but a benzimidazolebenzoselenazole trimethinecyanine (Kt **945**)[121] was quite soon adopted for use as a sensitizer for the green in an AGFA color film. Presumably the disclosure of this fact, and the appearance of the relevant patents from AGFA and IG, was responsible for the subsequent activity in this field shown by most of the other photographic companies, but particularly by Gevaert. In addition to the resulting large number of patents, the Russian workers have studied the effects of varying the substituents in the benzimidazole ring as thoroughly as in their complementary work on benzothiazole dyes. The literature on benzimidazole dyes has been reviewed up to **1959** by Ciernik.[122]

Many of the patents dealing with novel benzimidazole cyanines claim that the trimethinecyanines are powerful J-band[123] sensitizers for the green region of the spectrum. This is in spite of the fact that they lack the meso substituent which is considered necessary in, for instance, benzoxazole or benzothiazole dyes, for J-aggregation; in fact benzimidazole trimethinecyanines with a *meso*-phenyl substituent have only quite recently been described (Section II,C,3), and alkyl-substituted dyes are unknown. The reason for this difference has been explained by Brooker *et al.*[124] in terms of the spatial configuration of the dyes.

Reference to Table I gives an indication of the nature of the substituents that have been incorporated into benzimidazole dyes. Columns four and five give the absorption maxima for dyes of two series: the symmetrical trimethinecyanines (LXVII) and the 3-ethylrhodanine dimethinemerocyanines (LXVIII), respectively, (see Section III,C).

Levkoev *et al.*[125] have reported that the introduction of electron-attracting groups into the 5- or 6-positions of the benzimidazole ring has a beneficial effect on the sensitizing properties of the resulting trimethinecyanines. Only chlorine and $-CF_3$ were given as examples, but the even more strongly electron attracting $-SO_2CF_3$ group was discussed in a

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[120] T. Ogata, *Proc. Imp. Acad.* (*Tokyo*) **9**, 602 (1933); *J. Chem. Soc. Japan* **55**, 394 (1934); *CA* **28**, 2007, 5816 (1934).

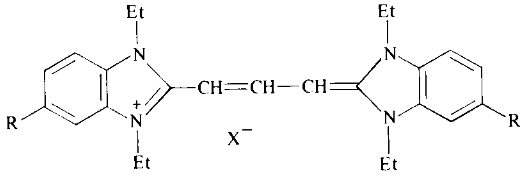
[121] Cf. *CSD II*, pp. 1167–1169.

[122] J. Ciernik, *Chem. Listy* **55**, 44 (1961); *CA* **55**, 6217 (1961).

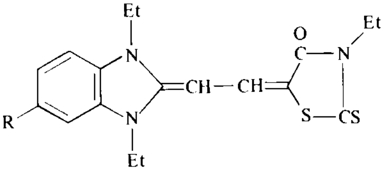
[123] For a definition of this term and a discussion of the different types of spectral sensitization, see, for instance, C. E. K. Mees and T. H. James.[2]

[124] L. G. S. Brooker, F. L. White, D. W. Heseltine, G. H. Keyes, S. G. Dent, and E. J. VanLare, *J. Phot. Sci.* **1**, 173 (1953).

[125] I. I. Levkoev, E. B. Lifshits, S. V. Natanson, N. N. Sveshnikov, and Z. P. Sytnik, *Wiss. Phot., Intern. Konf., Koeln, 1956* p. 109. Verlag Helwich, Darmstadt, 1958.



(LXVII)



(LXVIII)

patent.[125a] However, a later paper examined a greater range of substituents and attempted to correlate the photographic activity with the electronic properties of the substituents as measured by their effect on the basicity of the dyes.[126]

1. *Halogen Substituents*

The most frequently used substituent in benzimidazole dyes has been chlorine, and a number of patents claim trimethinecyanines with one or two chloro substituents in each benzimidazole ring.[127] Ciernik *et al.* have published two papers dealing with the photographic properties of a series of unsymmetrical trimethinecyanines with a 5,6-dichlorobenzimidazole nucleus, the other nucleus being either benzoselenazole or benzoxazole.[128] Papers and patents have appeared concerning dyes with the following substitution: 4,5,7-trichloro,[129] 5,6-difluoro,[130] 5,6-dibromo,[131] 5-bromo-6-chloro,[132] and 5-amino-6-chloro.[133]

[125a] I. I. Levkoev, E. B. Lifshits, L. M. Yagupol'skii, and A. V. Borin, *RP* 118,091; *CA* **53**, 19650 (1959).

[126] E. B. Lifshits, I. I. Levkoev, L. M. Yagupol'skii, and N. S. Barvyn, *Zh. Nauchn. i Prikl. Fotogr. i Kinematogr.* **11**, 175 (1966); *CA* **65**, 6566 (1966).

[127] Gevaert Photo-Producten, *BP* 812,924; 815,172; E. J. VanLare and Eastman Kodak, *USP* 2,739,149; D. W. Heseltine, L. L. Lincoln, E. J. VanLare, and Eastman Kodak, *FP* 1,470,055; H. Glockner, K. Küffner, and Perutz Photowerke, *DBP* 1,159,577; Ferrania SpA, *BeP* 691,230.

[128] J. Ciernik, J. Straka, and J. Kalina, *Chem. Prumysl* **12**, 348 (1962); *CA* **57**, 13332 (1962); J. Ciernik, V. Trnka, and F. Ptak, *Chem. Prumysl* **12**, 539 (1962); *CA* **58**, 4667 (1963).

[129] A. V. Stetsenko and Yu. I. Bogodist, *Ukr. Khim. Zh.* **26**, 92 (1960); *CA* **54**, 15938 (1960).

[130] Gevaert Photo-Producten, *BP* 1,087,315.

2. *Fluorine-Containing Substituents*

The other substituent mentioned by Levkoev *et al.*,[125] viz. trifluoromethyl, has also proved of some interest, and Bannert and Fry have patented various novel dyes with this substituent.[134] Other papers and patents are concerned with fluorine-containing substituents of the type listed in Table I, together with some other substituent such as chlorine or methoxy.[135]

3. *Quinonoid Derivatives*

Stetsenko *et al.*[136] have described dyes from naphtho- and anthraquinonoimidazoles, corresponding to the thiazole bases (XLVI) and (XLVII).

4. *Imidazoles with Additional Fused Heterocyclic Rings*

Fridman has prepared a number of benzimidazole bases, and hence dyes, in which a heterocyclic ring such as triazole or thiadiazole was fused in the 5,6-position[137]; the base (LXIX) was also described, and the benzo derivative of (LXIX) has been used.[138] More recently, Brooker *et al.* have prepared dyes from (LXX) and (LXXI),[139] and the bis quaternary salt (LXXII) has also been used.[140]

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[131] M. J. Libeer and Gevaert Photo-Producten, *BP* 980,234.

[132] M. J. Libeer, H. Depoorter, J. M. Nys, and Gevaert Photo-Producten, *BP* 979,251.

[133] H. Depoorter, M. J. Libeer, J. M. Nys, and Gevaert Photo-Producten, *BP* 983,700.

[134] K. J. Bannert, D. J. Fry, and Ilford, *BP* 1,020,295; 1,033,390.

[135] L. M. Yagupol'skii and V. I. Troitskaya, *Zh. Obshch. Khim.* **29**, 2730 (1959); *CA* **54**, 11001 (1960); L. M. Yagupol'skii, V. I. Troitskaya, I. I. Levkoev, E. B. Lifshits, P. A. Yufa, and N. S. Barvyn, *Zh. Obshch. Khim.* **37**, 191 (1967); *CA* **66**, 96202 (1967); E. B. Lifshits, L. M. Yagupol'skii, T. D. Rybnikova, and V. I. Troitskaya, *RP* 184,616; *CA* **66**, 15495 (1967); K. J. Bannert, D. J. Fry, and Ilford, *BP* 1,111,903; Ilford, *BeP* 697,245.

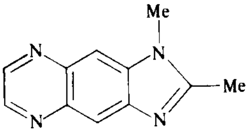
[136] A. V. Stetsenko and G. V. Chernyavskii, *Ukr. Khim. Zh.* **27**, 237 (1961); *CA* **55**, 22829 (1961); A. V. Stetsenko and V. K. Lishko, *Ukr. Khim. Zh.* **28**, 218 (1962); *CA* **58**, 6818 (1963); A. V. Stetsenko and V. A. Korinko, *Ukr. Khim. Zh.* **30**, 944 (1964); *CA* **62**, 11942 (1965).

[137] S. G. Fridman and L. I. Kotova, *Zh. Obshch. Khim.* **32**, 2871 (1962); *CA* **58**, 11495 (1963); *Khim. Geterotsikl. Soedin.* p. 497 (1967); *CA* **68**, 40976 (1968).

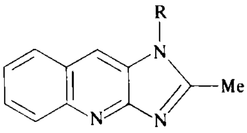
[138] Yu. S. Rozum and V. A. Gladkaya, *Ukr. Khim. Zh.* **32**, 1200 (1966); *CA* **66**, 66722 (1967).

[139] P. W. Jenkins, L. G. S. Brooker, and Eastman Kodak, *USP* 3,326,688; L. G. S. Brooker, E. J. VanLare, and Eastman Kodak, *BP* 1,075,653.

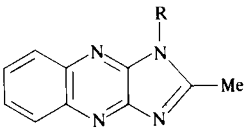
Benzimidazole nuclei with the following substituents have been incorporated into trimethincyanines: 4,5,6,7-tetrachloro/bromo,[140a] 5-



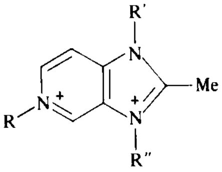
(LXIX)
560 nm (Me)



(LXX)



(LXXI)



(LXXII)

iodo-,[140b] 5-2′-cyanovinyl-[140c] 5-alkysulphonyl-,[140d] 5-arylsulphonyl-,[140e] 5-sulphamoyl-6-chloro-,[140f] and 5-2′-benzimidazolyl,[140g] Lifshits *et al.* have continued their studies on the relationship of structure to sensitizing properties of benzimidazole cyanines.[140h]

Fridman and Kiprianov have prepared dyes from the quaternary salts (LXXIIa) and (LXXIIb), both of which possess two reactive methyl groups.[140i]

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[140] A. F. Vompe, A. V. Kazymov, L. P. Shchelkina, E. M. Perel, E. G. Bren, E. B. Sumskaya, I. S. Basarova, N. V. Monich, and L. V. Ivanova, *RP* 165,969; *CA* **62,** 9278 (1965).

[140a] G. E. Ficken, D. J. Fry, K. J. Bannert, and Ilford, *BP* 1,132,528.

[140b] M. Gandino, L. Magnani, and Ferrania, *ItalianP* 786,601; *CA* **70,** 38910 (1969).

[140c] J. von Grossmann, *EGP*. 57,291.

[140d] Fuji, *BeP* 697,009. H. Depoorter, O. Riester, and Gevaert-Agfa, *BP* 1,161,797.

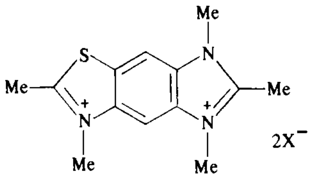
[140e] Ilford, *BeP* 707,214.

[140f] Fuji, *BeP* 704,296.

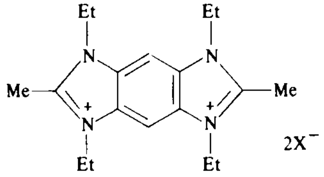
[140g] V. M. Zubarovskii and Y. P. Makovetskii, *Ukr. Khim. Zh.* **34,** 1151 (1968); *CA* **70,** 68251 (1969).

[140h] E. B. Lifshits, D. Y. Naroditskaya, and I. I. Levkoev, *Zh. Nauchn. Prikl. Fotogr. Kinematogr.* **13,** 119 (1968); E. B. Lifshits, L. M. Yagupol'skii, D. Y. Naroditskaya, V. I. Troitskaya, N. S. Barvyn, and I. I. Levkoev, *ibid.* p. 280; *CA* **69,** 68245, 112180 (1968).

[140i] S. G. Fridman and A. I. Kiprianov, *Zh. Organ. Khim.* **4,** 696 (1968), **5,** 373 (1969); *CA* **69,** 20394 (1968), **71,** 4498 (1969).



(LXXIIa)



(LXXIIb)

E. Indoles

Dyes such as (LXXIII), and the related mono- and trimethinecyanines in which the second nucleus is also 3-linked indole, appear to be of no use as sensitizers in normal photographic use. They have, however, been claimed as sensitizers for direct-positive emulsions, particularly when R′ is phenyl or pyridyl.[141]

Trimethinecyanines with the 3*H* indole nucleus (LXXIV), i.e., of the Astraphloxine type, have been examined by Sych, who has studied the effect of substituents such as nitro and amino on the light absorption.[142]

The 1,7-diazaindene (LXXV) and its 1,4- and 1,5-isomers have been prepared by Ficken and Kendall, and dyes obtained therefrom[143]; both the 1- and 7-methiodides of (LXXV) were made, and both activated the 2-methyl group (cf. the thiazoloquinoline (LXII), Section III,C,8).

Dokunikhin *et al.*[144] have prepared various dyes, mostly methinecyanines and merocyanines, containing the benzo[*cd*]indole nucleus by reaction of quaternary salts of (LXXVI) with reactive methyl or methylene groups. The unquaternized methylthio compound (LXXVI) is also highly reactive, enabling cyanine bases to be prepared.[145] Bayer have claimed a variety of benz[*cd*]indole dyes as textile dyes.[146] Cyanines with two of these nuclei have not as yet been prepared, but Packer and Smith have reacted naphthostyril with methylmagnesium iodide to ob-

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[141] J. Götze, *Mitt. Forschungslab. Agfa Leverkusen-Muenchen* **3,** 88 (1961); J. Götze, A. Randolph, O. Riester, and AGFA, *BP* 970,601.

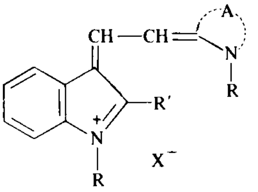
[142] E. D. Sych, *Ukr. Khim. Zh.* **19,** 643, 652, 657 (1953); *CA* **49,** 12429 (1955).

[143] G. E. Ficken and J. D. Kendall, *J. Chem. Soc.* p. 3202 (1959); p. 584 (1961); G. E. Ficken, J. D. Kendall, and Ilford, *BP* 841,588.

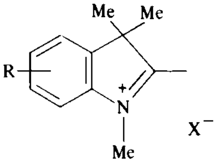
[144] N. S. Dokunikhin and L. A. Gaeva, *Khim. Nauka i Promy.* **3,** 126 (1958); *CA* **52,** 11427 (1958); N. S. Dokunikhin, G. M. Oksengendler, and Ya. B. Shteinberg, *Zh. Obshch. Khim.* **29,** 2742, 3361 (1959); *CA* **54,** 10993, 17368 (1960); N. S. Dokunikhin and Ya. B. Shteinberg, *Zh. Vses. Khim. Obshchestva im. D. I. Mendeleeva* **5,** 110, 239 (1960); *CA* **54,** 18475, 24795 (1960).

[145] G. E. Ficken and J. D. Kendall, *J. Chem. Soc.* p. 1537 (1960).

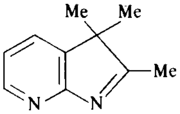
[146] FBy, *BP* 987,828; 1,014,403; 1,024,486; 1,055,832; 1,058,509; 1,064,584; 1,064,605; 1,074,786; 1,081,542; *BeP* 647,036; 647,743; 647,744.



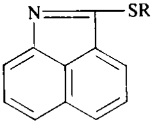
(LXXIII)



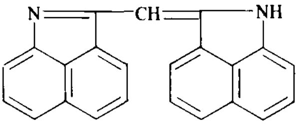
(LXXIV)



(LXXV)



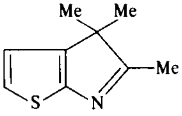
(LXXVI)



(LXXVII)
622 nm (in HCl)

tain the cyanine base (LXXVII); the spectrum of the monoprotonated species, presumably corresponding to a monomethinecyanine, was measured.[147]

Analogs of the well-known Astraphloxine dyes, in which the benzene rings are replaced by thiophene, have now been obtained by conventional reactions from (LXXVIIa) and an isomer.[147a]



(LXXVIIa)

F. Quinolines

In recent years the literature on quinoline cyanines has been dominated by Pilyugin and co-workers, who in a long series of papers (about 70 have so far appeared) have thoroughly examined the preparation of a variety of such dyes: mono- and trimethinecyanines with one or two quinoline rings, merocyanines, and styryl dyes of both the 2- and 4-linked series. The quinoline nitrogen atom generally carried a phenyl,

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[147] R. J. Packer and D. C. C. Smith, *Chem. & Ind.* (*London*) p. 1873 (1967).

[147a] V. G. Zhiryakov, P. I. Abramenko, and N. I. Sennikova, *RP* 202,728; *CA* **69**, 52935 (1968).

optionally substituted, or naphthyl group, and both the 5,6- and 7,8-benzoquinolines were used extensively. The effect on the light absorption of these structural variations has been discussed.[148]

Meyer *et al.* have examined the sensitizing properties of some quinoline monomethinecyanines (LXXVIII; Y = S or Se) with an amino group in one of the rings.[149]

Quaternary salts such as (LXXIX) react preferentially at the methylene group,* the spectra of the resulting dyes being bathochromically shifted by about 50 nm compared with the corresponding dyes from quinaldine. If this position is blocked, e.g., by formation of the benzylidene derivative, then dye formation occurs by reaction at the 4-methyl group.[150]

Kröhnke *et al.* have shown that the so-called xanthoapocyanine, one of the products of reaction of quinoline ethiodide with ethanolic potash, does not have the structure hitherto assigned to it.[151] They consider that the correct structure is in fact (LXXX), and propose a mechanism for its formation.[152] Some related dyes have been prepared.[153]

Corresponding to the thienothiazoles described in Section III,C,8, various quinoline analogs with a thiophene ring replacing the benzene ring have also been used to prepare cyanines. These include the thieno[2,3*b*]pyridine (LXXXI), the [3,2*b*] isomer, the bases with a benzene ring fused to the thiophene ring, and base (LXXXII) and an isomer. In all cases, the pairs of isomeric bases with either R or R′ = Me were used.[154]

Pailer and Renner-Kuhn have prepared some dyes from 1,8-naphthyridines (LXXXIII) (reaction at the 2-Me in the quaternary salts),

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[148] Part I: G. T. Pilyugin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* p. 512 (1952); *CA* **46,** 10983 (1952); Part LXX: O. M. Stashkevich and G. T. Pilyugin, *Ukr. Khim. Zh.* **33,** 614 (1967); *CA* **67,** 100989 (1967).

[149] K. Meyer and E. Krietsch, *Z. Wiss. Phot., Photophysik Photochem.* **48,** 126 (1953); K. Meyer and K. H. Bauer, *ibid.* **54,** 171 (1960).

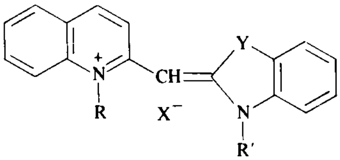
[150] G. Kempter, H. Dost, and W. Schmidt, *Chem. Ber.* **98,** 945, 955 (1965).

[151] Cf. *CSD II,* p. 1147.

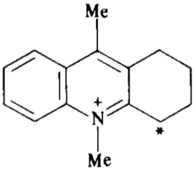
[152] F. Kröhnke, H. Dickhäuser, and I. Vogt, *Ann. Chem.* **644,** 93 (1961).

[153] G. Niederdellmann and F. Kröhnke, *Ann. Chem.* **688,** 196 (1965); V. P. Goguadze and M. I. Tarenko, *Soobshch. Akad. Nauk Gruz.* **36,** 69 (1964); *CA* **62,** 11942 (1965).

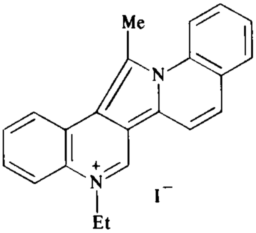
[154] V. G. Zhiryakov and P. I. Abramenko, *Zh. Obshch. Khim.* **35,** 150 (1965); *CA* **62,** 14861 (1965); P. I. Abramenko and V. G. Zhiryakov, *Zh. Organ. Khim.* **1,** 1132 (1965); *CA* **63,** 15017 (1965); V. G. Zhiryakov, P. I. Abramenko, and N. I. Sennikova, *RP* 175,819; 175,820; *CA* **64,** 8360, 8361 (1966); V. G. Zhiryakov, P. I. Abramenko, and G. F. Kurepina, *RP* 177,280; 179,189; *CA* **64,** 14328 (1966); **65,** 7330 (1966).



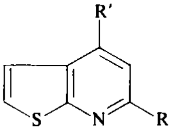
(LXXVIII)



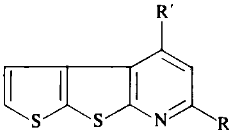
(LXXIX)



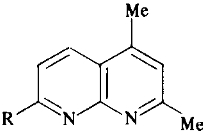
(LXXX)



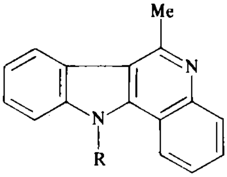
(LXXXI)



(LXXXII)



(LXXXIII)



(LXXXIV)

the dyes from the correspondingly substituted quinolines being made for comparison.[155]

The indoloquinolines (LXXXIV; R = H or Me) have been synthesized by Mann and Prior, and dyes prepared from the quaternary metho-*p*-toluenesulfonates by reaction at the *C*-methyl group.[156]

Mono- and tri-methinecyanines of the 4-linked quinoline series with an 8-fluoro substituent have been described.[156a]

Zhiryakov and Abramenko[156b] have now published their work on dyes

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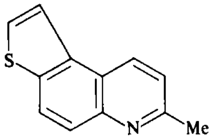
[155] M. Pailer and E. Renner-Kuhn, *Monatsh. Chem.* **84**, 85 (1953).

[156] F. G. Mann and A. F. Prior, *J. Chem. Soc.* p. 1331 (1956).

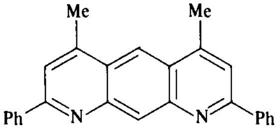
[156a] Fuji, *BeP* 718,499.

[156b] V. G. Zhiryakov and P. I. Abramenko, *Khim. Geterotsikl. Soedin.* pp. 621, 830 (1967); *CA* **68**, 96791 (1968); **69**, 3703 (1968).

from (LXXXI), (LXXXII) and related bases, previously reported in patents. New bases used to prepare cyanines include the thieno[3,2-*f*]-quinoline (LXXXIVa) and related bases[156c]; also the 1,8-diazaanthracene (LXXXIVb), the bis-quaternary salts of which contain two reactive methyl groups.[156d]



(LXXXIVa)



(LXXXIVb)

G. SUBSTITUENTS ON THE NITROGEN ATOMS

1. *General*

The N-heterocyclic quaternary salts, commonly with a 2-methyl substituent, required for cyanine dye synthesis are normally prepared by reaction of the base with a suitable quaternizing agent (this is, of course, not applicable to *N*-aryl quaternary salts).[157] In those cases where quaternization is difficult with the conventional reagents, due, for instance, to the very feeble basicity of the nitrogen atom, a useful reagent is methyl 2,4-dinitrobenzenesulfonate; its use enabled dyes to be prepared for the first time from 2-methyl-6-nitrosobenzothiazole, etc.[158]

Levkoev and Lifshits have examined a series of symmetrical trimethinecyanines with various alkyl groups on the nitrogen atoms; in the benzothiazole, benzoxazole, and 2-linked quinoline series, the *N*,*N′*-dimethyl dyes were less effective sensitizers than the diethyl dyes, while in the other series examined little difference was observed between the *N*-methyl and ethyl dyes.[159]

[156c] V. G. Zhiryakov, P. I. Abramenko, and N. I. Sennikova, *RP* 198,130; *CA* **70**, 79169 (1969). P. I. Abramenko and N. I. Sennikova, *RP* 200,426; *CA* **68**, 88212 (1968).

[156d] A. I. Kiprianov and T. M. Verbovskaya, *Zh. Organ. Khim.* **4**, 1991 (1968); *CA* **70**, 48607 (1969).

[157] For a discussion of the quaternization of heterocyclic compounds, see G. F. Duffin. *Advan. Heterocyclic Chem.* **3**, 1 (1964).

[158] A. I. Kiprianov and A. I. Tolmachev, *Zh. Obshch. Khim.* **27**, 142 (1957); *CA* **51**, 12912 (1957).

[159] I. I. Levkoev and E. B. Lifshits, *Zh. Nauchn. i Prikl. Fotogr. i Kinematogr.* **3**, 419 (1958); *CA* **53**, 18703 (1959).

2. *Acidic Substituents*

The first cyanines all carried simple alkyl substituents on the nitrogen atoms, but subsequently substituted alkyl groups and aryl groups were introduced.[160] One such substituent in alkyl groups was carboxyl, such dyes being claimed by Kodak and by Agfa in 1937.[160] It has been claimed for dyes with *N*-carboxyalkyl substituents that, in comparison with similar dyes with *N*-alkyl groups, they are sometimes better sensitizers[161] and can show a reduced tendency to be adversely affected by the presence of anionic color couplers.[162] Meyer and Rusche have examined a series of dyes of structure (LXXXV) and have found that the strongest J-band sensitization is observed when $n = 2$.[163]

Some interest has been shown in dyes carrying a sulfoalkyl group on one or both of the nitrogen atoms. First prepared by Kodak,[164] such dyes have also been claimed as being resistant to the desensitizing action of anionic color couplers.[165] An improved method of preparation of the *N*-sulfoalkyl quaternary salts required for their synthesis involves reaction of the appropriate heterocyclic base with a sultone, in preference to a bromoalkanesulfonic acid.[166]

The related sulfatoalkyl group, $-(CH_2)_nOSO_3H$, has likewise been incorporated into cyanines[167]; these dyes are also said to be resistant to anionic color couplers.[168]

Other acidic groups that have been used as N-substituents in cyanines include the following:

$-CH_2CH{=}CHSO_3H$[169]
$-CH_2CHClCH_2SO_3H$[170]
$-CH_2CH(OR)CH_2SO_3H$ ($R{=}H$ or acetyl)[171]

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[160] Cf. F. M. Hamer,[5] pp. 297–310.

[161] J. Ciernik, A. Mistr, J. Vavrova, and M. Vavra, *Zh. Nauchn. i Prikl. Fotogr. i Kinematogr.* **10**, 35 (1965); *CA* **62**, 9974 (1965).

[162] J. Spence, B. H. Carroll, and Eastman Kodak, *USP* 2,640,776; S. V. Natanson, E. B. Lifshits, and I. I. Levkoev, *Zh. Nauchn. i Prikl. Fotogr. i Kinematogr.* **1**, 174 (1956); *CA* **51**, 2432 (1957); K. Meyer, *Z. Wiss. Phot., Photophysik Photochem.* **52**, 170 (1957); M. S. Magson and ICI, *BP* 841,119; H. Glockner, H. Zorn, F. Müller, and Perutz Photowerke, *DBP* 1,127,714; E. B. Lifshits, S. V. Natanson, and I. I. Levkoev, *Usp. Nauchn. Fotogr., Akad. Nauk SSSR, Otd. Khim. Nauk* **8**, 44 (1962); *CA* **58**, 5185 (1963); J. Ciernik and J. Aufart, *CzechP* 115,442; *CA* **65**, 204 (1966).

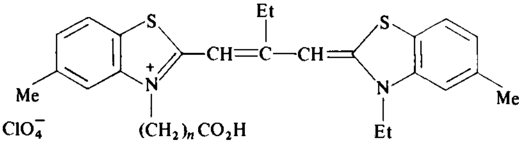
[163] K. Meyer and J. Rusche, *Z. Wiss. Phot., Photophysik Photochem.* **56**, 147 (1962).

[164] R. H. Sprague and Eastman Kodak, *USP* 2,503,776.

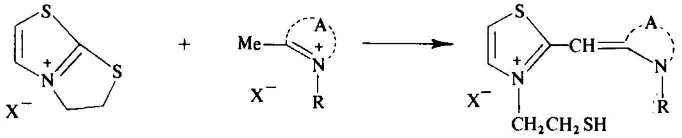
[165] J. E. Jones, J. Spence, and Eastman Kodak, *USP* 2,912,329; H. von Rintelen and AGFA, *DBP* 1,072,765; J. Götze and AGFA, *BP* 959,959; G. E. Ficken, R. W. Burrows, G. L. Care, and Ilford, *BP* 1,096,406.

[166] AGFA, *BP* 742,112.

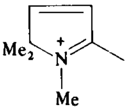
$-CH_2CH(OH)CH_2O(CH_2)_3SO_3H$[172]
$-(CH_2)_2O(CH_2)_2CO_2H$[173]
$-(CH_2)_mO(CH_2)_nSO_3H$[174]
$-(CH_2CH_2O)_2SO_3H$[175]
$-(CH_2CH_2O)_2(CH_2)_3SO_3H$[176]
$-CH_2CH(CH_2OMe)O(CH_2)_3SO_3H$[177]
$-(CH_2)_mCOO(CH_2)_nSO_3H$[178]
$-(CH_2)_nPO_3H_2$[179]
$-(CH_2)_nSO_2NHCOR$, $-(CH_2)_nCONHSO_2R$, etc. (acidic NH groups)[180]



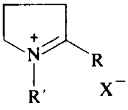
(LXXXV)



(LXXXVII) (LXXXVI)



(LXXXVIII)



(LXXXIX)

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[167] J. Brunken, J. Müller, and VEB Filmfabrik AGFA Wolfen, *DBP* 1,028,718; G. Bach, G. Beulig, and VEB Filmfabrik AGFA Wolfen, *DBP* 1,113,873.

[168] J. Brunken, *Veroeffentl. Wiss. Photolab. AGFA* 9, 58 (1961); J. Brunken, G. Glöckner, and E. J. Poppe, *ibid.* p. 61.

[169] H. Kampfer, O. Riester, J. Götze, and AGFA, *BP* 1,077,611.

[170] H. Kampfer, J. Götze, O. Riester, E. Böckly, and Agfa-Gevaert, *BP* 1,090,626.

[171] J. Götze and AGFA, *BP* 1,044,734; J. Götze, H. Kampfer, and AGFA, *BP* 1,093,444.

[172] Fuji, *BP* 1,091,739.

[173] Fuji, *BeP* 668,894.

[174] L. G. S. Brooker, G. H. Keyes, and Eastman Kodak, *USP* 3,352,857.

[175] Fuji, *BeP* 669,934.

[176] Fuji, *BeP* 669,133.

3. *Other Substituents*

Aryl groups as N-substituents have figured to a lesser extent in the literature on cyanines (but see Section III,F for Pilyugin's work on *N*-arylquinoline dyes, also Rogovik[181]). Neunhoeffer and Keiler have examined the effect on sensitizing properties of *o*-, *m*-, or *p*-substitution of Cl or Br in the phenyl group of a series of 1-ethyl-3-phenylbenzimidazole trimethinecyanines.[182]

Among some of the less usual N-substituents incorporated into cyanines, the following should be mentioned: cyclohexyl,[183] tetrahydrofurfuryl,[184] 2-thienylmethyl,[185] 2-benzothiazolylmethyl,[186] and 2-pyridyl.[187] The *N*-2-mercaptoethyl substituent, as in (LXXXVI), was obtained by carrying out a conventional methinecyanine synthesis (Section II,B,2) with the quaternary salt (LXXXVII) as alkylthio component.[188]

IV. The Use of Novel Heterocyclic Rings

In addition to varying the substituents in the common heterocyclic nuclei, much interest has been displayed in preparing cyanines with completely novel ring systems. A number of these have already, for convenience, been discussed in Section III, and the remainder will now be considered, classified according to the nature and number of the heteroatoms present.

A. NITROGEN HETEROCYCLIC RINGS

1. *One Nitrogen Atom*

a. Pyrroles. Cyanines with pyrrole nuclei are of little value as photographic sensitizers, and those discussed by Hamer[189] were of use only

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[177] Fuji, *BeP* 668 014.

[178] J. M. Nys, H. Depoorter, and Gevaert Photo-Producten, *BP* 886,271.

[179] J. M. Nys, M. J. Libeer, and Gevaert Photo-Producten, *BP* 886,270.

[180] J. M. Nys, H. Depoorter, and Gevaert Photo-Producten, *BP* 904,332.

[181] M. I. Rogovik, *Nauk. Zap., Chernivets'k. Derzh. Univ.* **53,** 74 (1961); *CA* **61,** 4518 (1964).

[182] O. Neunhoeffer and J.-A. Keiler, *J. Wiss. Phot., Photophysik Photochem.* **58,** 142, 147 (1964).

[183] I. K. Ushenko, *Ukr. Khim. Zh.* **21,** 738 (1955); *CA* **50,** 16752 (1956).

[184] Gevaert Photo-Producten, *BP* 670,799.

[185] H. G. Derbyshire and G, *USP* 3,136,772.

[186] I. K. Ushenko, *Soobshch. o Nauchn. Issled. Rabot. Chlenov Primorsk. Otd. Vses. Khim. Obshchestva* p. 1 (1953); *CA* **49,** 8265 (1955).

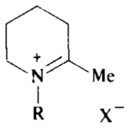
[187] Ferrania SpA, *BeP* 678,673.

[188] L. T. Bogolyubskaya and V. A. Bogolyubskii, *RP* 177,769; *CA* **65,** 7330 (1966).

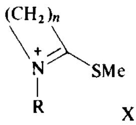
[189] F. M. Hamer,[5] pp. 314–318.

in light filtering layers; dyes with a 5-linked 2*H*-pyrrole ring, e.g. (LXXXVIII), have, however, been claimed as sensitizers.[190]

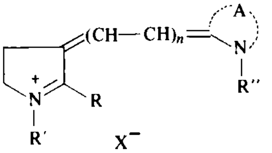
Dyes with a reduced pyrrole ring appear to be of more interest as sensitizers. Such dyes were first described by Hoechst, and were prepared by conventional reactions at the 2-methyl group of a pyrroline quaternary salt (LXXXIX; R = Me); trimethinecyanines and dimethinemerocyanines were claimed.[191] The use of 2-alkylthiopyrroline quaternary salts e.g., (LXXXIX; R = SMe) similarly gave monomethinecyanines and no-chain merocyanines.[192] Dyes of similar types, but with larger rings in place of the reduced pyrrole ring, have been prepared similarly from the quaternary salts (XC)[193] and (XCI; n = 4–7).[192,194]



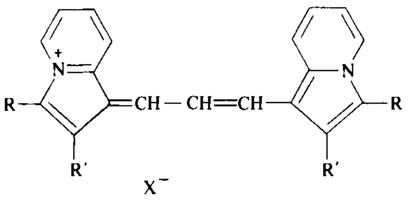
(XC)



(XCI)



(XCII)



(XCIII)

R = R′= Me	642 nm
3,3′-linked isomer	691 nm
1,3′-linked isomer	669 nm

Reaction of a quaternary salt (LXXXIX; R = Me) with, e.g., an alkylthio or acetanilidovinyl quaternary salt will, as described above, take place at the 2-methyl group. In a quaternary salt (LXXXIX) with a group at position 2 other than alkyl, reaction will occur at the 3-methyl-

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[190] D. J. Fry, B. A. Lea, J. D. Kendall, and Ilford *BP* 906,804.

[191] A. Sieglitz, L. W. Berlin, P. Heimke, and FH, *DBP* 883,025; A. Sieglitz, L. Berlin, P. Heimke, B. Schacke, and FH, *DBP* 902,290; 902,291. Similar dyes have been described by D. J. Fry, J. D. Kendall, and Ilford (*BP* 906,805) and by Ilford (*BeP* 697,631; 697,632).

[192] O. Riester, F. Bauer, and AGFA, *DBP* 927,043; O. Riester and AGFA, *DBP* 1,009,020.

[193] K. Küffner and Perutz Photowerke, *DBP* 1,073,133.

[194] D. J. Fry, B. A. Lea, and Ilford, *BP* 795,134.

ene group to give (XCII; $n = 0$ or 1); merocyanines may be prepared similarly. A 2-alkylthio group in such dyes (XCII; R = —SR′) is reactive, and gives trinuclear dyes with a methyl quaternary salt.[195]

b. Indolizines. Cyanine dyes containing the indolizine (pyrrocoline) nucleus were first prepared by Brooker and Sprague[196]; they included symmetrical dyes of type (XCIII) which were obtainable by reaction of an indolizine with 1,3,3-trimethoxy-1-propene in the presence of acetic acid. Subsequently, unsymmetrical dyes of structure (XCIV) were prepared by reaction of an indolizine with an acetanilidovinyl quaternary salt, for example; merocyanines and styryl dyes were also prepared.[197] Similar dyes have been prepared by Stepanov *et al.*,[198] from whose work the light absorption data are taken, and by Turchinovich[199]; azadimethinecyanines have also been prepared.[200] By reaction of a methylenedi(3-indolizine) with chloranil, Fraser *et al.* obtained the bridged monomethinecyanine (XCV) *inter alia,* which absorbs at a very high wavelength.[201]

Dyes have been prepared from 5,6,7,8-tetrahydroindolizines (XCVI) (reaction at position 3), and are best considered as *N*-alkylpyrrole dyes[202]; like the indolizine dyes described above, they are of no value as photographic sensitizers.

c. Other Ring Systems. Unlike quinoline cyanines, which were of course the first to be prepared, and are very well known, little work has been done on cyanines from isoquinoline. However, Brooker *et al.* have prepared a few dyes from 3-methylisoquinoline, and have discussed their spectra.[203]

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[195] D. J. Fry, B. A. Lea, and Ilford, *BP* 941,552; 944,291; cf. *BP* 918,433.

[196] L. G. S. Brooker, R. H. Sprague, and Eastman Kodak, *USP* 2,268,798; R. H. Sprague and Eastman Kodak, *USP* 2,571,775.

[197] R. H. Sprague, L. G. S. Brooker, and Eastman Kodak, *USP* 2,511,222; R. H. Sprague and Eastman Kodak, *USP* 2,622,082; 2,706,193; J. Bailey and Kodak Ltd., *BP* 999,874.

[198] F. N. Stepanov and L. I. Lukashina, *Zh. Obshch. Khim.* **29,** 2792 (1959); **30,** 2850 (1960); **33,** 2364 (1963); *CA* **54,** 10993 (1960); **55,** 15481 (1961); **60,** 695 (1964); F. N. Stepanov and N. A. Aldanova, *Khim., Tekhnol. i Primenenie Proizv. Piridina i Khinolina, Materialy Soveshch., Inst. Khim. Akad. Nauk Latv. SSR, Riga, 1957* p. 203. *Izd. Akad. Nauk Latv. SSR., 1960; CA* **55,** 23529 (1961).

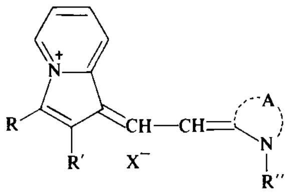
[199] G. Yu. Turchinovich, *Tr. Kievsk. Politekhn. Inst.* **43,** 81 (1963); *CA* **62,** 10559 (1965); *Vestn. Kievsk. Politekh. Inst., Ser. Khim. Mashinostr. Tekhnol.* **2,** 26 (1966); *CA* **67,** 118074 (1967).

[200] F. G. Holliman and H. A. Schickerling, *J. Chem. Soc.* p. 914 (1951).

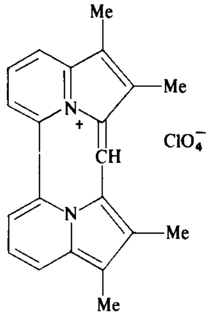
[201] M. Fraser, A. Melera, and D. H. Reid, *J. Chem. Soc., B* p. 483 (1966).

[202] J. Bailey and Kodak Ltd., *BP* 1,069,243.

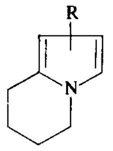
[203] L. G. S. Brooker, F. L. White, and R. H. Sprague, *J. Am. Chem. Soc.* **73,** 1087 (1951); L. G. S. Brooker, and F. L. White, *ibid.* p. 1094.



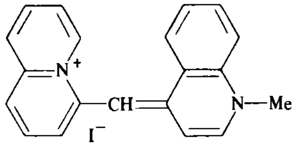
(XCIV)



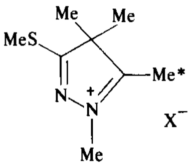
(XCV)
860 nm



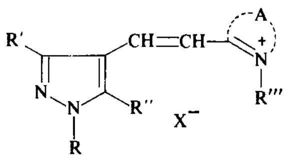
(XCVI)



(XCVII)
545 nm



(XCVIII)



(XCIX)

Boekelheide and Gall have prepared dye (XCVII) by reaction of 4-methylthioquinolizinium iodide with 1,4-dimethylquinolinium iodide.[204]

2. *Two Nitrogen Atoms*

a. Pyrazoles. The methyl group* in a 4*H*-pyrazole quaternary salt such as (XCVIII) is reactive, enabling cyanines to be prepared.[205] Reaction of a 4-pyrazolealdehyde with reactive methyl quaternary salts gives dimethinecyanines (XCIX), which have been claimed as textile dyes[206]; the 1-pyrazoline-3-aldehyde (C) similarly gives dimethinecyanines.[207] Styryl dyes from 3-methyl (or 3,5-dimethyl)-1,2-disubstituted pyrazolium salts are said to be useful sensitizers for high-energy electrons.[208]

b. Imidazoles. By making use of the reactive methyl- and alkylthio groups in 4*H*-imidazolium salts (CI), Duffin and Kendall were able to

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[204] V. Boekelheide and W. G. Gall, *J. Org. Chem.* **19**, 499 (1954).

[205] J. D. Kendall, G. F. Duffin, and Ilford, *BP* 730,489.

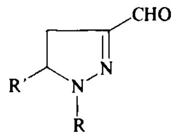
[206] J. D. Kendall, G. F. Duffin, and Ilford, *BP* 797,144.

[207] A. F. Plue and G, *USP* 3,013,015; 3,073,820.

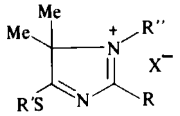
[208] R. Wizinger and CIBA, *USP* 2,671,783.

prepare two series of cyanines; if both groups were reacted appropriately, then trinuclear dyes of type (CII) could be obtained.[209]

True imidazole cyanines, analogous to the well-known benzimidazole dyes, have only recently been obtained; reaction of a 1,3-disubstituted-2-cyanomethylimidazolium salt with the usual reagents gave dyes of type (CIII).[210]

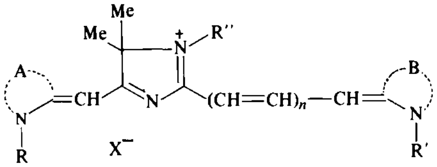


(C)

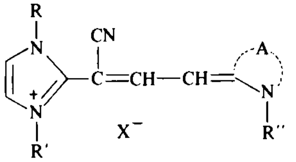


(CI)

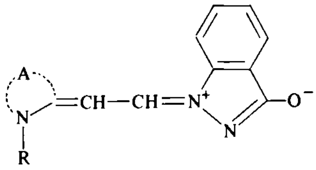
R = –Me or –SMe etc.



(CII)



(CIII)



(CIV)

c. Indazoles. Conventional cyanines containing the indazole nucleus are apparently unknown, although 3-indazolealdehyde has been condensed with ketomethylene compounds to give merocyanines.[211] However, reaction of 3-indazolone with, e.g., acetanilidovinyl quaternary salts gave novel hemicyanine dyes of type (CIV), in which the positive charge

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[209] G. F. Duffin and J. D. Kendall, *Compt. Rend. 27th Congr. Intern. Chim. Ind., Brussels, 1954* Vol. 3; see *Ind. Chim. Belge* **20,** Spec. No., 599 (1955); cf. K. Lempert and K. Zauer, *Acta Chim. Acad. Sci. Hung.* **50,** 303 (1966).

[210] H. Depoorter, M. J. Libeer, J. M. Nys, and Gevaert, *BP* 1,058,303.

[211] M. A. Kazanbieva, B. A. Tertov, and F. T. Pozharskii, *Khim. Geterotsikl. Soedin,* p. 394 (1965); *CA* **63,** 14847 (1965).

is shared with the nitrogen atom of ring A by normal cyanine mesomerism (these are "holopolar" dyes on Brooker's terminology[124]).[212]

d. Pyridazine and Its Benzo Derivatives. A quaternized $N_{(1)}$ in pyridazine activates a 4- or 6-methyl group or a 6-methylthio group for dye formation; dyes have been prepared from 4,5-dihydropyridazines similarly.[213]

Cyanine and styryl dyes have been prepared from 4-methylcinnoline salts,[214] and by reaction of the methylthio group in the indenophthalazine (CV) (merocyanines also).[215]

e. Benzo Derivatives of Pyrimidine. Fry *et al.* have shown that 4-methyl- and 4-methylthioquinazoline are both quaternized on $N_{(1)}$, thereby proving the structure of the dyes prepared some years earlier from these quaternary salts.[216] The methyl groups in the quaternary salts (CVI)[217] and (CVII)[218] are reactive.

Jeffreys has prepared a series of cyanines, merocyanines, and some trinuclear dyes by reactions involving the reactive methyl group of perimidine quaternary salts (CVIII); the spectra of the products have been compared with those of related benzimidazole dyes.[219]

f. Quinoxalines and Phenazines. Dyes have been prepared from 1-quaternized 3-hydroxy-2-methylquinoxaline and its 7,8-benzo derivative.[217]

A 5-ethylphenazinium salt reacted with methyl quaternary salts under oxidizing conditions to give the novel phenazine cyanines (CIX); merocyanines were prepared similarly.[220] The methylene group* in the tetrahydrophenazine quaternary salt (CX) is reactive, enabling cyanines to be prepared in the normal manner.[221]

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[212] F. G. Webster, L. G. S. Brooker, and Eastman Kodak, *USP* 2,961,317.

[213] R. H. Mizzoni and P. E. Spoerri, *J. Am. Chem. Soc.* **76,** 2201 (1954); G. F. Duffin and J. D. Kendall, *J. Chem. Soc.* p. 3789 (1959).

[214] A. B. Lal. *J. Indian Chem. Soc.* **36,** 64 (1959); *Chem. Ber.* **94,** 1723 (1961).

[215] N. S. Dokunikhin and S. A. Mikhalenko, *Zh. Obshch. Khim.* **33,** 1974 (1963); *CA* **59,** 10037 (1963); *Khim. Geterotsikl. Soedin.* p. 598 (1965); p. 435 (1966); *CA* **64,** 3525 (1966); **66,** 3806 (1967).

[216] D. J. Fry, J. D. Kendall. and A. J. Morgan. *J. Chem. Soc.* p. 5062 (1960).

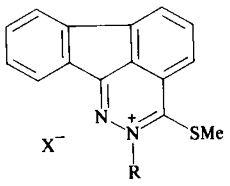
[217] L. Mandasescu, L. Stoicescu-Crivat. and I. Gabe, *Acad. Rep. Populare Romine, Filiala Iasi, Studii Cercetari Stiint., Chim.* **11,** 311 (1960); *CA* **56,** 11751 (1962); L. Mandasescu, L. Stoicescu-Crivat, I. Gabe, S. Lica. and M. Stefanescu, *ibid.* **13,** 115 (1962); *CA* **59,** 4069 (1963).

[218] L. W. Berlin, P. Heimke, and FH. *BP* 829,877.

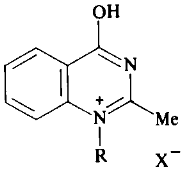
[219] R. A. Jeffreys, *Compt. Rend. 27th Congr. Intern. Chim. Ind., Brussels, 1954* Vol. 3; see *Ind. Chim. Belge* **20,** Spec. No., 618 (1955); *J. Chem. Soc.* p. 2394 (1955).

[220] A. I. Kiprianov and E. A. Ponomareva, *Ukr. Khim. Zh.* **26,** 78 (1960); *CA* **54,** 15935 (1960); A. I. Kiprianov, E. A. Ponomareva, and Ya. P. Skavinskii, *Ukr. Khim. Zh.* **26,** 237 (1960); *CA* **54,** 21765 (1960).

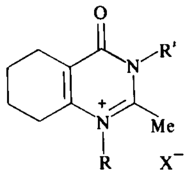
[221] A. I. Kiprianov and E. A. Ponomareva, *Ukr. Khim. Zh.* **26,** 633 (1960); *CA* **55,** 11853 (1961).



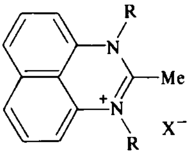
(CV)



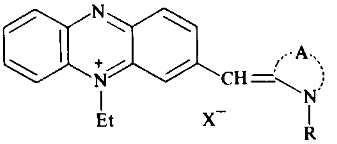
(CVI)



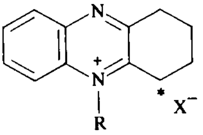
(CVII)



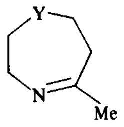
(CVIII)



(CIX)



(CX)



(CXI)

g. Diazepines. The diazepine derivative (CXI; Y = NH) has a reactive methyl group, even in the unquaternized base, enabling cyanine bases to be prepared; the benzodiazepine (CXII; Y = NR) likewise gave cyanine bases or, if quaternized, cyanines.[222,222a] The benzodiazepinone (CXIII), however, reacts at the methylene group adjacent to the carbonyl.[223]

3. *Triazoles, Tetrazoles, and Triazines*

Duffin *et al.* have prepared cyanines from 1,2,4-triazole quaternary salts possessing a reactive methyl group (CXIV; Y = CR).[224] The same

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[222] L. K. Mushkalo, *Nauk. Zap., Kiivs'k. Derzh. Univ.* **16,** 133 (1957), *CA* **53,** 18057 (1959).

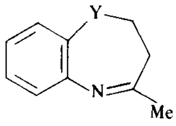
[222a] L. K. Mushkalo and Z. I. Shokol, *Ukr. Khim. Zh.* **27,** 372 (1961); *CA* **56,** 10327 (1962).

[223] H. Depoorter, M. J. Libeer, and Gevaert-Agfa, *BP* 1,074,428.

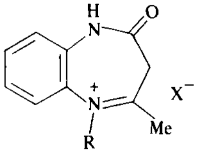
[224] G. F. Duffin, J. D. Kendall, and H. R. J. Waddington, *J. Chem. Soc.* p. 3799 (1959).

authors have also prepared dyes by reaction at a 5-methyl group in a 1,4-disubstituted tetrazolium salt (CXIV; Y = N).[225] It is to be noted that dyes prepared from azoles become progressively paler in color as the number of nitrogen atoms is increased.

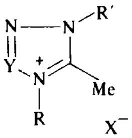
Quaternary salts of 1,2,4-triazine have a reactive 6-methyl group, and dyes have been prepared.[226]



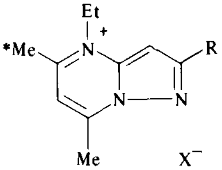
(CXII)



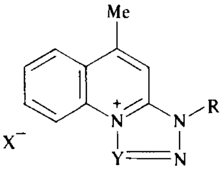
(CXIII)



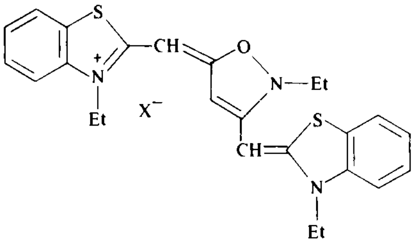
(CXIV)



(CXV)



(CXVI)



(CXVII)

4. *Complex Nuclei with Three or More Nitrogen Atoms*

A number of polyaza analogs of indolizine have been used to prepare cyanines, of which quaternary salt (CXV) may be cited as typical (the reactive methyl is indicated*).[227] The remaining examples resemble this

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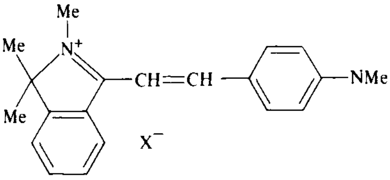
[225] A. Sieglitz, H. Hamal, and FH, *BP* 801,275; H. R. J. Waddington, G. F. Duffin, J. D. Kendall, and Ilford, *BP* 785,334.

[226] C. Cogrossi, B. Mariani, and R. Sgarbi, *Chim. Ind. (Milan)*, **46**, 530 (1964); *CA* **61**, 5821 (1964).

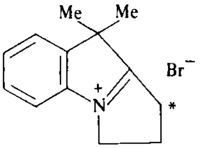
[227] W. Ried and E.-U. Köcher, *Ann. Chem.* **647**, 144 (1961).

in having, in addition to the bridgehead nitrogen, another two- three, or four nitrogen atoms, one of which is quaternized and activates an adjacent methyl group (in either ring).[228] The quaternary salts (CXVI; Y = CH or N), with a reactive methyl group in the 4-position of the quinoline ring, have also been used to prepare cyanines.[229]

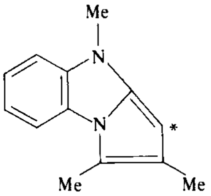


(CXVIIa)

True cyanines with an isoindole ring are as yet unknown, but Fabrycy and Kosmider have recently prepared 1,1,2-trimethyl-3-methyleneisoindoline which, like the isomeric Fischer's base, reacts with *p*-dimethylaminobenzaldehyde to give the styryl dye (CXVIIa).[229a]



(CXVIIb)



(CXVIIc)

Cyanine and merocyanine dyes have been prepared by reaction at position* in the dihydropyrroloindolium salts (CXVIIb).[229b]

The pyrrolo[1,2-*a*]indole (CXVIIc) reacts, like the indolizines, at position* to give cyanine and styryl dyes; if the 2- and 3-positions were substituted, the reaction occurred at position 1.[229c]

[228] L. G. S. Brooker, E. J. VanLare, and Eastman Kodak. *USP* 2,786,054; 2 852 384; 2,870 014; F. G. Webster. D. W. Heseltine, L. G. S. Brooker. and Eastman Kodak, *USP* 2,887,480; G. F. Duffin, J. D. Kendall, H. R. J. Waddington. and Ilford. *BP* 839,020; 862,825; L. Basaglia and B. Mariani, *Ann. Chim.* (*Rome*) **53**, 755 (1963); *CA* **59**, 15411 (1963); B. Mariani and R. Sgarbi, *Chim. Ind.* (*Milan*) **46**, 630 (1964); *CA* **61**, 12117 (1964); W. Ried and K. P. Peuchert, *Ann. Chem.* **682**, 141 (1965).

[229] L. G. S. Brooker and Eastman Kodak, *USP* 2,689,849; 2,743,274.

[229a] A. Fabrycy and A. Kosmider, *Angew. Chem. Intern. Ed. Engl.* **7**, 373 (1968).

[229b] G. L. Oliver and Eastman Kodak, *BP* 1,135,205–7.

[229c] F. S. Babichev and A. F. Babicheva, *Khim. Geterotsikl. Soedin.* p. 917 (1967); *CA* **69**, 60031 (1968).

B. NUCLEI CONTAINING NITROGEN AND OXYGEN OR SULFUR

1. *Isoxazoles*

A 3,5-dimethylisoxazole quaternary salt has two reactive methyl groups, so that a trinuclear cyanine (CXVII) or a bis-styryl dye may be prepared.[230] Novel cyanines have been prepared from 3-methylbenzisoxazole quaternary salts.[231]

2. *Thiazines*

Although cyanines containing a 5,6-dihydro-4*H*-1,3-thiazine or a 4*H*-3,1-benzothiazine nucleus had been known for some time, dyes containing a simple thiazine ring were described as recently as 1957; the quaternary salt (CXVIII) was used conventionally by reaction at the 2-methyl group.[232] Phenothiazine cyanines have been prepared by reaction of the aldehyde (CXIX) with reactive methyl compounds.[233]

3. *Thiazepines*

Corresponding to the use of diazepines (Section IV,A,2,g) Mushkalo *et al.* have prepared dyes from the 1,4-thiazepine and benzothiazepine derivatives (CXI; Y = S) and (CXII; Y = S); as the unquaternized bases were used, the products were cyanine bases.[222a,234]

4. *Complex Nuclei with a Bridgehead Nitrogen*

Babichev and Bubnovskaya have prepared cyanines from (CXX), which effectively reacts as a 4-methylpyridinium quaternary salt.[235] Similar dyes (CXXI), but of a "holopolar" type, have been prepared by Brooker *et al.*[236]

The methylene group* in (CXXII) or (CXXIII) is reactive; the resulting dyes may alternatively be considered as N,α-bridged thiazole or benzothiazole dyes (see Section V,B,3), although the absorption maxima given for the symmetrical monomethine dyes are considerably shifted

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[230] W. Lampe and J. Smolinska, *Roczniki Chem.* **28**, 163 (1954); **29**, 934 (1955); *CA* **49**, 8922 (1955); **50**, 10710 (1956).

[231] E. B. Rauch and G, *USP* 3,071,467.

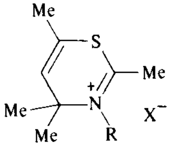
[232] H. R. J. Waddington, G. F. Duffin, J. D. Kendall, and Ilford, *BP* 848,016.

[233] L. P. Roosens and Gevaert Photo-Producten, *BP* 869,138.

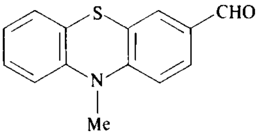
[234] L. K. Mushkalo, *Zh. Obshch. Khim.* **29**, 1030, 1034 (1959); *CA* **54**, 1538, 1539 (1960); L. K. Mushkalo and Z. I. Shokol, *Zh. Obshch. Khim.* **31**, 3069 (1961); *CA* **57**, 4796 (1962); L. K. Mushkalo and N. K. Mikhailyuchenko, *Ukr. Khim. Zh.* **30**, 202 (1964); *CA* **61**, 749 (1964).

[235] F. S. Babichev and V. N. Bubnovskaya, *Ukr. Khim. Zh.* **30**, 848 (1964); *CA* **62**, 1766 (1965).

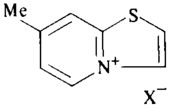
[236] L. G. S. Brooker, E. J. VanLare, and Eastman Kodak, *USP* 2,748,115.



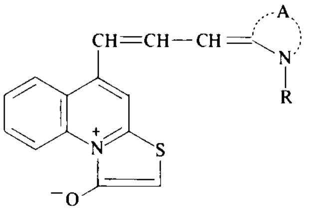
(CXVIII)



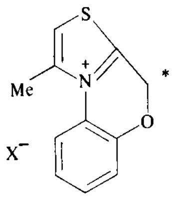
(CXIX)



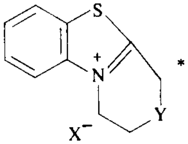
(CXX)



(CXXI)



(CXXII)
756 nm



(CXXIII)
638 nm; Y = O or S

bathochromically compared to a conventional trimethinecyanine.[237] Related dyes have been prepared by Gevaert[238,238a] and Agfa.[239]

Babichev *et al.* have also prepared dyes from the pyrrolo[2,1-*b*]-thiazole (CXXIV), i.e., an indolizine analog, with S replacing –CH=CH–, also the dibenzo analog (CXXV). Like indolizine itself, condensation occurs in the pyrrole ring, adjacent to the N atom, the dyes being of type (CXXVI). If the dyes are symmetrical, then they are mono- or trimethinecyanines, light absorption data being given for the former.[240] In the benzo derivative (CXXVII), the usual reaction site being blocked, condensation occurs at the indicated* position.[241]

[237] A. I. Kiprianov and T. M. Verbovskaya, *Zh. Obshch. Khim.* **32,** 3946 (1962); *CA* **58,** 12707 (1963); F. S. Babichev and V. P. Khilya, *Zh. Organ. Khim.* **1,** 562 (1965); *CA* **63,** 1914 (1965); A. I. Kiprianov and V. P. Khilya, *Zh. Organ. Khim.* **2,** 1478 (1966); *CA* **66,** 66721 (1967).

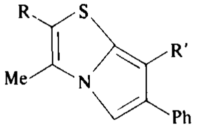
[238] M. J. Libeer, H. Depoorter, G. G. van Mierlo, R. G. Lemahieu, and Gevaert Photo-Producten, *BP* 1,001,061.

[238a] M. J. Libeer, H. A. Pattyn, J. M. Nys, and Gevaert Photo-Producten, *BP* 1,001,067.

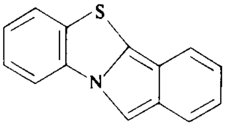
[239] O. Riester and AGFA, *BP* 1,082,977.

[240] F. S. Babichev and V. K. Kibirev, *Zh. Obshch. Khim.* **33,** 2000, 3646 (1963); *CA* **59,** 10019 (1963); **60,** 12139 (1964), F. S. Babichev, V. K. Kibirev, and L. G. Khil'ko, *Ukr. Khim. Zh.* **32,** 64 (1966); *CA* **65,** 834 (1966); cf. S. McKenzie, B. B. Molloy, and D. H. Reid, *J. Chem. Soc., C* p. 1908 (1966).

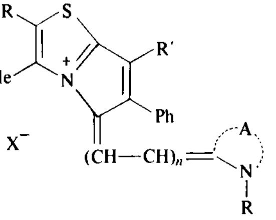
[241] A. I. Kiprianov and V. P. Khilya, *Zh. Organ. Khim.* **2,** 1474 (1966); *CA* **66,** 66720 (1967).



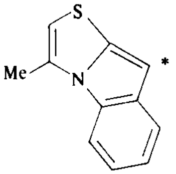
(CXXIV)
597 nm; R=H, R'=Me



(CXXV)
648 nm

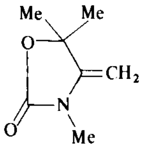


(CXXVI)

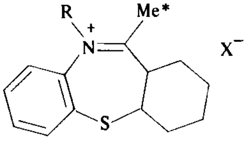


(CXXVII)
552 nm

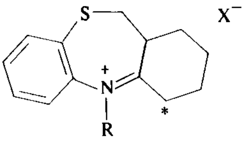
Baumann *et al.* have shown that the methylene group in the oxazolidinone (CXXVIIa) is reactive as in Fischer's base, enabling novel cyanines and styryl dyes to be prepared.[241a]



(CXXVIIa)



(CXXVIIb)



(CXXVIIc)

Mushkalo has continued his work on 7-membered heterocycles, preparing dyes by reaction at the positions indicated* in (CXXVIIb) and (CXXVIIc).[241b] Kiprianov and Khilya,[241c] and Bubnovskaya[241d] have

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[241a] H. Baumann, G. Hansen, H. R. Müller, and M. Seefelder, *Ann. Chem.* **717**, 124 (1968).

[241b] L. K. Mushkalo and N. K. Mikhailyuchenko, *Khim. Geterotsikl. Soedin.* p. 468 (1968); *CA* **70**, 30024 (1969).

[241c] A. I. Kiprianov and V. P. Khilya, *Zh. Organ. Khim.* **3**, 1091, 1097 (1967); V. P. Khilya, G. P. Kutrov, and F. S. Babichev, *Khim. Geterotsikl. Soedin.* p. 1043 (1967); *CA* **69**, 37080, 37081 (1968); **70**, 12646 (1969).

[241d] V. N. Bubnovskaya, V. S. Shvarts, and F. S. Babichev, *Ukr. Khim. Zh.* **33**, 924 (1967); *CA* **69**, 11405 (1968).

prepared cyanines from a number of novel quaternary salts with a bridgehead nitrogen, analogous to compounds (CXXII) and (CXXIII).

C. HETEROCYCLIC RINGS NOT CONTAINING NITROGEN

Although formula (I) adequately represents the traditional concept of a cyanine dye, it is now realized that various alterations in the structure are possible while still retaining the characteristic polymethine mesomeric system, represented in the case of the cyanines by the extreme canonical forms (Ia) and (Ib).

One such change concerns the nature of the terminal heteroatom. Clearly, any heterocycle containing an element —X— which, by use of a pair of unshared electrons, is able to go to the form $—X^+=$ can replace one or both of the nitrogen heterocycles in (I) (see Dähne[3]). So far, the only heterocycles so used have contained oxygen or sulfur (not, apparently, selenium), although phosphorus has been used in noncyclic terminal groups (see Section VIII,E).

Historically, the first dyes of this type were styryl derivatives of pyrylium salts, described in 1935[242]; although subsequently true cyanines containing this and the thiopyrylium nucleus were prepared. It was not until much later (1958) that dyes derived from a five-membered heterocycle (with two S atoms) were prepared, and dyes with a simple furan ring have only very recently been described.

1. *Furan and Thiophene Rings*

Fabrycy *et al.* have recently described methods for the preparation of dyes containing a simple furan ring. These were mostly of the styryl type such as (CXXVIII) or with the linkage in the 3-position of the furan ring; however, true cyanines, such as (CXXIX) were also described. These products were claimed as textile dyes.[243]

Hartmann has described the preparation of dyes from 2-morpholino-3,4-diphenylthiophene; various styryl-type dyes were claimed, also the symmetrical trimethinecyanine (CXXX).[244]

Dyes with a naphtho[1,8-*bc*]furan nucleus are unknown, but Packer and Smith ascribe the blue color formed by (CXXXI) with hydrogen chloride in acetic acid to the symmetrical methinecyanine (CXXXII).[245]

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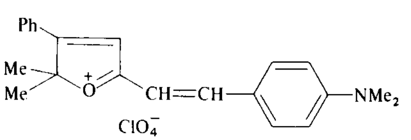
[242] Cf. *CSD II*, p. 1173.

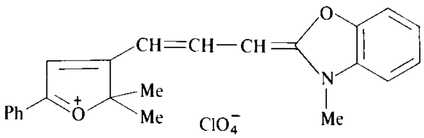
[243] A. Fabrycy, *Chimia (Aarau)* **15**, 552 (1961); *Roczniki Chem.* **40**, 1657 (1966); *CA* **66**, 94840 (1967); A. Fabrycy and K. Kozlowski, *Monatsh. Chem.* **97**, 1088 (1966); *Roczniki Chem.* **41**, 251 (1967); *CA* **67**, 33822 (1967); R. Wizinger, A. Fabrycy, and S. *SP* 429.758; 430.011.

[244] H. Hartmann, *EGP* 53,830.

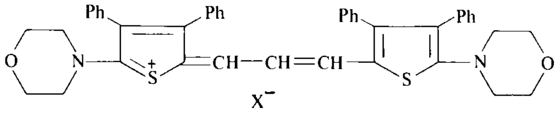
[245] R. J. Packer and D. C. C. Smith, *J. Chem. Soc., C* p. 2194 (1967).



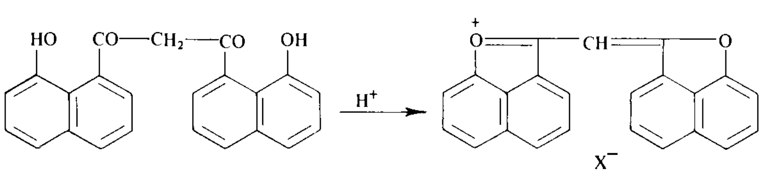
(CXXVIII)



(CXXIX)



(CXXX)



(CXXXI) (CXXXII)

2. *Dithiole Rings*

Some considerable interest has been displayed in recent years in the synthesis of dyes derived from dithiolium salts. The first such dyes were prepared by Wizinger and Soder, who showed that a 1,2-benzenedithiol would condense with malonic and glutaconic acids to give symmetrical mono- and trimethinecyanines, respectively (CXXXIII; $n = 0$ or 1); styryl dyes were also prepared.[246] Subsequently, Wizinger and Dürr prepared analogous dyes containing the 1,3-benzoxathiolium (CXXXIV) and 4,5-dihydro-1,3-dithiolium (CXXXV) nuclei[247]; light absorption data are given for the trimethinecyanines. Also, Gompper *et al.* have prepared various unsymmetrical cyanines and merocyanines containing nucleus (CXXXV).[248]

In the 1,2-dithiolium series, Schmidt *et al.* have shown that the 3-methylthio salt (CXXXVI; R = —SMe) reacts very much like an alkyl-

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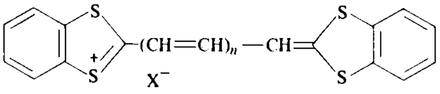
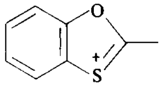
[246] R. Wizinger and L. Soder, *Chimia (Aarau)* **12,** 79 (1958); L. Soder and R. Wizinger, *Helv. Chim. Acta* **42,** 1733, 1779 (1959); cf. O. Neunhoeffer and A. Nowak, *Naturwissenschaften* **45,** 491 (1958).

[247] R. Wizinger and D. Dürr, *Helv. Chim. Acta* **46,** 2167 (1963).

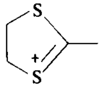
[248] R. Gompper, R. Schmidt, and E. Kutter, *Ann. Chem.* **684,** 37, (1965); R. Gompper and E. Kutter, *Chem. Ber.* **98,** 1365 (1965); R. Gompper, E. Kutter, and R. Schmidt, *ibid.* p. 1374.



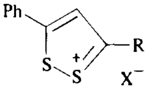
(CXXXIII)
654 nm



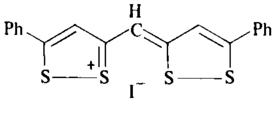
(CXXXIV)
558 nm



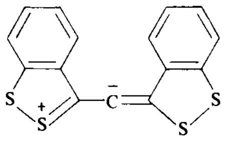
(CXXXV)
548 nm



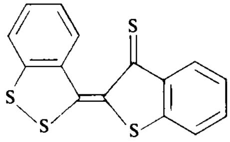
(CXXXVI)



(CXXXVII)



(CXXXVIII)



(CXXXIX)

thio-*N*-heterocyclic quaternary salt; with reactive methyl quaternary salts it gave methinecyanines, and merocyanines could be prepared likewise.[249] Klingsberg has shown that the salts (CXXXVI; R = —SMe) and (CXXXVI; R = -Me) react together to give the symmetrical dye (CXXXVII)[250]; the detailed structure of this dye, based on an X-ray analysis,[251] has been discussed by Klingsberg[250] and by Easton *et al.*[252]

By reaction of a 3-methylthio-1,2-benzodithiolium salt with malonic acid, Schmidt obtained a colored product which he claimed was the betaine (CXXXVIII); this was protonated in acid solution to the true

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[249] U. Schmidt, R. Scheuring, and A. Lüttringhaus, *Ann. Chem.* **630,** 116 (1960). Related dyes have also been described by D. Leaver, W. A. H. Robertson, and D. M. McKinnon, *J. Chem. Soc.* p. 5104 (1962); E. Campaigne and R. D. Hamilton, *J. Org. Chem.* **29,** 1711 (1964); E. Klingsberg, *ibid.* **31,** 3489 (1966); R. Pinel and Y. Mollier, *Compt. Rend.* **C264,** 1768 (1967); Y. Mollier, F. Terrier, R. Pinel, and N. Lozac'h, *Bull. Soc. Chim. France* p. 2074 (1967); M. Stavaux and N. Lozac'h, *ibid.* p. 2082.

[250] E. Klingsberg, *J. Heterocyclic Chem.* **3,** 243 (1966).

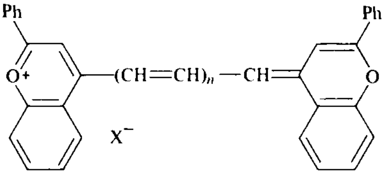
[251] A. Hordvik, *Acta Chem. Scand.* **19,** 1253 (1965).

[252] D. B. J. Easton, D. Leaver, and D. M. McKinnon, *J. Chem. Soc., C* p. 642 (1968).

methinecyanine.[253] This has now been disproved, however, by Easton *et al.* who have shown that Schmidt's compound is in fact the merocyanine (CXXXIX).[252]

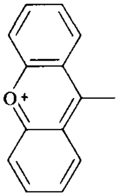
3. *Pyrans and Thiopyrans*

The earlier work on pyrylium and thiopyrylium dyes was largely concerned with the preparation of styryl dyes; a few genuine cyanine analogs, mostly symmetrical, were, however, also prepared. This work has been summarized by Hamer.[254]



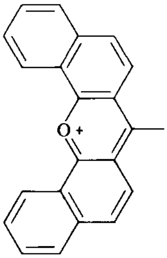
(CXL)

703 nm



(CXLI)

705 nm



(CXLII)

756 nm

Subsequently, Wizinger *et al.* have prepared symmetrical dyes, with chain lengths 1, 3, 5, and 7, of the "flavylocyanine" series (CXL), and with xanthylium nuclei (CXLI); the spectra (absorption maxima are given for the trimethinecyanines) were compared with those of the corresponding 4-quinoline and 9-acridine dyes.[255] Kamel and Shoeb have

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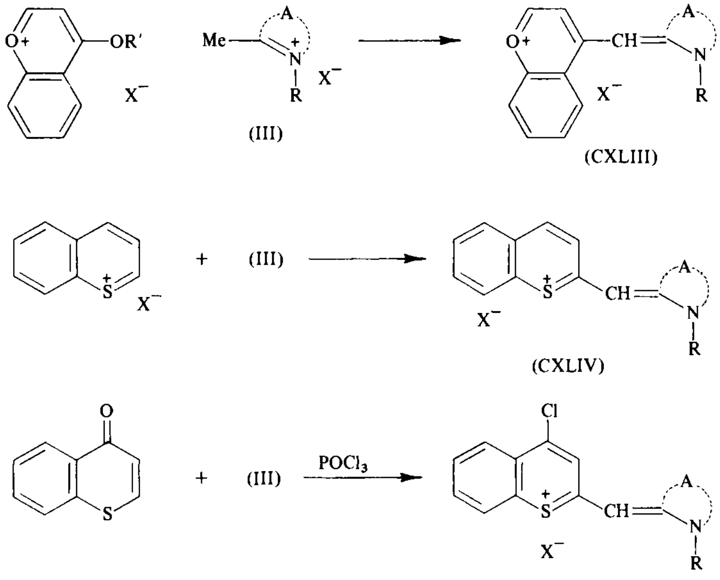
[253] U. Schmidt, *Ann. Chem.* **635**, 109 (1960).

[254] F. M. Hamer,[5] pp. 495–502.

[255] R. Wizinger and H. von Tobel, *Helv. Chim. Acta* **40**, 1305 (1957); R. Wizinger and U. Arni, *Chem. Ber.* **92**, 2309 (1959); R. Wizinger and W. Haldemann, *ibid.* **93**, 1533 (1960).

used the more complicated nuclei, dibenzo[*ch*]xanthylium (CXLII) and the [*ah*] and [*bh*] isomers.[256]

Dyes with only one pyrylium or thiopyrylium nucleus, the other being a conventional nitrogen heterocycle, were first prepared by Kiprianov and Tolmachev; reaction of a 4-alkoxybenzopyrylium salt with a reactive methyl quaternary salt gave a monomethinecyanine (CXLIII).[257] Subsequently, methinecyanines were prepared with a simple pyran or thiopyran nucleus, generally by reaction of, e.g., a 4-pyrone with the reactive methyl quaternary salt; no-chain merocyanines were obtainable similarly.[258]



(III)

(CXLIII)

(CXLIV)

(CXLV)

Other methods for the preparation of related dyes include the reaction of a methyl quaternary salt with (i) a benzothiopyrylium salt (an oxidation is involved) or (ii) with a 1-thiochromone in the presence of

---

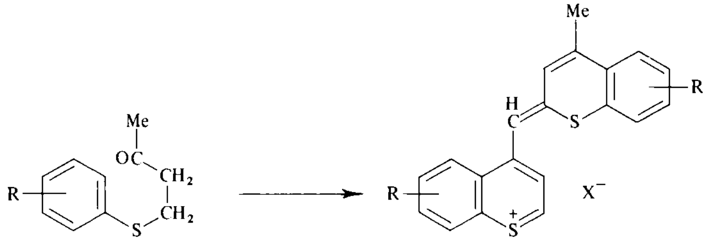
[256] M. Kamel and H. Shoeb, *Tetrahedron* **20**, 483 (1964); *Ann. Chem.* **699**, 168 (1966).

[257] A. I. Kiprianov and A. I. Tolmachev, *Zh. Obshch. Khim.* **30**, 638 (1960); *CA* **54**, 24703 (1960).

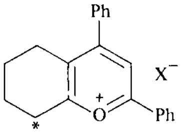
[258] M. Ohta and H. Kato, *Bull. Chem. Soc. Japan* **32**, 707 (1959); *CA*, **56**, 1422 (1962); J. Kelemen and R. Wizinger, *Helv. Chim. Acta* **45**, 1908, 1918 (1962); A. I. Tolmachev and V. P. Sribnaya, *Zh. Obshch. Khim.* **35**, 316 (1965); *CA* **62**, 16416 (1965); *Khim. Geterotsikl. Soedin.* p. 183 (1966); *CA* **65**, 20254 (1966).

phosphorus oxychloride; the products have structure (CXLIV)[259] and (CXLV),[260] respectively.

Tilak has described the formation of benzothiopyrylium dyes (CXLVI) during the polyphosphoric acid cyclization of an arylthioketone (CXLVII), and has suggested a mechanism for the reaction.[261] As this involves a hydride transfer at one stage, the yield of dye can be improved by incorporation of a hydride acceptor, e.g., trityl chloride (cf. the isocyanine synthesis, Section II,B,1).



(CXLVII) (CXLVI)



(CXLVIII)

Wizinger *et al.* have prepared dyes by reaction at the reactive methylene group* of a tetrahydrobenzopyrylium salt (CXLVIII) or of a tetrahydroxanthylium salt.[262]

In addition to preparing dyes with a simple furan ring,[243] Fabrycy has

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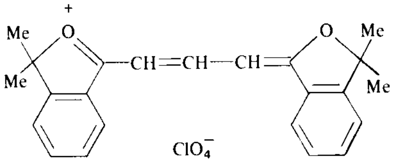
[259] A. I. Tolmachev and V. P. Sribnaya, *Zh. Obshch. Khim.* **33**, 3864 (1963); *CA* **60**, 13351 (1964); cf. R. Wizinger and H. J. Angliker, *Helv. Chim. Acta* **49**, 2046 (1966).

[260] A. I. Tolmachev and V. P. Sribnaya, *Zh. Obshch. Khim.* **32**, 383 (1962); *CA* **58**, 1446 (1963); cf. A. I. Tolmachev, V. P. Sribnaya, and L. V. Shcheglova, *Zh. Obshch. Khim.* **33**, 440 (1963); *CA* **59**, 4071 (1963).

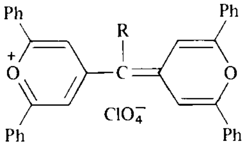
[261] B. D. Tilak, *Chimia (Aarau)* **20**, 272 (1966).

[262] L. Roosens and R. Wizinger, *Bull. Soc. Chim. Belges* **66**, 109 (1957); L. Roosens and S. Creyf, *ibid.* p. 125; W. Stevens and R. Wizinger, *Helv. Chim. Acta* **44**, 1708 (1961); H.-D. Kirner and R. Wizinger, *ibid.* pp. 1766, 1773, 1778.

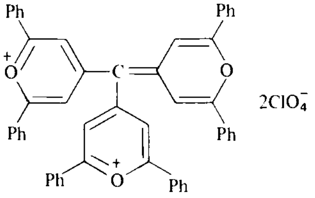
prepared the isobenzofuran cyanine (CXLVIIIa)[262a]; Malent'eva *et al.* have synthesized a number of merocyanines of this series.[262b]



(CXLVIIIa)



(CXLVIIIb)



(CXLVIIIc)

One of the products of reaction of 2,6-diphenyl-4-pyrone with cyanoacetic acid is the methin-substituted pyrylium dye (CXLVIIIb; R = —CN); the same paper also described the preparation of the novel trinuclear dye (CXLVIIIc).[262c] Reaction of the pyrone with 4-styrylpyrylium perchlorate in acetic anhydride gave the dye (CXLVIIIb; R = —CHPh.OAc).[262d]

Tilak has now published the details of his synthesis of benzothiapyrylium dyes (CXLVI) as a by-product of the cyclization of (CXLV)[262e]; the same author has also prepared a number of dyes from 4-methyl-2-phenyl-1-benzothiopyrylium and 4-methyl-2-phenylnaphtho[1,2-*b*]thiopyrylium salts.[262f]

The first cyanine in which the heterocyclic ring contained a phosphorus atom was prepared by Märkl[262g] (see the phosphinines, section VIIIE);

[262a] A. Fabrycy, *Roczniki Chem.* **36,** 243 (1962); *CA* **57,** 15041 (1962).

[262b] T. G. Melent'eva, L. A. Pavlova, and E. D. Venus-Danilova, *Zh. Obshch. Khim.* **33,** 1851, 2126, 2548 (1963); *CA* **59,** 8740, 13913 (1963); **60,** 516 (1964).

[262c] J. A. VanAllan, G. A. Reynolds, and D. P. Maier, *J. Org. Chem.* **33,** 4418 (1968).

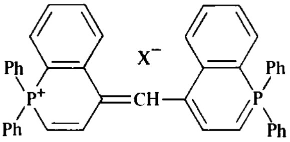
[262d] M. Simalty, J. Carretto, and S. Sib, *Tetrahedron Letters* p. 1567 (1969).

[262e] B. D. Tilak and S. K. Jain, *Indian J. Chem.* **7,** 17 (1969).

[262f] B. D. Tilak and G. T. Panse, *Indian J. Chem.* **7,** 311 (1969).

[262g] G. Märkl, *Angew. Chem. Intern. Ed. Engl.* **4,** 1023 (1965).

this dye (CXLVIIId) was obtained by reaction of 1,1-diphenyl-1-phosphanaphthalene with ethyl orthoformate.



(CXLVIIId)

D. Carbocyclic Rings

Referring to the generalized polymethine formula (II), any elements from Groups IV, V, or VI may act as the terminal atoms X and X′, at least in theory.[3] Clearly, carbon is not excluded, provided that it is capable of forming a carbonium ion in one of the extreme canonical forms. Probably the most interesting development in cyanine dye chemistry in the past few years has been the synthesis of dyes of this type, i.e., in which one or both of the terminal rings are carbocyclic.

The first examples were cyanines with azulene rings, described independently by Hafner and Treibs in 1958. Unsymmetrical dyes of structure (CXLIX; $n = 1$) were prepared by the method shown (A completes a benzothiazole, benzoselenazole, or 3*H*-indole ring), and a dye in which $n = 2$ was also prepared. Moreover, reaction of azulene with ethyl orthoformate in the presence of phosphorus oxychloride gave the symmetrical dye (CL), the first example of a cyanine in which the cation was composed solely of carbon and hydrogen.[263]

Shortly afterwards Stepanov and Aldanova described the independent synthesis of (CL) by a similar method, or by the reaction of azulene with azulene aldehyde, and compared the light absorption with that of related indolizine dyes.[264] Also, Kirby and Reid prepared a number of dyes of types (CXLIX) and (CL), including several of the latter in which the two azulene rings were differently substituted.[265] The synthesis of tri- and pentamethine vinylogs of (CL) has also been described.[266]

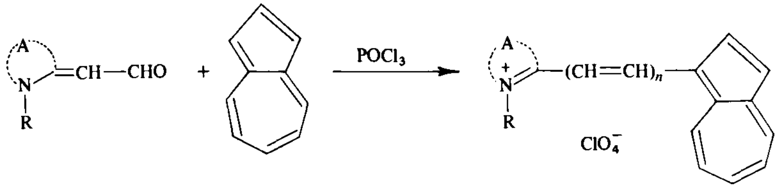
Almost simultaneously with the first preparation of azulenocyanines,[263]

[263] K. Hafner, *Angew. Chem.* **70,** 413, 419 (1958); E. J. Poppe and W. Treibs, *Naturwissenschaften* **45,** 517 (1958): *Veroeffentl. Wiss. Photolab. AGFA* **9,** 88 (1961); G. Bach, E. J. Poppe, and W. Treibs, *Naturwissenschaften* **45,** 517 (1958).

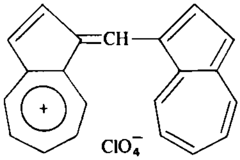
[264] F. N. Stepanov and N. A. Aldanova, *Angew. Chem.* **71,** 125 (1959); *Zh. Obshch. Khim.* **29,** 339 (1959); *CA* **54,** 462 (1960).

[265] E. C. Kirby and D. H. Reid, *J. Chem. Soc.* p. 494 (1960); pp. 163, 1724 (1961).

[266] C. Jutz, *Angew. Chem.* **71,** 380 (1959); E. C. Kirby and D. R. Reid, *J. Chem. Soc.* p. 3579 (1961).



(CXLIX)



(CL)
617 nm

Behringer *et al.* reacted guaiazulene with 5-chloromethylene-3-ethylrhodanine to obtain an azulene analog of a merocyanine (CLI).[267] Dorofeenko *et al.* have prepared azulene cyanines (dimethine) in which the other nucleus is a pyrylium ring.[268]

Some time after the first preparation of azulene cyanines, Hafner *et al* showed that a simple tropylium ring could also be incorporated into cyanines. The methyl group in methyltropylium perchlorate was reactive giving a styryl dye with *p*-dimethylaminobenzaldehyde and the symmetrical trimethinecyanine (CLII) with ethyl orthoformate.[269] Other dyes containing a tropylium ring have been described by Jutz and Voithenleitner.[270]

The tropylium ion owes its stability to the presence of the aromatic sextet of π-electrons, conforming to Hückel's $(4n + 2)$ rule, and in recent years analogs in which $n = 0$ have also been described, viz., derivatives of the cyclopropenylium ion.[271] Very recently Eicher and Hansen have

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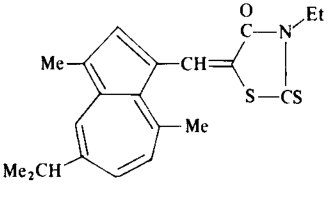
[267] H. Behringer, E. Dillinger, H. Suter, and K. Kohl, *Chem. Ber.* **91**, 2773 (1958); cf. also W. Treibs, C. Vollrad, and M. Reimann, *Ann. Chem.* **648**, 164 (1961); F. N Stepanov and A. G. Yurchenko, *Zh. Organ. Khim.* **2**, 150 (1966); *CA* **64**, 17753 (1966).

[268] G. N. Dorofeenko, Yu. A. Zhdanov, A. D. Semenov, V. A. Palchkov, and S. V Krivun, *Zh. Obshch. Khim.* **36**, 1728 (1966); *CA* **66**, 55327 (1967).

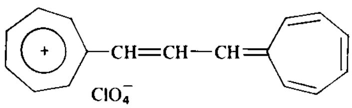
[269] K. Hafner, H. W. Riedel, and M. Danielisz, *Angew. Chem.* **75**, 344 (1963).

[270] C. Jutz and F. Voithenleitner, *Chem. Ber.* **97**, 29, 1590 (1964); C. Jutz, *ibid* p. 2050; cf. Y. Kitahara, I. Murata, and T. Asano, *Bull. Chem. Soc. Japan* **37**, 924 (1964); *CA* **61**, 10623 (1964).

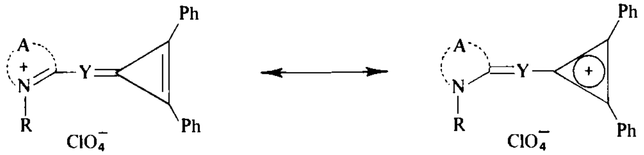
[271] This topic has been reviewed by A. W. Krebs, *Angew. Chem. Intern. Ed. Engl* **4**, 10 (1965).



(CLI)



(CLII)
604 nm



(CLIII)

Y = —CH=, —C(CN)=, —C(CO$_2$Me)=, or —N=

prepared some compounds (CLIII), in which one of the extreme resonance forms contains such an ion, and which can therefore be considered as cyanines of the cyclopropenylium series.[272] The synthesis of symmetrical cyanines in this series is awaited with interest.

In his studies of the Vilsmeier formylation of unsaturated hydrocarbons, Jutz has prepared the aldehyde (CLIV) from the methylenecyclohexadiene (CLV) as shown. This aldehyde reacted with reactive methyl quaternary salts to give cyanines such as (CLVI); with the hydrocarbon (CLV) it gave the remarkable symmetrical dye (CLVII), in which the positive charge is delocalized by mesomerism over the whole conjugated system, but in which neither of the terminal rings is aromatic.[273]

Jutz has also described methods for the preparation of symmetrical mono- or trimethine dyes from ferrocene, which can presumably be regarded as cyanines (CLVIII).[274]

Complementary to the above dyes with a mesomeric carbonium ion are a number of polymethine dyes with a mesomeric anion. In fact, as Dähne has pointed out, the latter dyes are the true analogs of the cyanines, merocyanines, oxonols, etc., insofar as they all have $(p + 1)$ π-electrons spread over p atoms. The carbonium dyes, such as (CL), (CLII), and

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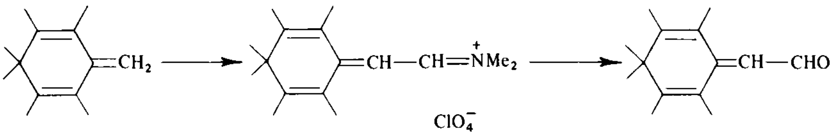
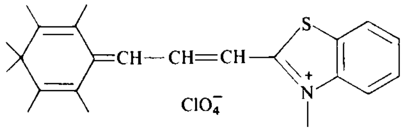
[272] T. Eicher and A. Hansen, *Tetrahedron Letters* p. 4321 (1967).

[273] C. Jutz, W. Müller and E. Müller, *Chem. Ber.* **99**, 2479 (1966); C. Jutz, *Compt. Rend. 36th Congr. Intern. Chim. Ind., Brussels, 1966* Vol. 3; see *Ind. Chim. Belge* **32**, Spec. No., 127 (1967).

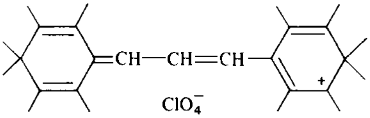
[274] C. Jutz, *Tetrahedron Letters* No. 21, 1 (1959); cf. A. Treibs and R. Zimmer-Galler, *Chem. Ber.* **93**, 2359 (1960).



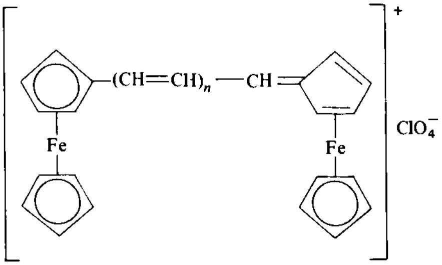
(CLV) (CLIV)



(CLVI)
503 nm



(CLVII)
650 nm



(CLVIII)
785 nm; $n = 1$

(CLVII), on the other hand, are exceptional in having only $(p-1)\pi$-electrons, although still conveniently classed as polymethines.[3]

The first such anionic dye was prepared by Kuhn and Fischer, who treated the hydrocarbon (CLIX) with alkali in tetrahydrofuran to obtain an intensely blue solution containing the anion (CLX); an alternative mesomeric form can, of course, be written with the negative charge on the other fluorene ring.[275] In a number of subsequent papers on highly acidic hydrocarbons, Kuhn and his co-workers have prepared colored anions from many compounds related to (CLIX); these include mono- and pentamethine analogs of (CLX) and various aza derivatives.[276]

Shortly after Kuhn's first publication,[275] Jutz and Amschler described the preparation of similar anionic dyes, including those from cyclopentadiene (CLXI) and indene. The method of preparation involved reaction

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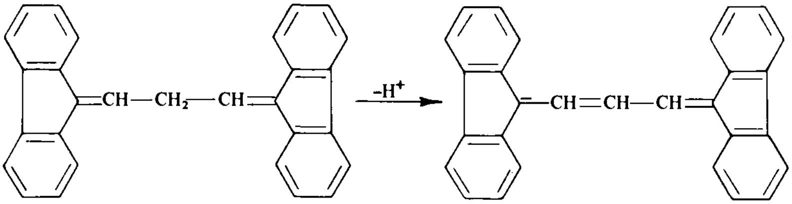
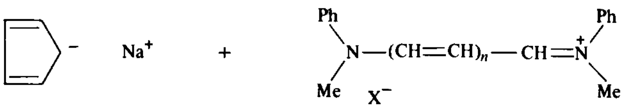
[275] R. Kuhn and H. Fischer, *Angew. Chem.* **73**, 435 (1961).

[276] R. Kuhn and D. Rewicki, *Tetrahedron Letters* p. 3513 (1965), and earlier papers; cf. C. Jutz and H. Amschler, *Angew. Chem.* **76**, 302 (1964).

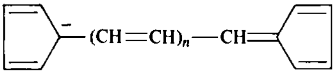


(CLIX)

(CLX)
633 nm



(CLXII)



$n = 0, 1$ or 2

(CLXI)

(CLXIIIa) (CLXIIIb)

of the sodio (or lithio) derivative of the hydrocarbon with compounds of type (CLXII); unsymmetrical products were also obtained.[277]

Reference must also be made to various heterocyclic derivatives of cyclopentadiene or its benzo derivatives (e.g., CLXIII; Y = O or $\rangle$N—R). A number of these are now known, and dipole moment measurements indicate a high contribution from the zwitterionic structure (CLXIIIb), so that they can be regarded as analogs of the merocyanines in which the cyclopentadiene ring takes the place of the usual ketomethylene component.[278]

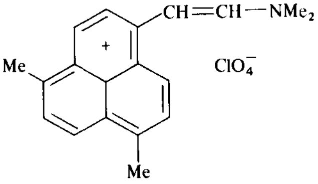
[277] C. Jutz and H. Amschler, *Angew. Chem.* **73**, 806 (1961).

[278] J. A. Berson, E. M. Evleth, and Z. Hamlet, *J. Am. Chem. Soc.* **87**, 2887 (1965) (this refers to earlier work also); J. A. Berson, E. M. Evleth, and S. L. Manatt, *ibid.* pp. 2901, 2908; J. H. Crabtree and D. J. Bertelli, *ibid.* **89**, 5384 (1967); G. Seitz, *Angew. Chem. Intern. Ed. Engl.* **6**, 82 (1967); cf. E. D. Bergmann, *Chem. Rev.* **68**, 41 (1968).

A useful discussion of *inter alia* cyanines with carbocyclic end-groups is contained in a paper by Hünig.[278a]

Further examples of dyes containing a cyclopropenylium ring (see ref. 272) have been provided by Hill and Battiste.[278b]

The compound (CLXIIIc), recently prepared by Dingwall *et al.*, may be regarded as the first example of a polymethine (actually a hemicyanine) of the phenalene series.[278c]



(CLXIIIc)

V. Variations in the Polymethine Chain and the Anion

A. Substituents on the Chain

1. *General*

It was discovered about 40 years ago that trimethinecyanines could be prepared with an alkyl group on the meso carbon atom of the chain, a modification that frequently led to dyes of improved sensitizing properties. Since then, a great variety of other substituents have been introduced into the polymethine chain, including difunctional substituents attached to two atoms of the chain (see the following section, B).

The literature to 1959 on chain-substitution has been adequately reviewed by Hamer,[279] so that the following discussion will concentrate on the more interesting work published since then.

Kiprianov and Suleimanova have discussed the effect on light absorption of benzothiazole trimethinecyanines with a variety of substituents in the α- or α, α'-positions.[280,280a] The relationship between the electronic

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[278a] S. Hünig, *1964 Opt. Anregung Org. Syst., Int. Farbensymp., 2nd, Schloss Elmau, Ger.* 184 (1966).

[278b] J. H. M. Hill and M. A. Battiste, *Tetrahedron Letters* pp. 5537. 5541 (1968).

[278c] J. G. Dingwall, D. H. Reid, and K. Wade, *J. Chem. Soc. C*, p. 913 (1969).

[279] F. M. Hamer,[5] particularly pp. 77–80 (methinecyanines), pp. 148–162 (trimethinecyanines), pp. 270–277 (bridged chains), pp. 520–527 (merocyanines), and pp. 696–698 (color and constitution).

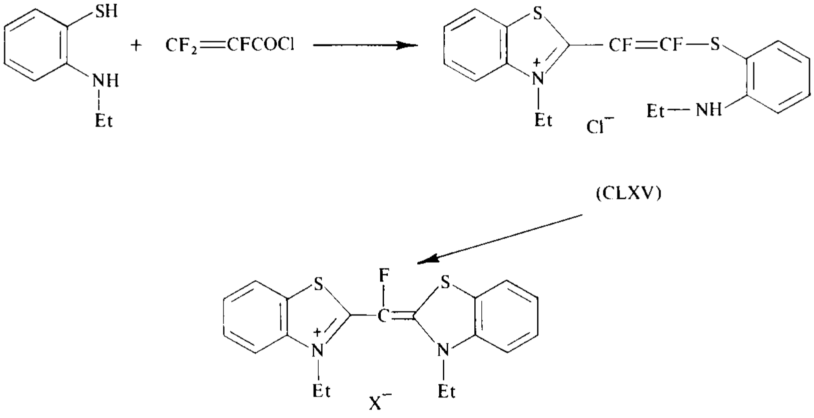
[280] A. I. Kiprianov and M. G. Suleimanova. *Ukr. Khim. Zh.* **31**, 1281 (1965); *CA* **64**, 14318 (1966).

[280a] A. I. Kiprianov and M. G. Suleimanova, *Ukr. Khim. Zh.* **33**, 589 (1967); *CA* **68**, 40977 (1968).

character of some substituents in the meso position of benzothiazole heptamethinecyanines and the photographic properties of the dyes has been discussed by Kheinman.[281]

2. *Halogens*

Although *meso*-chloro- and *meso*-bromopentamethinecyanines were prepared as long ago as 1930 (the spectra of these dyes have been discussed by Jezewski[282]) and bromo-substituted trimethinecyanines in 1948,[283] it is only comparatively recently that halogen-substituted monomethinecyanines have been prepared. Thus, dye (CLXIV) could be prepared conventionally by reaction of a 2-fluoromethylbenzothiazolium salt with an alkylthiobenzothiazolium salt.[284] Later, it was prepared directly from *o*-ethylaminothiophenol by reaction with trifluoroacrylyl chloride; by working at —30°, the intermediate (CLXV) could be isolated.[285] Tri- and pentamethinecyanines and merocyanines with α-fluoro substituents



(CLXV)

(CLXIV)
453 nm

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[281] A. S. Kheinman, S. V. Natanson, N. S. Spasokukotskii, A. F. Vompe, and R. V. Karaul'shchikova, *Zh. Nauchn. i Prikl. Fotogr. i Kinematogr.* **13,** 44 (1968); *CA* **68,** 100650 (1968).

[282] Z. Jezewski, A. Szuchnik, and J. Swiderski, *Roczniki Chem.* **30,** 467 (1956); *CA* **51,** 13570 (1957).

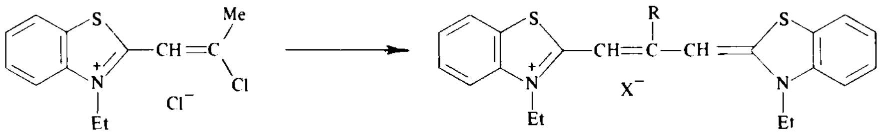
[283] F. M. Hamer[279]; cf. also A. I. Kiprianov and Ya. Shtets, *Zh. Obshch. Khim.* **33,** 3519 (1963); *CA*, **60,** 10839 (1964).

[284] L. M. Yagupol'skii and B. E. Gruz, *Zh. Obshch. Khim.* **31,** 3955 (1961); *CA* **57,** 9989 (1962).

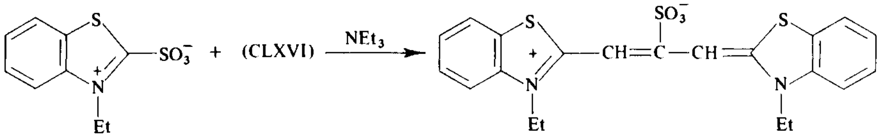
[285] B. E. Gruz, R. I. Sterlin, and L. M. Yagupol'skii, *Zh. Obshch. Khim.* **34,** 4122 (1964); *CA* **62,** 16225 (1965).

were also prepared.[284] So far, monomethinecyanines with one of the other halogens on the methine link have not been prepared.

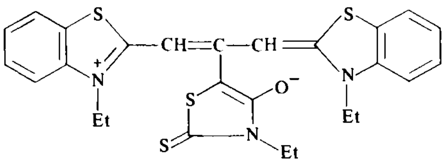
It appears that a halogen atom in the meso position of a trimethinecyanine would be too reactive for the dye to be isolated. This would explain the intriguing products obtained by Levkoev *et al.* in reactions of the chloropropenyl quaternary salt (CLXVI); thus, with an alkylthio quaternary salt the dye (CLXVII; R = SEt) was obtained, presumably by reaction of the initially formed chloro dye (CLXVII; R = Cl) with the liberated ethanethiol. Reaction of (CLXVI) with the betaine (CLXVIII) and triethylamine in ethanol gave dye (CLXVII; R = OEt) among a variety of other products, some of them too unstable to isolate; in chloroform, however, the main product of this reaction was the dye (CLXIX). The $-SO_3^-$ group in the latter was very reactive, giving with sodium methoxide and aniline, for instance, the dyes (CLXVII; R = OMe) and (CLXVII; R = -NHPh); with 3-ethylrhodanine the "holopolar" trinuclear dye (CLXX) was formed.[286]



(CLXVI) (CLXVII)



(CLXVIII) (CLXIX)



(CLXX)

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[286] I. I. Levkoev, N. N. Sveshnikov, and N. I. Shirokova, *Dokl. Akad. Nauk SSSR* **153,** 350 (1963); *CA* **60,** 8164 (1964).

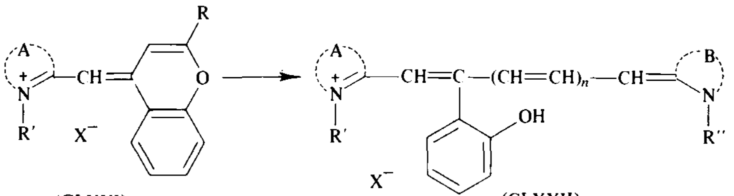
3. *Cycloalkyl Groups*

Neunhoeffer and Bohg prepared a benzothiazole trimethinecyanine with a *meso*-cyclopentyl substituent; this dye aggregates well and is a good sensitizer, so presumably the cycloalkyl group is twisted out of the plane of the remainder of the molecule.[287] The cyclopropyl, cyclobutyl, and cyclohexyl substituents were subsequently used by Kheifets and Sveshnikov.[288]

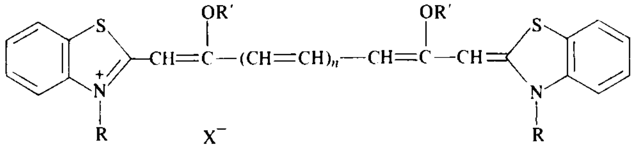
4. *Aryl Groups*

The steric hindrance in *meso*-phenyl pyridocarbocyanines, and in indocarbocyanines has been discussed.[289]

Tolmachev and Shcheglova have described the formation of *o*-hydroxyphenyl-substituted dyes by reactions of benzopyrylium cyanines which involve opening of the heterocyclic ring. Thus, reaction of (CLXXI; R = H) with a 2-methyl quaternary salt gives a pentamethinecyanine (CLXXII; $n = 1$), while (CLXXI; R = Cl) with an *o*-alkylaminothiophenol gives a trimethinecyanine (CLXXII; $n = 0$).[290]



(CLXXI) (CLXXII)



(CLXXIII)

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[287] O. Neunhoeffer and K. Bohg, *Chem. Ber.* **91,** 1319 (1958).

[288] S. A. Kheifets and N. N. Sveshnikov, *Kinotekhn., Nauchn.-Tekhn. Sb.* p. 19 (1963); *CA* **61,** 13454 (1964).

[289] A. I. Kiprianov and G. G. Dyadyusha, *Dopovidi Akad. Nauk Ukr. RSR* p. 1119 (1959); *CA* **55,** 565 (1961); N. I. Shirokova, I. I. Levkoev, and N. N. Sveshnikov, *Zh. Vses. Khim. Obshchestva im. D. I. Mendeleeva* **7,** 587 (1962); *CA* **58,** 6954 (1963).

[290] A. I. Tolmachev, *Zh. Obshch. Khim.* **30,** 2892, 3640 (1960); *CA* **55,** 17313, 22829 (1961); A. I. Tolmachev and L. V. Shcheglova, *Zh. Obshch. Khim.* **33,** 448 (1963); *CA* **59,** 4072 (1963).

5. *Alkoxy Groups*

A group of Russian patents describe hepta-, nona-, and undecamethinecyanines with the β- and β'-carbon atoms carrying alkoxy groups (CLXXIII; $n = 1$, 2, or 3).[291] Reaction of such a heptamethinecyanine (CLXXIII; $n = 1$) with ammonia or an amine is said to replace one of the alkoxy groups by an amino group.[292]

Tri- and pentamethinecyanines with a β-substituent of type $-Y(CH_2)_nSO_3^-$ (where Y is O or S) have been claimed as sensitizers.[293]

6. *Acyl Groups*

Taki has shown that a by-product in the formation of a thiazole trimethinecyanine, by reaction of the 2-methyl quaternary salt with ethyl orthoformate and acetic anhydride, is the α-acetyl trimethinecyanine. Such dyes can also be prepared by reaction of the unsubstituted dye with acetic anhydride.[294]

7. *Nitro Groups*

Riester has shown that a 2-alkylthio quaternary salt will react with nitromethane to form the nitromethylene base (CLXXIV), from which α-nitrotrimethinecyanines can be prepared by conventional reactions.[295]

Reichardt has reinvestigated the formation of a γ-nitropentamethinecyanine (CLXXV; A = B) by reaction of a methyl quaternary salt with nitromalonaldehyde. By carrying out the reaction in ethanol plus piperidine he was able to isolate an intermediate (CLXXVI), which he considered as a novel type of merocyanine; further reaction of this with a quaternary salt gave the pentamethinecyanine.[296]

8. *Azo Substituents*

Treibs and Zimmer-Galler have shown that a trimethinecyanine will undergo azo coupling with an aryldiazonium salt, the arylazo group

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[291] N. N. Sveshnikov, S. A. Kheifets, and N. S. Stokovskaya, *RP* 109,457; *CA* **53,** 3718 (1959); S. A. Kheifets and N. N. Sveshnikov, RP 162,902-3; *CA* **61,** 16212, 14830 (1964).

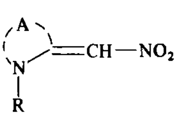
[292] S. A. Kheifets, N. N. Sveshnikov and G. F. Kurepina, *RP* 126,206; *CA* **54,** 16851 (1960).

[293] I. I. Levkoev, E. B. Lifshits, V. V. Durmashkina, and G. F. Kurepina, *RP* 184,614-5; *CA* **66,** 10926, 24431 (1967); G. E. Ficken and Ilford, *BP* 1,051,056.

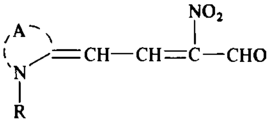
[294] K. Taki, *J. Sci. Res. Inst. (Tokyo)* **49,** 185, 254, 331 (1955); *Rept. Sci. Res. Inst. (Tokyo)* **32,** 81 (1956); *CA* **51,** 373 (1957).

[295] O. Riester, *Mitt. Forschungslab. Agfa Leverkusen-Muenchen* **1,** 44 (1955).

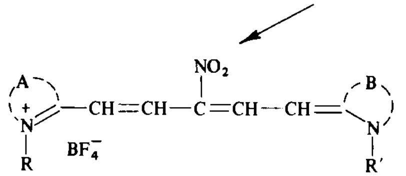
[296] C. Reichardt, *Tetrahedron Letters* p. 429 (1965).



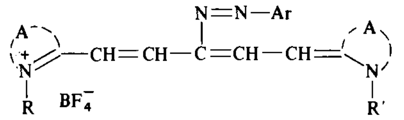
(CLXXIV)



(CLXXVI)



(CLXXV)



(CLXXVII)

entering at the α-carbon atom.[297] An alternative method of preparation of this type of dye has been given by Wahl.[298]

For the preparation of a γ-arylazopentamethinecyanine (CLXXVII), Reichardt reacted a methyl quaternary salt with the arylhydrazone, $ArNHN{=}C(CHO)_2$; no intermediate was isolated.[299]

9. *Other Substituents*

Babichev and Kiprianov have demonstrated that the reaction product (VII) of a benzothiazolium methylene base with methyl iodide has a reactive methyl group; with a sulfobetaine of type (CLXVIII) it gives the meso-substituted dye (CLXXVIII).[300]

By the use of conventional reactions, von Rintelen has prepared trimethinecyanines (also merocyanines) with *meso*-3- and 4-pyridyl substituents. The light absorption of symmetrical *N,N′*-diethylbenzothiazole dyes was similar to that of the *meso*-phenyl dye, although the sensitizing

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[297] A. Treibs and R. Zimmer-Galler, *Ann. Chem.* **627,** 166 (1959).

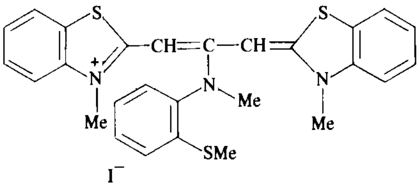
[298] H. Wahl, *Chimia* (*Aarau*) **15,** 126 (1961); P. Lochon and H. Wahl, *ibid.* **19,** 218 (1965).

[299] C. Reichardt, *Angew. Chem.* **77,** 508 (1965).

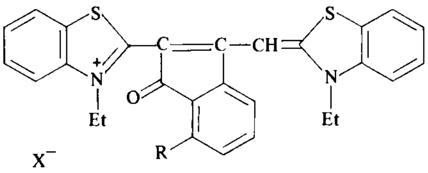
[300] F. S. Babichev and A. I. Kiprianov, *Zh. Obshch. Khim.* **28,** 209 (1958); *CA,* **52,** 12848 (1958).

action was not quite as great. If the pyridyl groups were quaternized, however, the absorption was shifted bathochromically and the intensity was reduced, while the sensitization was much weaker; this indicates severe steric hindrance in these quaternized pyridyl dyes.[301]

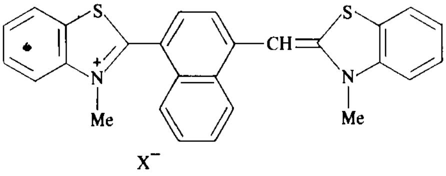
Among the α-substituted trimethinecyanines examined by Kiprianov and Suleimanova were some with a quaternary pyridine substituent (attached by the nitrogen); light absorption was hypsochromic, with reduced intensity.[280a]



(CLXXVIII)
493 nm



(CLXXIX)



(CLXXX)
514 nm

Sych and Umanskaya have discussed the effect on the light absorption of various electronegative substituents in the α and αα′ positions of thiazole trimethinecyanines.[301a]

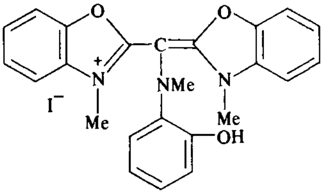
Yagupol'skii has extended his work on cyanines with chain fluorine substituents (see refs. 284, 285) to the synthesis of trimethinecyanines with β-fluoro and α, β-difluoro substituents. Fluorine atoms in the α-positions cause a bathochromic shift of the light absorption, whilst a β-fluoro substituent is hypsochromic. Dyes with a β-CH_2F substituent have also been prepared.[301b]

[301] H. von Rintelen, *Mitt. Forschungslab. Agfa Leverkusen-Muenchen* **2,** 141 (1958).

[301a] E. D. Sych and L. P. Umanskaya, *Ukr. Khim. Zh.* 34, 604 (1968); *CA* **70,** 20966 (1969).

[301b] L. M. Yagupol'skii and B. E. Gruz, *Zh. Obshch. Khim.* 37, 2470 (1967); L. M. Yagupol'skii, B. E. Gruz, and L. I. Katerinenko, *ibid.* 38, 1732 (1968); *CA* **68,** 106061 (1968); **70,** 5212 (1969).

Wanzlick and Steinmaus have shown that treatment of 3-methylbenzoxazolium iodide with triethylamine leads to the formation of the substituted monomethinecyanine (CLXXXa).[301c]



(CLXXXa)

B. Bridged Chains

1. *Chains Incorporating a Carbocyclic Ring*

In addition to the examples discussed by Hamer,[279] the following rings have been incorporated into the polymethine chain:

a. Indanone. Jeffreys has shown that trimethinecyanines (and merocyanines) with a *meso-o*-carboxyphenyl substituent can be cyclized by the action of acetic anhydride to give dyes of structure (CLXXIX).[302]

b. Naphthalene. Kiprianov and Shulezhko have prepared the dye (CLXXX) and the isomer in which the chain is incorporated into the naphthalene ring at the 1,5-positions; the latter dye absorbs at the lower wavelength.[303]

c. Cyclohexene. The most valuable procedure to date for synthesizing long-chain polymethinecyanines (up to 13 methine links) involves the incorporation of one or two β,δ-neopentylene bridges. In addition to the patents reviewed by Hamer,[279] these dyes have been discussed by Brooker and Vittum.[304] Corben *et al.* have described the formulation of a photographic emulsion with a sensitizing maximum at 1060 nm which uses such a dye (CLXXXI).[305]

d. Cyclobutenone. Treibs and Jacob have recently shown that "squaric

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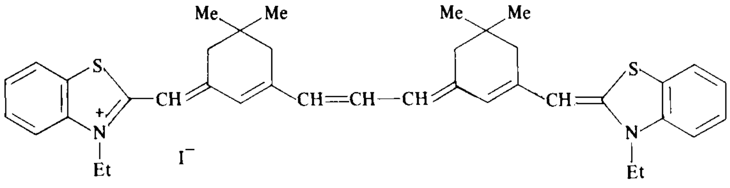
[301c] H. W. Wanzlick and H. Steinmaus, *Chem. Ber.* **101,** 244 (1968).

[302] R. A. Jeffreys, *J. Chem. Soc.* p. 5824 (1963).

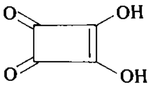
[303] A. I. Kiprianov and A. A. Shulezhko, *Zh. Organ. Khim.* **2,** 1852 (1966); *CA* **66,** 47297 (1967).

[304] L. G. S. Brooker and P. W. Vittum, *J. Phot. Sci.* **5,** 71 (1957); cf. C. E. K. Mees and T. H. James,[2] p. 204. Related dyes have also been prepared by A. I. Tolmachev and V. P. Sribnaya, *RP* 172,435; *CA* **64,** 2206 (1966).

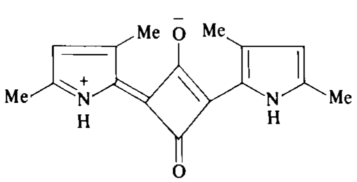
[305] L. Corben, F. Dow, and R. Wilkins, *J. Phot. Sci.* **15,** 265 (1967).



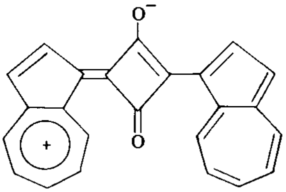
(CLXXXI)



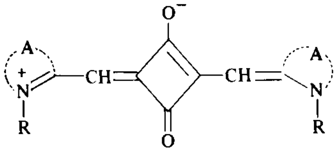
(CLXXXII)



(CLXXXIII)
550 nm



(CLXXXIV)
680 nm



(CLXXXV)

acid" (quadratic acid) (CLXXXII) condenses with pyrroles to form dyes of type (CLXXXIII).[306] Subsequently, Ziegenbein and Sprenger condensed squaric acid with azulene to give (CLXXXIV) and with reactive methyl quaternary salts to give dyes of structure (CLXXXV).[307] On paper, all of these dyes appear to be cyanines of the holopolar type (with the meso O^-) carrying an additional α,α' or β,β' CO bridge. However, Dähne and Leupold consider it problematical whether they should strictly be regarded as cyanines.[308]

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[306] A. Treibs and K. Jacob, *Angew. Chem.* **77**, 680 (1965); *Ann. Chem.* **699**, 153 (1966); A. Treibs, *Chimia (Aarau)* **20**, 329 (1966); cf. G. Maahs and P. Hegenberg, *Angew. Chem. Intern. Ed. Engl.* **5**, 888 (1966).

[307] W. Ziegenbein and H.-E. Sprenger, *Angew. Chem. Intern. Ed. Engl.* **5**, 893 (1966); H.-E. Sprenger and W. Ziegenbein, *ibid.* **6**, 553 (1967).

[308] S. Dähne and D. Leupold, *Angew. Chem. Intern. Ed. Engl.* **5**, 984 (1966).

2. *Chains Incorporating a Heterocyclic Ring*

Ficken and Kendall have described synthetic methods for cyanines with a heterocyclic ring such as furan, thiophene, or dihydropyran fused to adjacent carbon atoms of the chain, e.g. (CLXXXVI); the light absorption of the dyes was discussed.[309] Kiprianov and Shulezhko have prepared dyes (penta- and heptamethinecyanines) such as (CLXXXVII) in which the chain incorporates all four carbon atoms of a furan ring.[310]

3. *Dyes with an N, α Bridge*

Authentic quaternary salts of type (CLXXXVIII) were first prepared by the route shown by Babichev and Neplyuev[311]; these authors disproved earlier claims to have prepared such salts by reaction of 2-methylbenzothiazole with an alkylene dibromide. By reacting with conventional reagents at the methylene group*, dyes such as (CLXXXIX) were prepared, also related bridged styryl dyes and merocyanines. Subsequently, dyes were prepared from similar cyclic quaternary salts of the simple thiazole,[312] benzimidazole,[238,313] tetrazole,[238a] or 3*H*-indole[314] series. Dyes in which one of the methylene groups is replaced by a heteroatom have already been discussed (Section IV,B,4).

The synthesis of chain *o*-hydroxyphenyl cyanines by ring-opening of pyrylium dyes (CLXXI) has been extended to the preparation of complex bridged nonamethinecyanines such as (CLXXXIXa).[314a]

Shulezhko and Kiprianov have prepared a series of heptamethinecyanines in which the chain passes through a benzene ring as in (CLXXXIXb), or likewise through a naphthalene (1,4) or anthracene (9,10) nucleus.[314b]

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[309] G. E. Ficken and J. D. Kendall. *Chimia (Aarau)* **15**, 110 (1961).

[310] A. I. Kiprianov and A. A. Shulezhko, *Zh. Obshch. Khim.* **34**, 3932 (1964); *CA* **62**, 7902 (1965); *Zh. Organ. Khim.* **1**, 352 (1965); *CA* **63**, 709 (1965).

[311] F. S. Babichev and V. M. Neplyuev, *Zh. Obshch. Khim.* **32**, 857, 860 (1962); *CA* **58**, 4535 (1963); F. S. Babichev, *Zh. Obshch. Khim.* **33**, 3016 (1963); *CA* **60**, 1728 (1964); F. S. Babichev, N. V. Dzhigirei, and S. P. Gukalov, *Zh. Obshch. Khim.* **34**, 2433 (1964); *CA* **61**, 13454 (1964); F. S. Babichev and E. Shchetsinskaya, *Zh. Obshch. Khim.* **34**, 2441 (1964); *CA* **61**, 14816 (1964); cf. L. L. Lincoln, D. W. Heseltine, and Eastman Kodak, *USP* 3,282,932.

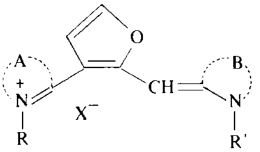
[312] F. S. Babichev, F. A. Mikhailenko, V. K. Kibirev, and V. A. Bogolyubskii, *Ukr. Khim. Zh.* **32**, 204, 991 (1966); *CA* **64**, 17749 (1966); **66**, 47308 (1967).

[313] L. L. Lincoln, L. G. S. Brooker, and Eastman Kodak, *BP* 1,054,107.

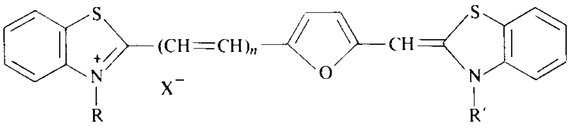
[314] Eastman Kodak, *BeP* 674,292; 674,376.

[314a] A. I. Tolmachev, V. P. Sribnaya, and I. K. Ushenko, *Khim. Geterotsikl. Soedin.* p. 459 (1968); *CA* **70**, 3907 (1969).

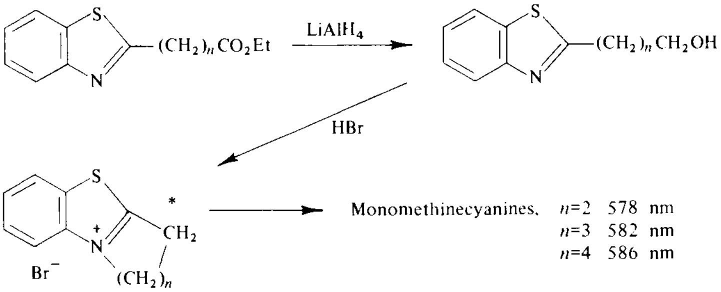
[314b] A. A. Shulezhko and A. I. Kiprianov, *Zh. Organ. Khim.* **4**, 1089 (1968); *CA* **69**, 78432 (1969).



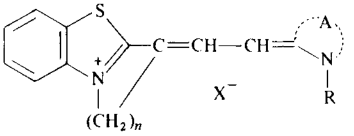
(CLXXXVI)



(CLXXXVII)
596 nm; $n = 0$



(CLXXXVIII)



(CLXXXIX)

A novel type of hydrocarbon bridge has been provided by Tolmachev *et al.*; the dye illustrated (CLXXXIXc) absorbs at 749 nm, very close to that of the unbridged dye.[314c]

The preparation of dyes from squaric acid (see refs. 306–308) has been reviewed by Sprenger and Ziegenbein,[314d] and further examples have been provided by Treibs and Jacob.[314e]

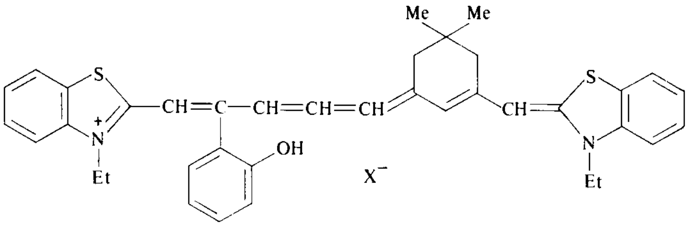
Dyes analogous to (CLXXXVII), but with a thiophene ring in place of furan, have now been described; this change causes a bathochromic shift in the light absorption.[314f]

[314c] A. I. Tolmachev, Yu. L. Slominskii, and A. I. Kiprianov, *Dokl. Akad. Nauk SSSR* **177,** 869 (1967); *CA* **69,** 11406 (1968).

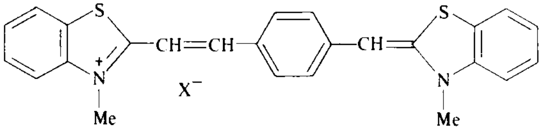
[314d] H.-E. Sprenger and W. Ziegenbein, *Angew. Chem. Intern. Ed. Engl.* **7,** 530 (1968).

[314e] A. Treibs and K. Jacob, *Ann. Chem.* **712,** 123 (1968).

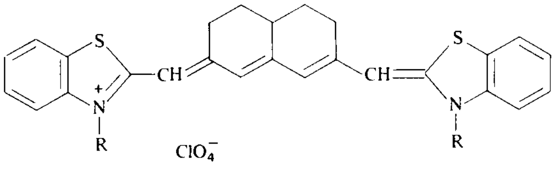
[314f] A. A. Shulezhko, *Zh. Organ. Khim.* **4,** 2207 (1968); *CA* **71,** 4496 (1969).



(CLXXXIXa)



(CLXXXIXb)



(CLXXXIXc)

C. AZACYANINES

Cyanines in which one or more of the methine links have been replaced by nitrogen have found little use in the photographic industry, since this change frequently leads to loss of spectral sensitivity and the acquisition of desensitizing properties.[315] Interest in these dyes has, however, been maintained for two reasons. Firstly, they have frequently been claimed as textile dyes, more particularly the α β-diazatrimethinecyanines and the diazastyryl dyes.[316]

The azacyanines are also of interest in connection with the spectral

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[315] Cf. *CSD II*, pp. 1183–1185; F. M. Hamer,[5] Chapter XII.

[316] The numerous patents dealing with such dyes will not be reviewed here.

changes caused by replacement of —CH= by —N=, and various rules have been propounded which aim to predict the effect of this change *inter alia,* such as those of Knott[317] and Dewar.[318] Several other authors[319-321] have discussed the effect on light absorption of the replacement of methine by nitrogen, frequently with reference to such rules. On a more theoretical level, Nikitine has discussed this change in terms of a perturbation in a linear metallic model.[322]

Knott and Williams[323] have used the shift in absorption maximum caused by the change —CH= → —N= in trimethinecyanines as a measure of the ±M effect of various heterocyclic nuclei. In general, the results correlate well with those obtained by a consideration of "Brooker deviations."[324]

Since the previous reviews[315] were written, the novel azamethinecyanines discussed below have been prepared

1. *Azatrimethinecyanines*

Kiprianov and Verbovs'ka have prepared β-azatrimethinecyanines by reaction of an aminomethyl quaternary salt (CXC) with a heterocyclic aldehyde, followed by quaternization of the azacyanine base (CXCI). Symmetrical dyes of structure (CXCII) could also be prepared simply by heating (CXC) in pyridine.[325]

Methods have been devised for the synthesis of triazatrimethinecyanines. In the first of these, due to Kiprianov *et al.*,[326] a heterocyclic

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[317] E. B. Knott, *J. Chem. Soc.* p. 1024 (1951).

[318] M. J. S. Dewar, *Chem. Soc. (London), Spec. Publ.* **4,** 64 (1956).

[319] B. Das, B. K. Patnaik, and M. K. Rout, *J. Indian Chem. Soc.* **37,** 603 (1960); B. K. Sabata, B. K. Patnaik, and M. K. Rout, *ibid.* **38,** 679 (1961); M. K. Rout, *J. Proc. Inst. Chemists (India)* **35,** 117 (1963); P. C. Rath, P. K. Jesthi, P. K. Mishra, and M. K. Rout, *Indian J. Chem.* **4,** 24 (1966).

[320] A. I. Kiprianov and F. A. Mikhailenko, *Zh. Obshch. Khim.* **33,** 1415 (1963); *CA* **60,** 3130 (1964); *Ukr. Khim. Zh.* **30,** 1309 (1964); *CA* **62,** 11941 (1965); A. I. Kiprianov and T. M. Verbovskaya, *Zh. Organ. Khim.* **2,** 1848 (1966); *CA* **66,** 47298 (1967).

[321] G. G. Dyadyusha, T. M. Verbovskaya and A. I. Kiprianov, *Ukr. Khim. Zh.* **32,** 357 (1966); *CA* **65,** 9060 (1966).

[322] S. Nikitine, *Compt. Rend.* **236,** 2051 (1953). S. Nikitine and S. E. El Komoss, *J. Chim. Phys.* **52,** 108 (1955).

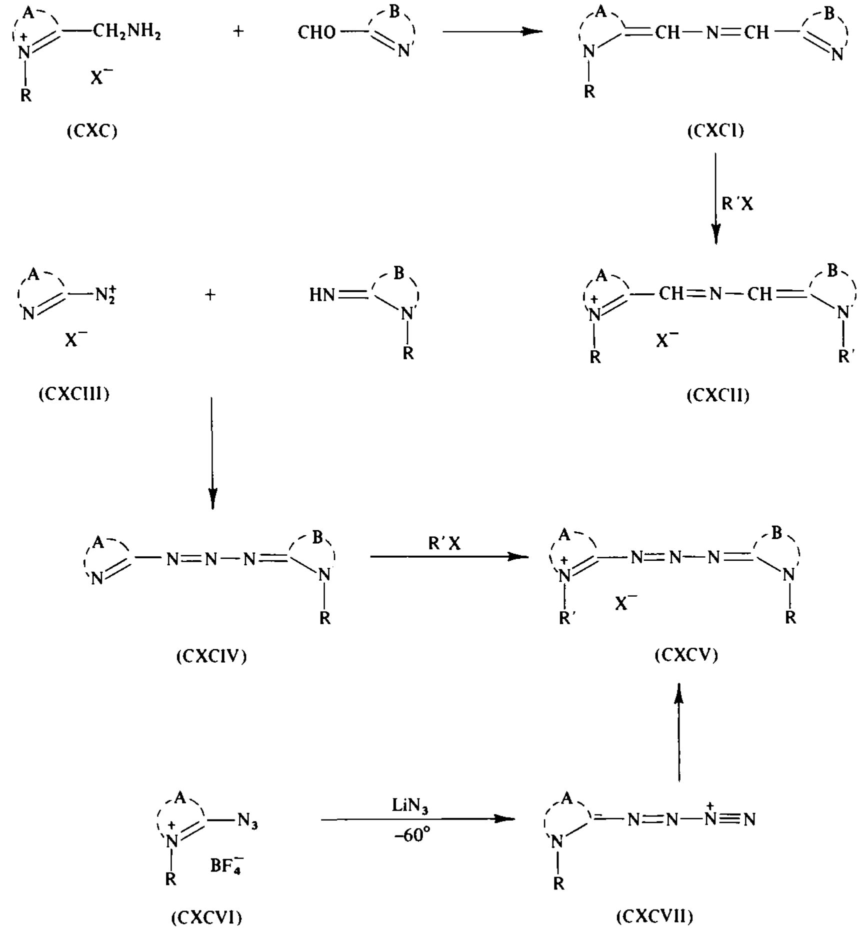
[323] E. B. Knott and L. A. Williams, *J. Chem. Soc.* p. 1586 (1951).

[324] L. G. S. Brooker, A. L. Sklar, H. W. J. Cressman, G. H. Keyes, L. A. Smith, R. H. Sprague, E. VanLare, G. VanZandt, F. L. White, and W. W. Williams, *J. Am. Chem. Soc.* **67,** 1875 (1945); L. G. S. Brooker, R. H. Sprague, and H. W. J. Cressman, *ibid.* p. 1889.

[325] A. I. Kiprianov and T. M. Verbovs'ka, *Dopovidi Akad. Nauk Ukr. RSR* p. 924 (1962); *CA* **58,** 1445 (1963); *Zh. Obshch. Khim.* **33,** 479 (1963); *CA* **59,** 2971 (1963).

[326] A. I. Kiprianov, V. Ya. Pochinok, and A. I. Tolmachev, *Ukr. Khim. Zh.* **20,** 204 (1954); *CA* **49,** 12834 (1955).

diazonium salt (CXCIII) was coupled with a 2-imino heterocyclic base and the resulting triazene (CXCIV) quaternized (but see Voltz[327]). An alternative route to (CXCV) involved reaction of a 2-heterocyclic azido quaternary salt (CXCVI) with an inorganic azide at 20–30°; by working



at a lower temperature, the reaction could be arrested at an intermediate stage [to which structure (CXCVII) was assigned], and reaction of this with a different compound of type (CXCVI) gave an unsymmetrical dye (CXCV).[328] These dyes are said to be stable to acids but labile towards

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[327] J. Voltz, *Chimia (Aarau)* **15,** 168 (1961).

[328] H. Balli, *Ann. Chem.* **647,** 11 (1961); H. Balli and F. Kersting, *ibid.* **663,** 96, 103 (1963); *Chimia (Aarau)* **20,** 318 (1966).

bases, even ammonia. After heating at 200° for 8 hours under anhydrous conditions they could be recovered unchanged, but in the presence of water smooth decomposition to the azamonomethinecyanine occurred. Other methods for the preparation of the triaza dyes (CXCV) have been described.[329]

2. *Azapentamethinecyanines*

Dyadyusha *et al.* have prepared γ-azapentamethinecyanines by reaction of an acetanilidovinyl quaternary salt with ammonia. The same authors also prepared $\alpha\alpha'$-diazapentamethinecyanines by reaction of a 2-amino quaternary salt with 1,1,3,3-tetramethoxypropane (cf. the preparation of pentamethinecyanines, Section II,D).[321]

Hünig *et al.* have described the reaction of a heterocyclic hydrazone (CXCVIII) with an aldehyde (including formaldehyde) to form the azine (CXCIX); reaction of this with a further molecule of (CXCVIII) (not necessarily the same as before) under oxidizing conditions (e.g., lead tetraacetate) gave the tetraazapentamethinecyanine (CC).[330] The same type of intermediate (CXCVIII) could also be used to prepare pentaazapentamethinecyanines (CCI). Reaction with sodium nitrite or lead tetraacetate led directly to symmetrical dyes, while reaction with an azido quaternary salt (CXCVI) gave an unsymmetrical dye.[331] These dyes were not surprisingly thermally unstable, giving a mixture of triazatrimethinecyanine and azamonomethinecyanine on heating to 110°.

3. *Miscellaneous Azacyanines*

Kiprianov *et al.* have described methods of synthesis for diaza and triaza polymethine dyes with one or two benzene rings in the chain (CCII; $Y = \text{CH}$ or N, $n = 0$ or 1).[326,332]

The synthesis of azacyanines has been reviewed by Balli.[332a]

A new method for the preparation of α,β-diazatrimethinecyanines con-

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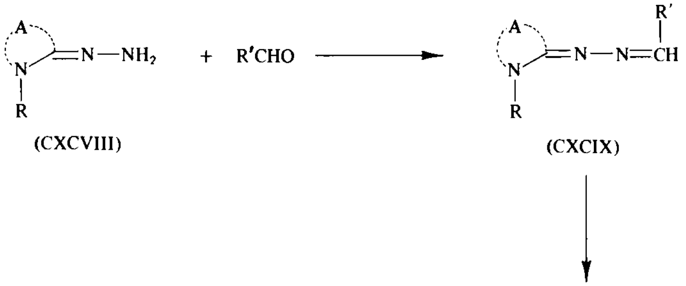
[329] A. Spiliadis, E. Badic, V. Cornea, M. Hilsenrath, D. Bretcan, and R. Neagoe, *Rev. Chim.* (*Bucharest*) **15**, 23 (1964); *CA* **62**, 5360 (1965); H. Quast and E. Frankenfeld, *Angew. Chem.* **77**, 680 (1965); H. Quast and S. Hünig, *Chem. Ber.* **99**, 2017 (1966); S. Hünig, H. Geiger, G. Kaupp, and W. Kniese, *Ann. Chem.* **697**, 116 (1966).

[330] S. Hünig and K. H. Fritsch, *Ann. Chem.* **609**, 172 (1957); S. Hünig, F. Brühne, and E. Breither, *ibid.* **667**, 72 (1963); cf. R. Sureau, G. Kremer, and CN, *FP* 1,353,497.

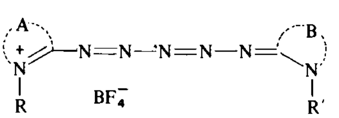
[331] S. Hünig, H. Balli, and H. Quast, *Angew. Chem.* **74**, 28 (1962).

[332] A. I. Kiprianov and T. M. Verbovskaya, *Zh. Organ. Khim.* **1**, 13 (1965); *CA* **62**, 14860 (1965).

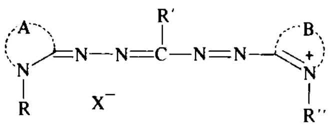
[332a] H. Balli, *Textilveredlung* **4**, 37 (1969).



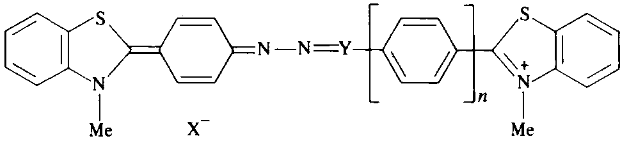
(CXCVIII) (CXCIX)



(CCI)

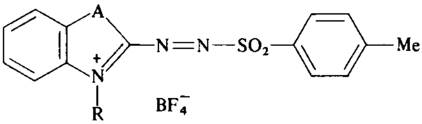


(CC)



(CCII)

sists in the reaction of an arylsulphonylazo quaternary salt (CCIIa) with a reactive methyl quaternary salt.[332b] Similar reaction of (CCIIa) with a 2-imino-heterocyclic base leads to a triazatrimethinecyanine.[332c]



(CCIIa)

The full details of Hünig's preparations of penta-azapentamethinecyanines[331] have now been published,[332d] and various reactions of these dyes have been described.[332e]

[332b] H. Quast, S. Hünig, and E. Schmitt, *Chem. Ber.* **101**, 1522 (1968); S. Hünig, *Angew. Chem. Intern. Ed. Eng.* 7, 335 (1968).

[332c] H. Quast and S. Hünig, *Chem. Ber.* **101**, 435 (1968).

[332d] S. Hünig and H. Quast, *Ann. Chem.* **711**, 139 (1968).

[332e] H. Quast and S. Hünig, *Ann. Chem.* **711**, 157 (1968).

D. Cyanines with Other Heteroatoms in the Chain

In view of the fact that so many cyanines are known with a nitrogen atom replacing a —CH= group of the polymethine chain, it could be predicted that a similar replacement by trivalent phosphorus would be possible. This was, however, achieved only as recently as 1964, and then only in the monomethinecyanine series. Dimroth and Hoffmann showed that if 2-chloro-3-ethylbenzothiazolium fluoroborate was reacted with tri(hydroxymethyl)phosphine, $P(CH_2OH)_3$, in dimethylformamide in the presence of an organic base, then the dye (CCIII) was formed. The 2-linked quinoline analog was obtained similarly, and some unsymmetrical dyes were also prepared.[333]

Allmann has shown by an X-ray analysis that the cation of (CCIII) is almost planar and symmetrical, with the two P—C bonds of equal length; this indicates that the dye is displaying true cyanine mesomerism, with the phosphorus atom providing one *p*-electron.[334] In the 2-quinoline dye, however, the two heterocyclic rings are considerably twisted out of coplanarity due to steric hindrance of the 3,3′-hydrogen atoms; there is some asymmetry in the bond lengths, indicating incomplete resonance.[334a]

An alternative method of preparing (CCIII) involved reaction of the chlorobenzothiazolium salt with tris(trimethylsilyl)phosphine; use of the related arsine gave the arsenic analog of (CCIII). This absorbed bathochromically (λ_{max} 491 nm) and hypochromically compared with (CCIII).[335]

Kabachnik *et al.* have prepared some dyes containing formally pentavalent phosphorus, and which were described as azacyanine analogs. Reaction of the phosphorus compound (CCIV) with the azido quaternary salt (CCV) gave the yellow tetraza dye (CCVI) which decomposed at a higher temperature to the colorless diaza compound (CCVII). In addition to the presumed normal cyanine mesomerism, canonical forms such as (CCVIIb) are possible.[336]

Knott has shown that in a compound such as (CCVIIIa) resonance with the dipolar form (CCVIIIb) occurs, i.e., it is showing merocyanine-like mesomerism; also that a sulfur atom in the middle ring of a trinuclear dye of the rhodacyanine type (Section VII,B) can act as a resonance transmitter. All attempts to prepare a cyanine analog with

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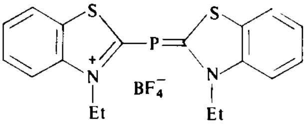
[333] K. Dimroth and P. Hoffmann, *Angew. Chem.* **76,** 433 (1964); *Chem. Ber.* **99,** 1325 (1966).

[334] R. Allmann, *Chem. Ber.* **99,** 1332 (1966).

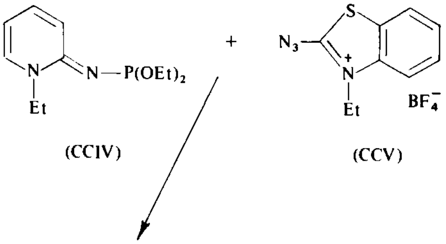
[334a] I. Kawada and R. Allmann, *Angew. Chem. Intern. Ed. Engl.* **7,** 69 (1968).

[335] G. Märkl and F. Lieb, *Tetrahedron Letters* p. 3489 (1967).

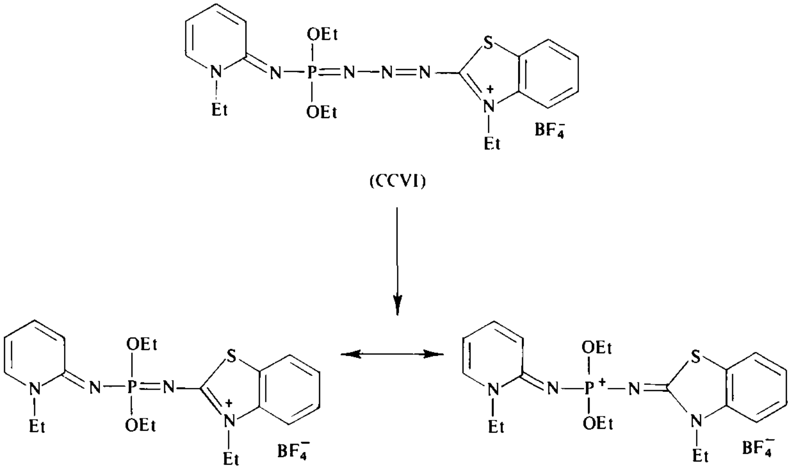
[336] M. I. Kabachnik, V. A. Gilyarov, and M. M. Yusupov, *Dokl. Akad. Nauk SSSR* **160,** 1079 (1965); **164,** 812 (1965); *CA* **62,** 14650 (1965); **64,** 3465 (1966).



(CCIII)
472 nm

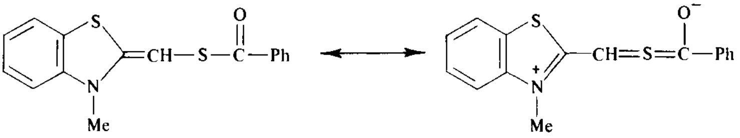


(CCIV) (CCV)



(CCVI)

(CCVIIa) (CCVIIb)



(CCVIIIa) (CCVIIIb)

—CH=CH— replaced by —S— were uniformly unsuccessful due to extrusion of sulfur. Thus attempts to synthesize dyes with a =CH—S—CH=CH— chain in fact gave a chain =CH—CH=CH— instead.[337]

It is to be noted that another obvious replacement for —CH= in a polymethine chain, viz., —SiR=, has not yet been achieved.

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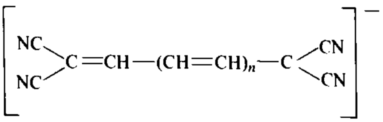
[337] E. B. Knott, *J. Chem. Soc.* pp. 916, 933, 937, 949 (1955); E. B. Knott and R. A. Jeffreys, *ibid.* p. 927

E. THE ANION

The anion has been less systematically studied than the cationic portion of the cyanine molecule, since it is generally considered that the nature of the anion has little effect on sensitizing properties. However, Natanson and Sennikova have examined the effect of the nature of the anion on the adsorption of the dye to silver halide; it appears that changing the anion can affect the degree of polymerization in those dyes which are prone to aggregate.[338]

Isolation of a dye as the cyclohexanesulfonate or butanesulfonate is said to lead to increased solubility in water or ethanol.[339] The use of an ion-exchange resin for the conversion of, e.g., an iodide or perchlorate into a more soluble salt such as chloride has been described.[340]

Ogata *et al.* have described the preparation of cyanine salts with various organic carboxylic acid anions,[341] and Hishiki has prepared various cyanine erythrosinates.[342] Franke claims that conversion of cyanines into their picrates leads to greater solubility and increased sensitizing power.[343] The use of tetrachloroaurates of cyanines as emulsion stabilizers or sensitizers has been patented.[344]



$$\left[(NC)_2C{=}CH{-}(CH{=}CH)_n{-}C(CN)_2\right]^-$$

(CCVIIIc)

Hishiki has prepared some cyanines in which the anion is of the type (CCVIIIc; $n = 0$).[344a]

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[338] S. V. Natanson and N. I. Sennikova, *Kinotekhn., Nauchn.-Tekhn. Sb.* p. 56 (1963); *CA* **61**, 10224 (1964).

[339] W. H. Vinton and DuP, *USP* 2,647,115-6.

[340] O. Riester, W. Schneider and VEB Filmfabrik Agfa Wolfen, *EGP* 9036.

[341] T. Ogata, R. Tanno, T. Shimizu, and T. Nishihama, *Rept. Sci. Res. Inst.* (*Tokyo*) **28**, 118 (1952); *CA* **48**, 170 (1954); T. Ogata and B. Ogura, *Ann. Rept. Hoshi Coll. Pharm.* **4**, 3, 7 (1954); T. Ogata and M. Noguchi, *ibid.* p. 5; *CA* **50**, 13924 (1956).

[342] Y. Hishiki, *Rept. Sci. Res. Inst.* (*Tokyo*) **29**, 72 (1953); *CA* **47**, 12067 (1953).

[343] W. Franke and Adox Fotowerke, *DBP* 1,132,796.

[344] R. E. Damschroder and Eastman Kodak, *USP* 2,597,856; H. C. Yutzy, J. A. Leermakers, and Eastman Kodak, *USP* 2,597,915; R. E. Damschroder, H. C. Yutzy, and Eastman Kodak. *USP* 2,642,361.

[344a] Y. Hishiki and O. Yoshida, *Chiba Daigaku Kogakubu Kenkyu Hokuku* **18**, 115 (1967).

VI. Merocyanines and Related Dyes

Many of the publications discussed in earlier sections, particularly III and IV, included dyes of the merocyanine type in addition to true cyanines. The present section will deal with the more interesting publications concerned purely with merocyanines; those already reviewed by Hamer[345] will not be included.

A. VARIATIONS IN THE COMMON KETOMETHYLENE RINGS

1. *Pyrazolinones*

The well-known 3-methyl-1-phenyl-2-pyrazolin-5-one, from which merocyanines have frequently been prepared by reaction at the methylene group in position 4, has been modified in the following directions: use of the 3-hydroxymethyl derivative,[346] and replacement of the phenyl group by a 5- or 6-benzothiazolyl group,[347] or by a 1,2,4-triazinyl group.[348]

2. *Rhodanines*

Merocyanines have been prepared from rhodanines with the following substituents at the 3-position: 5- or 6-benzothiazolyl or 2-benzothiazolylmethyl,[349] amino (and $-N{=}CHR$ etc.),[350] $-(CH_2)_5CO_2R$,[351] $-(CH_2)_n$-NR_2 (in other ketomethylene rings also),[352] and benzoyl.[353]

3. *Thiohydantoins*

The benzoyl group has also been introduced into the 2-thiohydantoin ring (at position 3) in merocyanines.[354]

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[345] F. M. Hamer,[5] Chapter XIV.

[346] G. F. Duffin, J. D. Kendall, and Ilford, *BP* 828,847.

[347] V. M. Zubarovskii and G. P. Khodot, *Zh. Obshch. Khim.* **30**, 1585 (1960); *CA* **55**, 1583 (1961).

[348] J. Hadacek and D. Matulova, *Spisy Prirodovedecke Fak. Univ. Brne* **462**, 161 (1965).

[349] V. M. Zubarovskii and T. M. Verbovskaya, *Zh. Obshch. Khim.* **27**, 2177 (1957); *CA* **52**, 6323 (1958).

[350] B. Mariani and R. Sgarbi, *Chim. Ind. (Milan)* **45**, 696 (1963); *CA* **61**, 9606 (1964).

[351] L. T. Bogolyubskaya, V. A. Bogolyubskii, R. V. Timofeeva, and Z. P. Sytnik, *RP* 173,775; *CA* **64**, 3747 (1966).

[352] R. C. Taber, L. G. S. Brooker, and Eastman Kodak, *USP* 3,352,680.

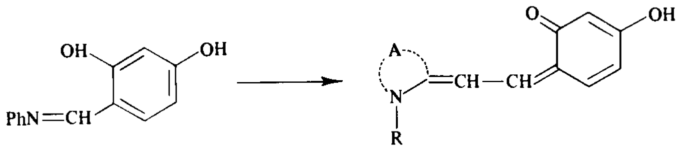
[353] D. J. Fry, J. D. Kendall, B. A. Lea, and Ilford, *BP* 829,644.

[354] D. J. Fry, B. A. Lea, J. D. Kendall, and Ilford, *BP* 829,790.

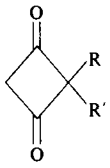
B. The Use of Novel Ketomethylene Rings

1. *Carbocyclic Rings*

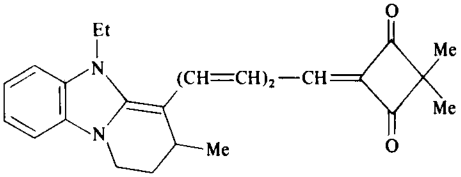
Reaction of resorcinol with *N,N′*-diphenylformamidine gave the intermediate (CCIX), from which merocyanines (CCX) could be prepared by reaction with methyl quaternary salts.[355]



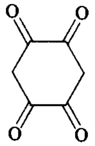
(CCIX) (CCX)



(CCXI)



(CCXII)



(CCXIII)

The methylene group in a 1,3-cyclobutanedione (CCXI) is reactive, enabling merocyanines to be prepared[356]; dyes of this type (CCXII), have been suggested for use as solvent polarity indicators (see Section VI,E).[357]

Both methylene groups in the cyclohexanetetrone (CCXIII) are reactive, and mono- and bis-merocyanines can be prepared; the dyes are photographic desensitizers.[358]

2. *Oxygen and Sulfur Heterocycles*

Dyes have been prepared by reaction at the methylene group in the compounds (CCXIV),[359] (CCXV),[360] (CCXVI),[361] (CCXVII),[362] and

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[355] B. Mariani, L. Basaglia, and Ferrania SpA, *FP* 1,377,346.

[356] D. W. Heseltine, L. G. S. Brooker, and Eastman Kodak, *USP* 3,140,182.

[357] L. G. S. Brooker, A. C. Craig, D. W. Heseltine, P. W. Jenkins, and L. L. Lincoln, *J. Am. Chem. Soc.* **87**, 2443 (1965).

[358] D. W. Heseltine, L. G. S. Brooker, and Eastman Kodak, *USP* 3,140,951. The spectra of these dyes have been discussed in C. E. K. Mees and T. H. James,[2] pp. 226–227.

[359] J. A. Ford, C. V. Wilson, and W. R. Young, *J. Org. Chem.* **32**, 173 (1967).

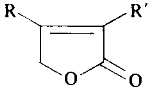
[360] E. B. Knott, *J. Chem. Soc.* p. 402 (1963).

[361] P. C. Rath, B. K. Sabata, and M. K. Rout, *J. Indian Chem. Soc.* **41**, 797, 803 (1964); P. K. Jesthi and M. K. Rout, *Indian J. Chem.* **3**, 461 (1965).

[362] Eastman Kodak, *BeP* 682,285.

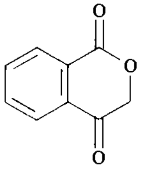
(CCXVIII).[363] If both R and R′ in the 3-thietanone-1,1-dioxide (CCXVIII) are hydrogen, then there are two reactive methylene groups.

The methyl group in a 4-methylcoumarin is reactive, and merocyanines of type (CCXIX) can be prepared.[364]

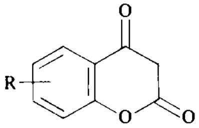


R = Aryl
R′= Me, Aryl, or CN

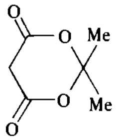
(CCXIV)



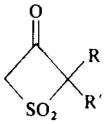
(CCXV)



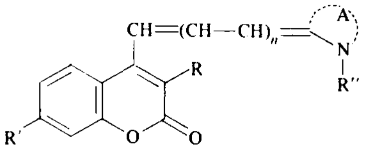
(CCXVI)



(CCXVII)



(CCXVIII)



R = H or CN

(CCXIX)

3. *Nitrogen Heterocycles*

The methylene groups* in (CCXX) and (CCXXI) are reactive (also in an analog of the former with arsenic replacing nitrogen), but only benzylidene derivatives have been prepared, by reaction with *p*-dimethylaminobenzaldehyde.[365]

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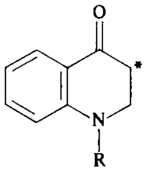
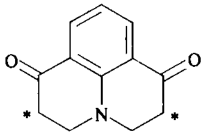
[363] A. C. Craig, L. G. S. Brooker, and Eastman Kodak, *USP* 3,148,065; A. C. Craig, L. G. S. Brooker, J. C. Martin, and Eastman Kodak, *USP* 3,277,084.

[364] J. D. Kendall, A. J. Axford, and Ilford, *BP* 672,741; J. D. Kendall, H. R. J. Waddington, G. F. Duffin, and Ilford, *BP* 856,068.

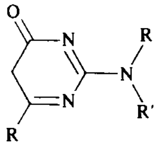
[365] J. T. Braunholtz and F. G. Mann, *J. Chem. Soc.* p. 398 (1955), F. G. Mann and A. J. Wilkinson, *ibid.* p. 3336 (1957); P. I. Ittyerah and F. G. Mann, *ibid.* p. 467 (1958).



(CCXX)

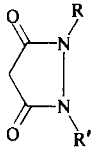


(CCXXI)

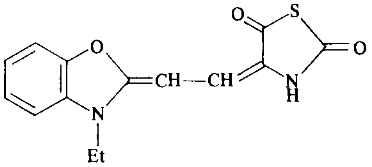


(CCXXII)

R = -OH or -NH$_2$



(CCXXIII)



(CCXXIV)

Pyrimidine derivatives of the type (CCXXII) have been used to prepare merocyanines,[366] as have 3,5-pyrazolidinediones (CCXXIII).[367]

4. *Nuclei with N and O or S*

Aubert *et al.* have described the preparation of 2,5-thiazolidinedione and a merocyanine (CCXXIV) obtained therefrom.[368]

The preparation of merocyanines (CCXXV) from a 2-thiazolin-4-one has been described[369,370]; if group R′ is methyl, it is activated by the carbonyl group in the thiazoline ring, and can be reacted to give trinuclear dyes of type (CCXXVI). Other ketomethylene compounds which can be used similarly to prepare trinuclear dyes include (CCXXVII) and (CCXXVIII).[370]

Knott has shown that a 2-hydroxy- or mercaptothiazole will react with the usual reagents to give merocyanines (CCXXIX) derived from the tautomeric 3-thiazoline-2-one or thione; further reactions of these merocyanines, leading to trinuclear dyes, were also described.[371]

[366] G. de W. Anderson and ICI, *BP* 834,751.

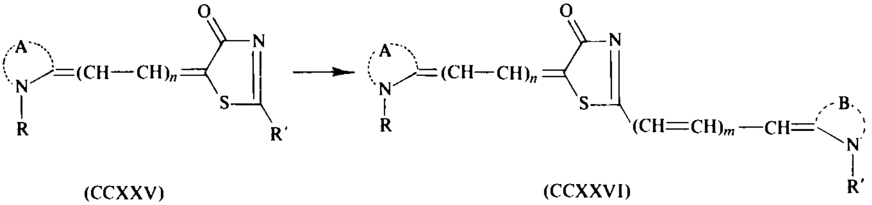
[367] P. W. Jenkins, L. G. S. Brooker, and Eastman Kodak, *BP* 1,075,391.

[368] P. Aubert, R. A. Jeffreys, and E. B. Knott, *J. Chem. Soc.* p. 2195 (1951).

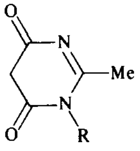
[369] F. N. Stepanov and Z. Z. Moiseeva, *Zh. Obshch. Khim.* **25,** 1977 (1955); *CA* **50,** 8604 (1956).

[370] D. W. Heseltine, L. G. S. Brooker, and Eastman Kodak, *USP* 2,927,026; 3,213.089.

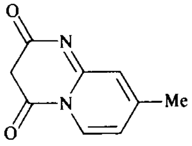
[371] E. B. Knott, *J. Chem. Soc.* p. 4244 (1960); *Chimia* (*Aarau*) **15,** 106 (1961).



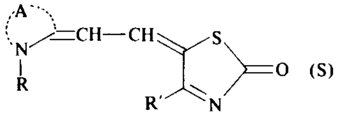
(CCXXV) (CCXXVI)



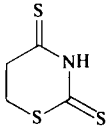
(CCXXVII)



(CCXXVIII)



(CCXXIX)



(CCXXX)

A *p*-dimethylaminobenzylidene derivative has been prepared from the 1,3-thiazine-2,4-dithione (CCXXX).[372]

Condensed ring systems with an active methylene group, which have been used to prepare merocyanines, include (CCXXXI),[373] (CCXXXII),[374] and (CCXXXIII).[375]

C. Noncyclic Carbonyl Components

Further examples have been described of merocyanines in which the carbonyl group does not form part of a ring system. Thus, Duffin and Kendall have prepared a number of such dyes (CCXXXIV) from modified cyanoacethydrazides.[376]

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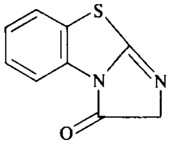
[372] A. P. Grishchuk and G. I. Roslaya, *Khim. Geterotsikl. Soedin.* p. 537 (1966); *CA* 66, 37861 (1967).

[373] E. B. Knott and Kodak, *BP* 908,428.

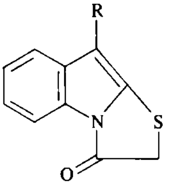
[374] G. E. Ficken, J. D. Kendall, and Ilford, *BP* 874,809.

[375] H. Depoorter, M. J. Libeer, and Gevaert-Agfa, *BP* 1,077,299.

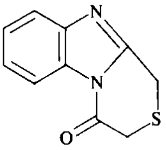
[376] G. F. Duffin and Ilford, *BP* 840,384; G. F. Duffin, J. D. Kendall, and Ilford, *BP* 849,741; 850,976.



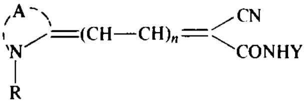
(CCXXXI)



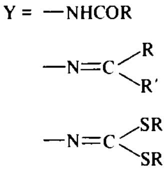
(CCXXXII)



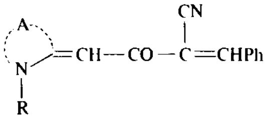
(CCXXXIII)



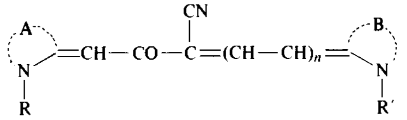
(CCXXXIV)



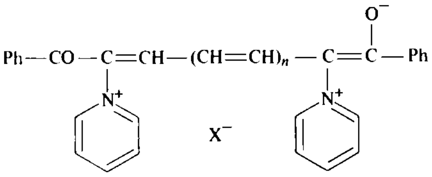
Reaction of a heterocyclic methylene base with a 2-cyanocinnamyl chloride gives dyes of structure (CCXXXV); an alternative synthesis involves reaction of a cyanoacetylmethylene heterocycle with an aromatic aldehyde.[377] More complicated dyes of similar type (CCXXXVI) have also been prepared.[378]



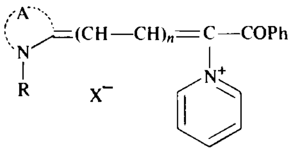
(CCXXXV)



(CCXXXVI)



(CCXXXVII)
n = 1 or 2



(CCXXXVIII)

Dickoré and Kröhnke described the preparation of the novel oxonols (CCXXXVII) from phenacylpyridinium salts.[379] Similar dyes were pre-

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[377] M. Coenen and FBy, *DBP* 824,818–9.

[378] O. Riester and FBy, *DBP* 821,524; M. Coenen, K. Zietan, and AGFA, *DBP* 960,605.

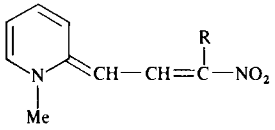
[379] K. Dickoré and F. Kröhnke, *Chem. Ber.* 93, 1068, 2479 (1960).

pared by Heseltine and Lincoln, who also described the related merocyanines (CCXXXVIII) and similar dyes in which a cyano or benzothiazolyl group replaces the benzoyl group.[380]

Merocyanines in which cyanoacetamide acts as the ketomethylene component have been known for some time (see ref. 5, Chapter XIV, Section 13); the corresponding thio- and seleno-acetamide dyes have now been described.[380a]

Novel merocyanines have been prepared from cyanomethyl sulphones, $NC \cdot CH_2 \cdot SO_2R$, as the active methylene components.[380b]

Condensation of an unsaturated nitroamine of the type $Me_2N \cdot CH = CR \cdot NO_2$ with a reactive methyl quaternary salt leads to a dye such as (CCXXXVIIIa); this is considered by the authors to constitute a novel type of merocyanine.[380c]



(CCXXXVIIIa)

D. Variations in the Chain

Sytnik *et al.* have examined the effect of introducing a range of electron-donating substituents (alkyl, alkoxy, amino, etc.) into the β-position of the dimethine chain, i.e., adjacent to the rhodanine ring. In all cases the light absorption was hypsochromic compared to the unsubstituted dye.[381] Benzothiazole-rhodanine dyes with a β-ethoxy-substituted dimethine chain have been suggested for use as green sensitizers in color films.[382]

Reaction of an intermediate of structure (CCXXXIX) (from, e.g., levulinic acid and 3-ethylrhodanine) with an alkylthio quaternary salt leads to merocyanines with a β-$(CH_2)_n$-CO_2H substituent.[383]

Some novel bridged-chain merocyanines have been described by Brooker

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[380] D. W. Heseltine, L. L. Lincoln, and Eastman Kodak, *USP* 3,094,418; 3,125,448; 3,311,618.

[380a] Gevaert-Agfa, *BeP* 715,498.

[380b] G. L. Oliver and Eastman Kodak, *BP* 1,128,113.

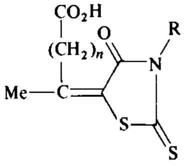
[380c] T. Severin and H. J. Böhme, *Chem. Ber.* **101,** 2925 (1968).

[381] Z. P. Sytnik, L. D. Zhilina, and E. B. Lifshits, *Dokl. Akad. Nauk SSSR* **114,** 343 (1957); *CA* **52,** 369 (1958).

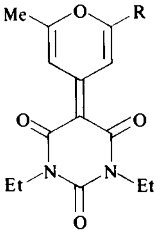
[382] Z. P. Sytnik, M. S. Lyubich, A. A. Abdullaev, R. B. Lifshits, M. K. Grechko, Yu. B. Vilenskii, R. V. Timofeeva, and R. A. Gershtein, *Kinotekhn., Nauchn.-Tekhn. Sb.* p. 54 (1963); *CA* **61,** 10806 (1964).

[383] D. J. Fry, B. A. Lea, and Ilford, *BP* 846,298.

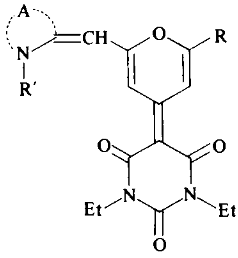
and Webster. Reaction of a 4-pyrone with a ketomethylene compound or with malononitrile, gives, e.g., (CCXL); the methyl group in this is reactive and with the usual reagents leads to dyes such as (CCXLI). If the group R is also methyl, then this is reactive too, and trinuclear dyes can be prepared.[384] The same authors have also described dyes such as (CCXLII).[385]



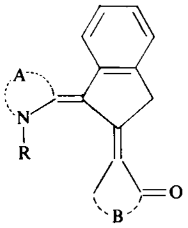
(CCXXXIX)



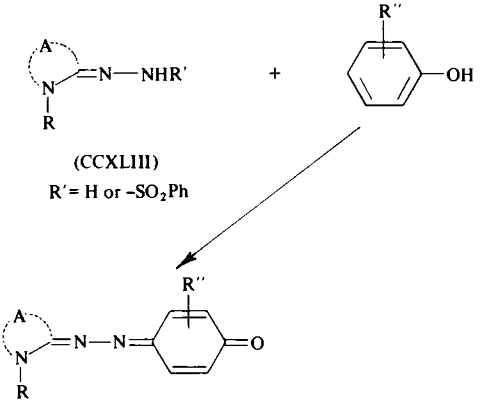
(CCXL)



(CCXLI)



(CCXLII)



(CCXLIII)
R′ = H or $-SO_2Ph$

(CCXLIV)

The literature on azamerocyanine dyes will not be reviewed in detail, but reference must be made to the work of Hünig *et al.*, who have described the reaction of hydrazones (CCXLIII) with reactive methylene compounds or phenols under oxidizing conditions to give diazamerocyanines (e.g., CCXLIV). Oxidative coupling of (CCXLIII) with tertiary aromatic amines likewise gives diazastyryl dyes.[386]

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[384] L. G. S. Brooker, F. G. Webster, and Eastman Kodak, *USP* 2,965,486.

[385] L. G. S. Brooker, F. G. Webster, and Eastman Kodak, *USP* 3,253,925.

[386] Part I: S. Hünig and K. H. Fritsch, *Ann. Chem.* **609,** 143 (1957); Part XXVIII: S. Hünig and G. Kaupp, *Tetrahedron* **23,** 1411 (1967).

E. Miscellaneous Topics

The solubility of merocyanines in water and hydrophilic organic solvents is frequently very slight, leading to considerable difficulty in their incorporation into photographic emulsions. Dyes have recently been described, however, which contain a sulfo substituent in the benzene ring of a benzoxazole, benzothiazole, etc., nucleus[387]; this substitution, like the earlier use of *N*-carboxyalkyl or *N*-sulfoalkyl substituents,[345] leads to improved water solubility.

A characteristic feature of the merocyanines is their sensitization of silver halides in the monomeric form; only very rarely do they show J-band sensitization. Lifshits has described a few dyes which display a tendency to form J-aggregates, this being most marked with dye (CCXLV).[388] More recently Brunken and Poppe have prepared two series of dimethinemerocyanines in which several members show J-band sensitization.[389] In series (CCXLVI), the nature of the alkyl groups on the thiohydantoin nitrogens was critical, since J-band sensitization was only observed when R was Me to *n*-Bu and when R′ was *n*-Pr to *n*-heptyl; outside these limits only M-band sensitization was obtained. If the benzimidazole ring was replaced by a different heterocycle, e.g., benzoxazole, then the range of values of R and R′ for J-band sensitization was even more restricted. In series (CCXLVII) the size of the groups on the benzimidazole nitrogens was likewise quite critical.

Götze and Riester have described the preparation of merocyanine (CCXLVIII) by reaction of 2-methylthiobenzothiazole (unquaternized) with 3-ethylrhodanine. Reaction of this dye with dimethyl sulfate was studied, some surprising intramolecular transmethylations involving the three reactive centres (–NH–, –CO–, and –CS–) being observed.[390]

Merocyanines show the phenomenon of solvatochromism, i.e., sensitivity of the absorption maximum to the nature of the solvent, to a marked degree. This effect, which has been correlated with the dielectric constant of the solvent, is frequently so great that the dyes can be used as solvent polarity indicators.[391] The first compounds of this type, de-

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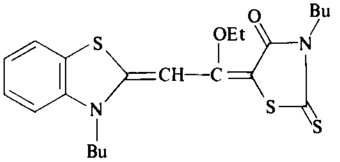
[387] D. W. Heseltine and Eastman Kodak, *USP* 3,148,187; O. Riester, M. Glass, and AGFA, *BP* 1,064,037.

[388] E. B. Lifshits, *Zh. Nauchn. i Prikl. Fotogr. i Kinematogr.* **6**, 64 (1961); *CA* **55**, 26802 (1961).

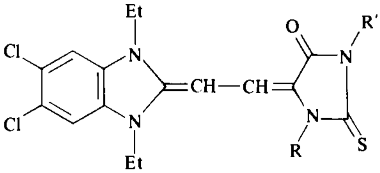
[389] J. Brunken and E. J. Poppe, *Veroeffentl. Wiss. Photolab. Wolfen* **10**, 101 (1965); E. J. Poppe, *ibid.* p. 115.

[390] J. Götze and O. Riester, *Mitt. Forschungslab. Agfa Leverkusen-Muenchen* **1**, 56 (1955).

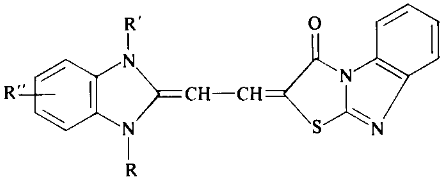
[391] L. G. S. Brooker, G. H. Keyes, and D. W. Heseltine, *J. Am. Chem. Soc.* **73**, 5350 (1951); cf. C. E. K. Mees and T. H. James,[2] pp. 219–221; F. M. Hamer,[5] pp. 592–594.



(CCXLV)

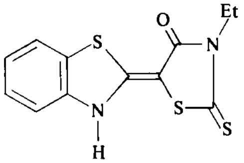


(CCXLVI)



R'' = 5-Cl
5-CN
5,6-Cl_2

(CCXLVII)



(CCXLVIII)

scribed by Brooker *et al.,* were anhydronium bases of *p*-hydroxystyryl dyes (CCXLIX); dyes of this type have also been examined by a number of other workers.[392] With these dyes, the absorption maximum moves to shorter wavelength as the polarity of the solvent is increased, and the same is true of Brooker's cyclobutanedione dye (CCXII).[357] Dyes showing large shifts in the opposite direction have also been prepared, the greatest effect being obtained with dye (CCL).[357]

Arnett and Hufford have examined the solvatochromism of the bridged-chain merocyanine (CCL) in aqueous *tert*-butyl alcohol; addition of ~4 mole % of the alcohol to the aqueous solution caused the very large red shift of 140 nm.[392a] Blandamer *et al.* have shown, however, that this is due largely to a monomer-dimer equilibrium, complete dimerization occurring in pure water.[392b]

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[392] A. I. Kiprianov and E. S. Timoshenko, *Ukr. Khim. Zh.* **18,** 347 (1952); *CA* **49,** 984 (1955); A. I. Kiprianov and F. A. Mikhailenko, *Zh. Obshch. Khim.* **31,** 1334 (1961); *CA* **55,** 27895 (1961); S. Hünig and O. Rosenthal, *Ann. Chem.* **592,** 161 (1955); S. Hünig, G. Bernhard, W. Liptay, and W. Brenninger, *Ann. Chem.* **690,** 9 (1965); J. P. Saxena, W. H. Stafford, and W. L. Stafford, *J. Chem. Soc.* p. 1579 (1959); J. T. Leach and J. P. Phillips, *J. Org. Chem.* **27,** 3309 (1962).

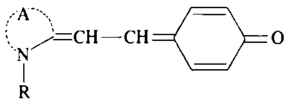
[392a] E. M. Arnett and D. Hufford, *J. Am. Chem. Soc.* **88,** 3140 (1966).

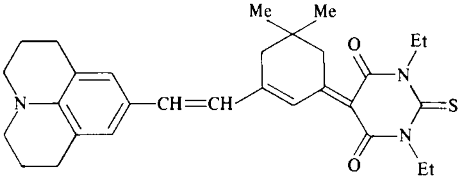
[392b] M. J. Blandamer, M. C. R. Symons, and M. J. Wootten, *Trans. Faraday Soc.* **63,** 2337 (1967).

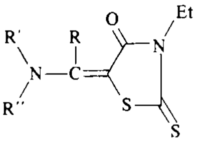
A structural determination by X-ray analysis has been made on a merocyanine-iodine complex.[392c]

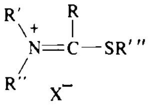
F. Hemioxonols and Oxonols

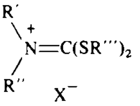
Riester has compared the spectra of some rhodanine hemioxonols (CCLI) with those of related merocyanines, including those obtained by reaction of quaternary salts (XCI) with 3-ethylrhodanine; the general method used to prepare (CCLI; R = H or alkyl) involved reaction of a salt (CCLII) (from a thioamide and a quaternizing agent) with 3-ethylrhodanine.[393] If the salt (CCLIII) (from a dithiocarbamate, R′R″N-CSSR‴, was used) then dyes (CCLI) in which R was an alkylthio group could be obtained; this group could be replaced by an amino group by reaction with an amine.[394]


(CCXLIX)


(CCL)


(CCLI)


(CCLII)


(CCLIII)

Corresponding to the use of a neopentylene bridge in cyanines and merocyanines (Section V,B,1,c), VanLare has prepared some pentamethinehemioxonols with this bridging group (CCLIV).[395]

Morris and Mooney have used NMR spectroscopy to show that the anion of a rhodanine oxonol is correctly represented by structure (CCLV), in which the negative charge is shared by mesomerism with the other oxygen atom. In the neutral molecule, however, the proton is

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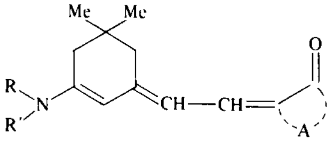
[392c] M. Bois d'Enghien-Peteau, J. Meunier-Piret, and M. Van Meerssche, *J. Chim. Phys. Physicochim. Biol.* **65**, 1221 (1968).

[393] O. Riester, *Chimia* (*Aarau*) **15**, 75 (1961); cf. O. Riester and AGFA, *DBP* 1,175,810.

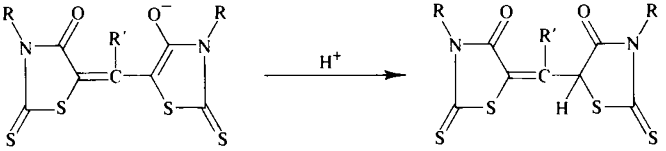
[394] H. von Rintelen and O. Riester, *Mitt. Forschungslab. Agfa Leverkusen-Muenchen* **1**, 65 (1955); *DBP* 947,185.

[395] E. J. VanLare and Eastman Kodak, *USP* 2,956,881.

attached not to an oxygen atom as previously thought, but to a carbon atom; in the resulting molecule (CCLVI) there is no resonance interaction between the two rings, which are not coplanar.[396]



(CCLIV)



(CCLV) (CCLVI)

The anions (CCVIIIc), derived from the highly acidic tetracyano unsaturated hydrocarbons, show mesomerism typical of an oxonol anion; these, and some related anions have been discussed as negatively-charged cyanines by Hünig.[278a] A recent paper by Bossa *et al.* deals with the electronic structure of the anions (CCVIIIc; $n = 0$, 1, and 2).[396a]

VII. Polynuclear Dyes

The chapter on cyanine dyes in Volume II discussed several examples of dyes with three heterocyclic nuclei, including the technically important "rhodacyanines." It is not possible to discuss here all of the numerous patents, which have appeared subsequently, dealing with modifications of known structural types; this section will therefore concentrate primarily on novel types of tri- and polynuclear dyes not included in Hamer's review.[397]

A number of such dyes, the preparation of which depended on the presence within a molecule of two reactive sites, have been referred to earlier: see Sections IV,A[195,209]; IV,B[230]; and VI,B[358,363,370,371].

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[396] E. A. Morris and E. F. Mooney, *Compt. Rend. 36th Congr. Intern. Chim. Ind., Brussels, 1966* Vol. 3; see *Ind. Chim. Belge* **32**, Spec. No., 86 (1967).

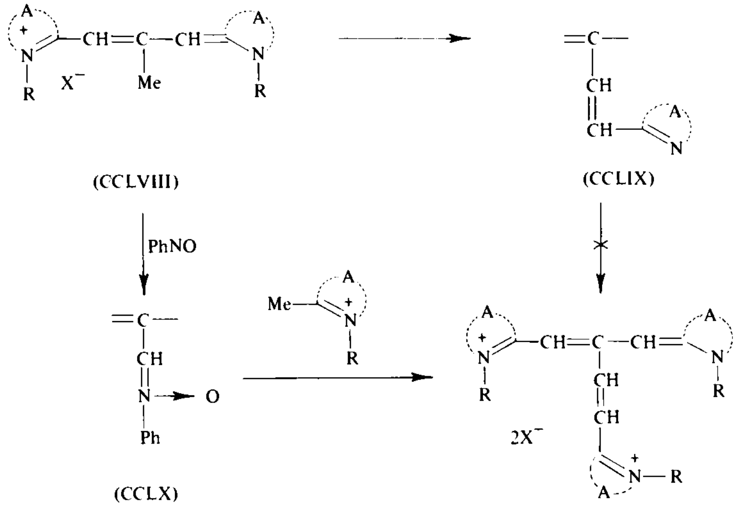
[396a] M. Bossa, G. Ciullo, and A. Sgamelotti, *Tetrahedron* **25**, 1991 (1969).

[397] F. M. Hamer,[5] Chapter XV.

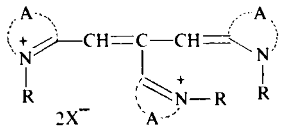
A. Dyes with a Branched Chain

1. *Neocyanine Isomers*

Before the structure of the neocyanines was finally established (see [1,397]), structure (CCLVII), among others, had been proposed for these dyes. When it was realized that the neocyanines did not in fact possess structure (CCLVII), it clearly became of interest to prepare dyes of this type. The first attempt was by Hamer, who condensed a *meso*-methyltrimethinecyanine (CCLVIII) with a heterocyclic aldehyde (or derivative) to obtain (CCLIX); all attempts to quaternize this to give (CCLVII) were, however, unsuccessful.[398]



(CCLVIII) (CCLIX) (CCLX) (CCLVII)



(CCLXI)

Subsequently Tanabe claimed to have synthesized such dyes by reaction of a *meso*-anilinotrimethinecyanine with an anilinovinyl quaternary

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[398] F. M. Hamer, *J. Chem. Soc.* p. 3197 (1952). Other dyes of type (CCLIX) have been described by W. Ried and R. Bender, *Chem. Ber.* **90,** 2650 (1957).

salt.[399] However, Kimura showed that Tanabe's products did not possess the assigned structure, and described methods for the unequivocal synthesis of the required dyes.[400] One of these methods involved the conversion of a *meso*-methyltrimethinecyanine into the phenylnitrone (CCLX) by reaction with nitrosobenzene, followed by the condensation of (CCLX) with a methyl quaternary salt to give (CCLVII). The method was, of course, not restricted to the synthesis of dyes in which all three heterocyclic nuclei were identical. Kimura also described methods for the synthesis of the lower vinylogs (CCLXI) of these dyes.[400]

2. *Holopolar Dyes*

Interest has been maintained in un-ionized dyes of the type (CCLXII), first described by Brooker *et al.*[124,401]; depending on the solvent, such dyes can exist either as a substituted trimethinecyanine (the "holopolar" form) or as a substituted merocyanine (the "meropolar" form).[402] The reality of the charge separation in the holopolar form of two such dyes has been demonstrated by measurement of their dipole moments.[403] Clearly, in theory any ketomethylene nucleus of the type commonly used in merocyanines may be incorporated into a dye of type (CCLXII), and indeed many of the nuclei included in Section VI,B have been so used. Thus, dyes (CCLXII) have been prepared in which D completes one of the following rings in addition to those disclosed in the original patent[401]: (CCXI),[356] (CCXVI),[404] (CCXVII),[362] and (CCXXIII).[367] Also, similar dyes but with an additional α,α'-ethylene or *o*-phenylene bridge have been described.[385,405]

3. *Other Dyes*

Ficken and Fry have discussed the preparation and light absorption of some trinuclear cyanines of type (CCLXIII) in which D completes

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[399] Y. Tanabe, *Yakugaku Zasshi* **73,** 855, 860 (1953); *CA* **48,** 8093, 8095 (1954).

[400] S. Kimura, *Bull. Soc. Sci. Phot. Japan* **9,** 29, 41 (1959); *Bull. Chem. Soc. Japan* **33,** 872, 875, 879 (1960); *CA* **55,** 3556 (1961).

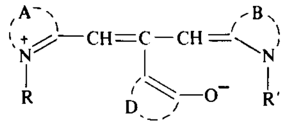
[401] L. G. S. Brooker, F. L. White, and Eastman Kodak, *USP* 2,739,964 (Re 24,292).

[402] For a discussion of this isomerism, see Brooker *et al.*[124,304] and C. E. K. Mees and T. H. James,[2] pp. 223–226; cf. also A. van Dormael, *Compt. Rend. 27th Congr. Intern. Chim. Ind., Brussels, 1954* Vol. 3; see *Ind. Chim. Belge* **20,** Spec. No., 658 (1955); A. van Dormael and J. Nys, *Compt. Rend. 31st Congr. Intern. Chim. Ind., Liege, 1958;* see *Ind. Chim. Belge* Suppl. **2,** 512 (1959).

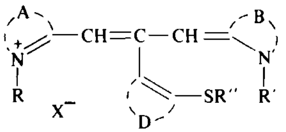
[403] A. J. Petro, C. P. Smyth, and L. G. S. Brooker, *J. Am. Chem. Soc.* **78,** 3040 (1956).

[404] J. E. Jones, N. W. Kalenda, and Eastman Kodak, *FP* 1,485,203.

[405] L. G. S. Brooker, F. L. White, and Eastman Kodak, *USP* 2,955,939; L. G. S. Brooker, F. G. Webster, and Eastman Kodak, *USP* 3,194,805.



(CCLXII)



(CCLXIII)

an indole, pyrazole, or thiophene nucleus[406]; these dyes resemble the holopolar form of dyes (CCLXII) in that the heterocyclic ring on the meso position of the trimethine chain is not coplanar with the rest of the molecule.

Coenen and Riester have described a new method for the preparation of dyes of structure (CCLXIV; $n = 0$) in which a dimethinemerocyanine (CCLXV; $n = 0$) is reacted with a heterocyclic aldehyde (CCLXVI), e.g., Fischer's aldehyde. Applied to tetramethinemerocyanines the novel dyes (CCLXIV; $n = 1$) were obtained.[407]

Reichardt has reacted a methyl quaternary salt with the trialdehyde $HC(CHO)_3$ in the presence of acetic anhydride and sodium acetate to give the trinuclear dye (CCLXVII), which possesses simultaneously three pentamethinecyanine segments.[408]

B. Rhodacyanines and Related Dyes

The most useful technically of the trinuclear dyes, and consequently the most thoroughly examined, are the linear trinuclear dyes with a central ketomethylene nucleus. Methods of synthesis of these dyes, to which the convenient name "rhodacyanines" has been applied, have been described fully previously (see reference 1 for the synthesis of the IG dyes Ma 1088, etc., also Hamer[397]).

Many of the variants in the heterocyclic nuclei and the polymethine chain, discussed in earlier sections, have been carried over into the rhodacyanines, and will not be reiterated here. Among the more interesting developments is the study of Brunken and Poppe of rhodacyanines with a central 4-imidazolidone ring (CCLXVIII); methods were described for the preparation of dyes in which $n = 1$, 2, or 3, the chain of seven carbon atoms in the last of these being the longest yet incorporated into a dye of this type.[409]

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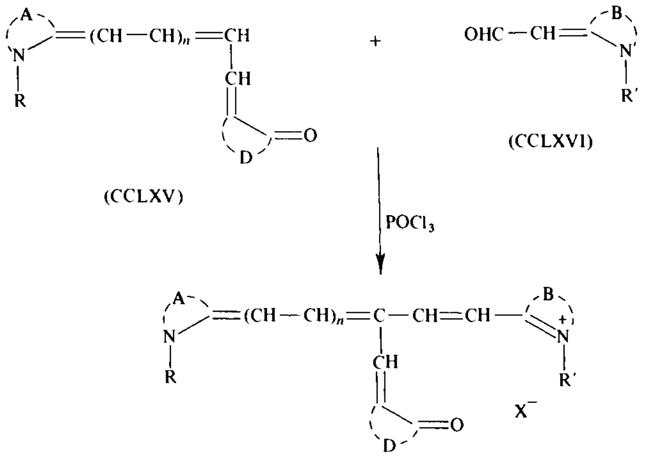
[406] G. E. Ficken and D. J. Fry, *Compt. Rend. 36th Congr. Intern. Chim. Ind., Brussels, 1966* Vol. 3; see *Ind. Chim. Belge* **32,** Spec. No., 44 (1967).

[407] M. Coenen, *Ann. Chem.* **633,** 92 (1960); M. Coenen and O. Riester, *ibid.* p. 110.

[408] C. Reichardt, *Tetrahedron Letters* p. 4327 (1967).

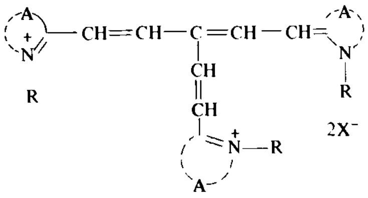
[409] J. Brunken and E. J. Poppe, *Veroeffentl. Wiss. Photolab. AGFA* **9,** 79 (1961).



(CCLXV)

(CCLXVI)

(CCLXIV)



(CCLXVII)

The trinuclear dye (CCLXIX) has been prepared by further reaction of the merocyanine (CCXLVIII)[390]; insofar as it is still a cationic dye, it can be regarded as a rhodacyanine. Dyes such as (CCXXVI), however, in which the nitrogen atom of the central ring lacks a substituent, are neutral substances related to rhodacyanines as cyanine bases are related to true cyanines. So too are dyes of type (CCLXX) in which the third ring is not quaternized.[410]

The commonest method of synthesizing a rhodacyanine is to react a merocyanine containing a -CS—NR- grouping with a quaternizing agent, followed by reaction of the alkylthio quaternary salt with a reactive methyl quaternary salt; use of a reactive methylene compound in the second stage leads to a trinuclear merocyanine.[1,397] If the intermediate

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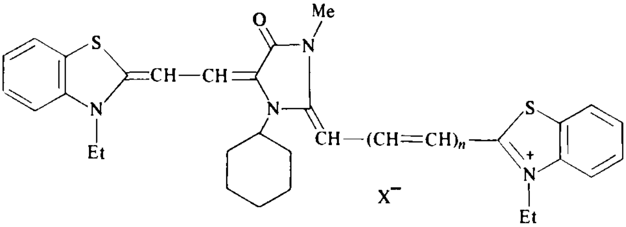
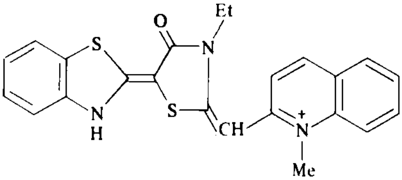
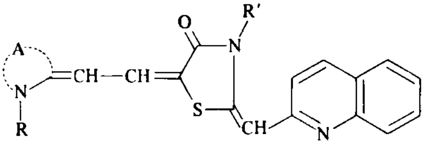
[410] R. H. Sprague, J. J. Urbancik, and Horizons, *USP* 3,109,736. Some related dyes have been described by F. Bauriedel, W. Franke, H. Lang, and DuP, *USP* 3,275,444.



(CCLXVIII)



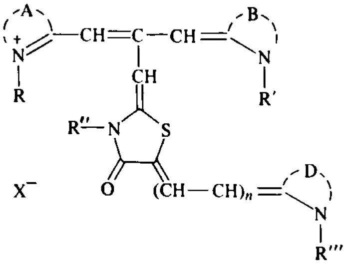
(CCLXIX)



(CCLXX)

quaternized merocyanine is reacted with a *meso*-methyltrimethinecyanine, then a tetranuclear dye of the novel structure (CCLXXI) results.[411]

This type of reaction has been adapted to oxonols in which one or both rings possess a -CS—NR- grouping. Thus reaction of the quaternary salt of an oxonol (CCLXXII) with (i) a methyl quaternary salt provides



(CCLXXI)

a new route to trinuclear dyes (CCLXXIII)[412] and with (ii) a ketomethylene compound gives dyes (CCLXXIV).[412,413] Dyes of the latter type in which A = B had previously been prepared by reaction of a rhodanine derivative (CCLXXV) with 2 moles of a ketomethylene

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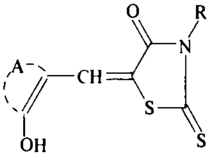
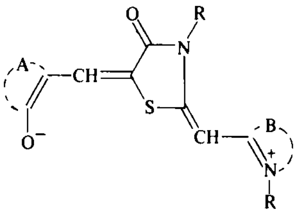
[411] Nederlandsche Fotografische Industrie, *DP* 69,344; *CA* **47,** 6288 (1953).

[412] E. B. Knott, *J. Chem. Soc.* p. 6204 (1964).

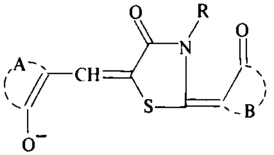
[413] B. Gaspar and Minnesota Mining and Manufacturing Co., *USP* 3,152,905.



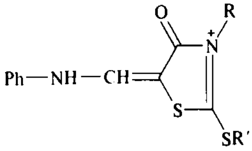
(CCLXXII)



(CCLXXIII)



(CCLXXIV)



(CCLXXV)

compound.[414] The complex tetranuclear dyes (CCLXXVI)[415] and (CCLXXVII)[416] have also been prepared by the use of similar reactions, the linkages formed in the final stage being indicated by vertical dashed lines.

C. Other Tetranuclear Dyes

In addition to the tetranuclear dyes discussed in Section B, others have been obtained by reaction at both methyl groups (using conventional reagents) in the bis-quaternary salt of a base such as (CCLXXVIII). In the first examples, the two heterocyclic rings were linked either directly or by a methylene group.[111] A different type of linking group, viz., $-NHCONH-$ or $-NHCO(CH_2)_nCONH-$ (where $n =$ 0–4), was used by Ushenko and Chovnik.[417]

Bis-merocyanines have likewise been prepared from bis-pyrazolinones (CCLXXIX), where the linking group Y is $-(CH_2)_4-$, *m* or *p*-phenylene, etc., or is a direct linkage.[418]

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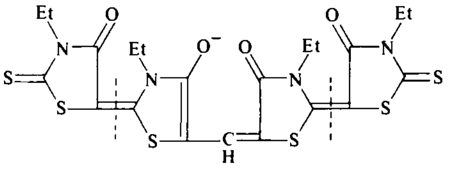
[414] Z. P. Sytnik, A. A. Abdullaev, R. A. Gershtein, and R. V. Timofeeva, *RP* 124,570; *CA* **54**, 11780 (1960).

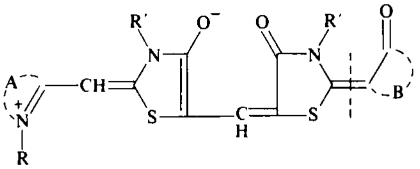
[415] M. S. Lyubich, Z. P. Sytnik, and R. V. Timofeeva, *Zh. Obshch. Khim.* **33**, 3979 (1963); *CA* **60**, 12140 (1964).

[416] A. A. Abdullaev, R. V. Timofeeva, M. K. Grechko, and Z. P. Sytnik, *RP* 170,595; *CA* **63**, 11750 (1965).

[417] I. K. Ushenko and L. I. Chovnik, *Zh. Obshch. Khim.* **30**, 2665 (1960); *CA* **55**, 11851 (1961).



(CCLXXVI)



(CCLXXVII)

Reaction of a bis-quaternary salt of type (CCLXXX) with, e.g., a 2-formylmethylenebenzothiazoline leads to a bis-trimethinecyanine in which the two moieties are linked by a $-(CH_2)_n-$ chain at their α-positions.[419]

Kiprianov and Mushkalo have described the synthesis of dyes such as (CCLXXXI) and similar bis-merocyanines, and have discussed the effect on the light absorption of linking the two chromophores in this manner.[420]

D. Polymeric Dyes

By reaction of the bis-ethiodide of base (CCLXXVIII; Y = a direct linkage) with ethyl orthoformate, Pailer and Renner-Kuhn prepared mixtures of low polymers of the structure (CCLXXXII), where a maximum value of n of about 5.8 was obtained.[421]

Some interest has been shown in the preparation of vinyl polymers with cyanine dye residues attached to the hydrocarbon chain. The first

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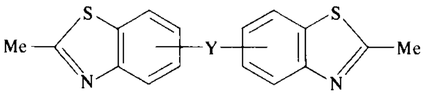
[418] J. Ciernik and A. Mistr, *Collection Czech. Chem. Commun.* **31**, 4669 (1966). The sensitizing efficiency of these dyes has been discussed by J. Ciernik, A. Mistr, and M. Vavra, *ibid.* **33**, 327 (1968).

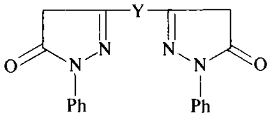
[419] E. D. Sych and E. K. Perkovskaya, *Zh. Organ. Khim.* **1**, 1479 (1965); *CA* **64**, 3733 (1966).

[420] A. I. Kiprianov and I. L. Mushkalo, *Zh. Organ. Khim.* **1**, 744 (1965); *CA* **63**, 13450 (1965).

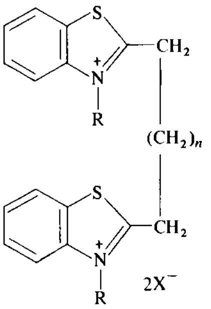
[421] M. Pailer and E. Renner-Kuhn, *Monatsh. Chem.* **85**, 601 (1954).



(CCLXXVIII)



(CCLXXIX)



(CCLXXX)

materials of this type were described by Sprague *et al.*, who reacted a cyanine possessing an *N*-hydroxyalkyl substituent with a polymer containing functional groups capable of esterifying the hydroxy group; poly(acrylyl chloride) or maleic anhydride copolymers were suggested as suitable for this purpose. The products, being nondiffusible, were useful, for instance, as light filters in photographic materials.[422] A different approach involved the use of a polymer containing sulfonic acid groups, e.g., the polyacetal formed by poly(vinyl alcohol) and *o*-sulfobenzaldehyde, as the anion of a cyanine dye (oxazoline styryl dyes were actually suggested); the resulting products could be dispersed in gelatin and used as light filters.[423]

Starting from a copolymer of styrene and 2-methyl-5-vinylpyridine (CCLXXXIII), Turchinovich has used known reactions to convert the pyridine rings into indolizine nuclei, and then into cyanine dye residues, giving the polymer (CCLXXXIV).[424] Kudryavtsev has quaternized the

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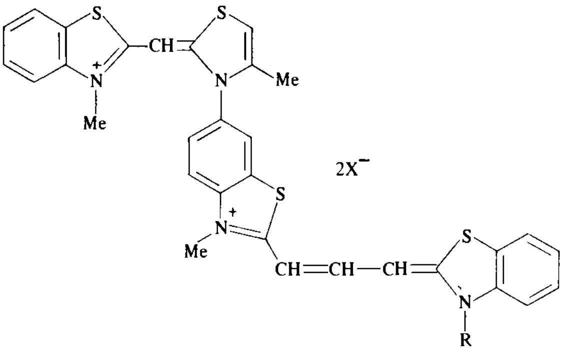
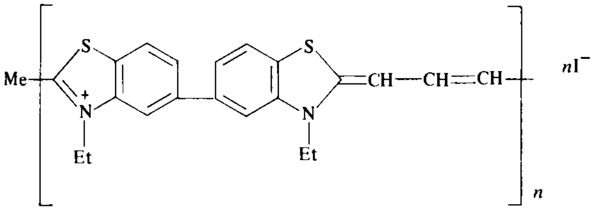
[422] R. H. Sprague, L. G. S. Brooker, S. G. Dent, and Eastman Kodak, *USP* 2,639,282.

[423] V. F.-H. Chu, J. Q. Umberger, and DuP, *USP* 3,182,029.

[424] G. Yu. Turchinovich, *Tr. Kievsk. Politekhn. Inst.* **43**, 91 (1963); *CA* **62**, 10558 (1965).



(CCLXXXI)



(CCLXXXII)

pyridine rings in a poly(2-methyl-5-vinylpyridine) and then reacted with *p*-dimethylaminobenzaldehyde to give (CCLXXXV).[425]

Little has suggested on theoretical grounds that a polymer consisting of a carbon chain with conjugated double bonds, the residues of a cyanine molecule being attached at regular intervals, should exhibit superconductivity even at room temperature or above.[426] A recent patent has described various methods of preparation for such polymers, but no figures were given to show that they were in fact superconductive. One of the methods leading to (CCLXXXVI), is shown.[427]

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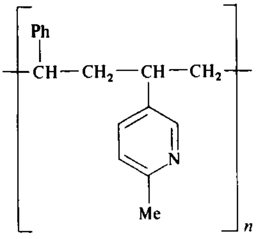
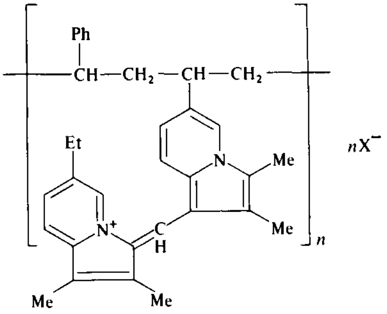
[425] G. I. Kudryavtsev, E. A. Vasil'eva-Sokolova, I. S. Pinskaya, and T. I. Volynskaya, *Faserforsch. Textiltech.* **16**, 256 (1965).

[426] W. A. Little, *Phys. Rev.* **134**, A1416 (1964). For later literature on this topic, see J. H. Lupinski, K. R. Walter, and L. H. Vogt, *Mol. Cryst.* **3**, 241 (1967).

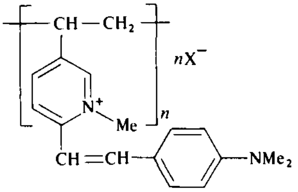
[427] Varian Associates, *FP* 1,458,963.



(CCLXXXIII)



(CCLXXXIV)



(CCLXXXV)

VIII. Other Dyes Related to Cyanines

A. CYANINE BASES

Reference to cyanine bases has already been made on a number of occasions in this chapter, viz., in Sections III,E[145,147]; IV,A[222]; IV,B[234]; and V,C.[325]

It has been shown that, in the preparation of such compounds by heating a cyanine dye with a high-boiling amine,[428] the alkyl group is lost from the more basic heterocyclic nucleus.[429,430]

A series of indole bases (CCLXXXVII) has been prepared by this dequaternization reaction; the light absorption of these, and of the isomeric bases with group R on the nitrogen atom of ring A, has been correlated with the basicities of A as measured by "Brooker deviations."[429]

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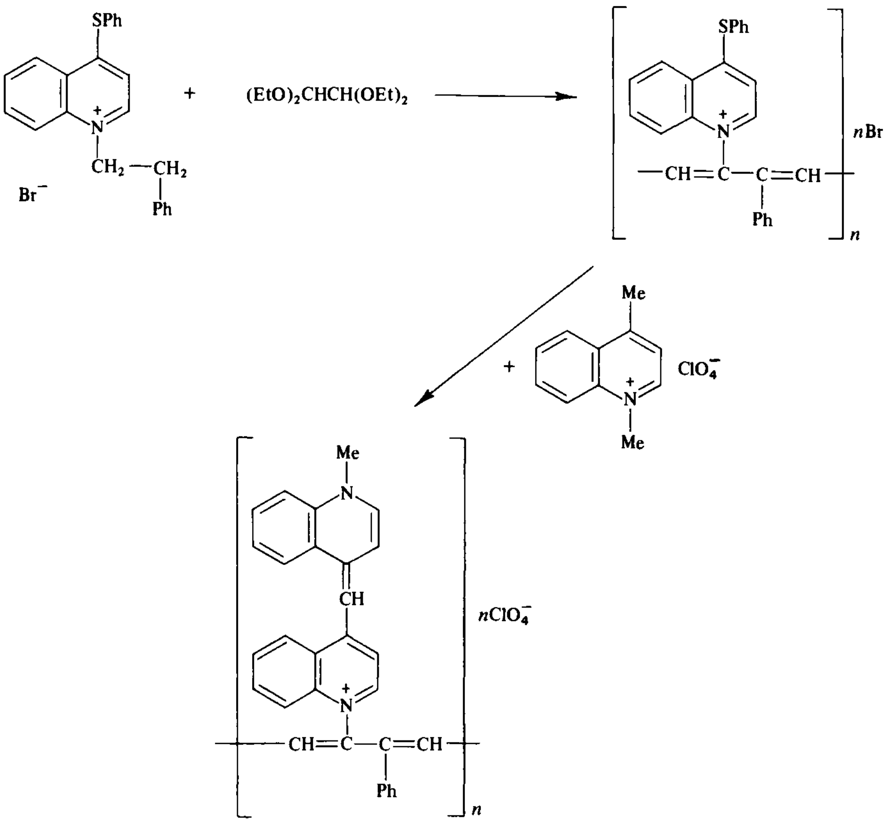
[428] This, and other methods of preparation of cyanine bases, are discussed by Hamer,[5] Chapter XI.

[429] G. E. Ficken and J. D. Kendall, *J. Chem. Soc.* p. 1529 (1960).

[430] A. I. Kiprianov and Yu. L. Slominskii, *Zh. Organ. Khim.* **1**, 1314 (1965); *CA* **63**, 15016 (1965).



(CCLXXXVI)

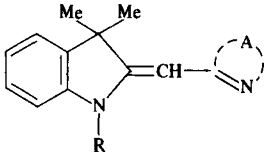
Kiprianov and Slominskii have likewise related the absorption maxima of some cyanine bases to their pK_a values.[430a]

B. Styryl Dyes

Frequent reference has been made in this chapter to styryl dyes, prepared by reaction of *p*-dialkylaminobenzaldehydes with reactive methyl quaternary salts[431]; many of the other references of Sections III and IV also include examples of such dyes. In addition, numerous papers and patents have appeared dealing specifically with styryl dyes, the patents

[430a] A. I. Kiprianov and Yu. L. Slominskii, *Zh. Organ. Khim.* **1**, 1321 (1965); *CA* **63**, 15016 (1965).

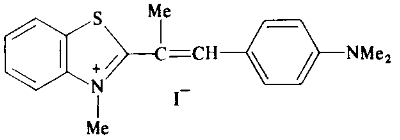
[431] Cf. *CSD II*, p. 1172, and F. M. Hamer[5] Chapter XIII, Sect. 1.



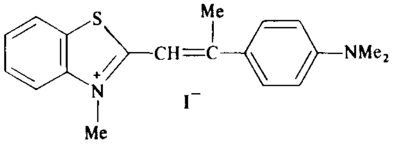
(CCLXXXVII)

generally claiming their use as textile dyes, not as photographic sensitizers.

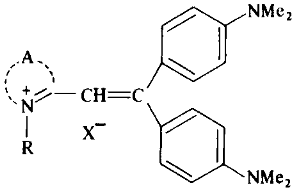
Kiprianov *et al.* have studied the effect on the light absorption of substituents in the dimethine chain of styryl dyes and styryl bases; they conclude, for instance, that there is considerable steric hindrance in (CCLXXXVIII), but little in the isomeric (CCLXXXIX).[432]



(CCLXXXVIII)



(CCLXXXIX)



(CCXC)

Oksengendler and Kiprianov have obtained a series of bis(*p*-dimethylaminophenyl)vinyl dyes (CCXC) by reaction of methyl quaternary salts with Michler's ketone. In most cases the light absorption was fairly close to that of the corresponding *p*-dimethylaminostyryl dye.[433]

Reference has already been made to Hünig's work on the preparation of diazastyryl dyes by the oxidative coupling of hydrazones with aromatic amines (Section VI,D). Other methods of preparation of these

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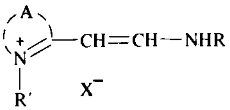
[432] A. I. Kiprianov and A. I. Tolmachev, *Ukr. Khim. Zh.* **25**, 337 (1959); *CA* **54**, 5621 (1960); A. I. Kiprianov and F. A. Mikhailenko, *Zh. Obshch. Khim.* **31**, 781 (1961); *CA* **55**, 24019 (1961).

[433] G. M. Oksengendler and A. I. Kiprianov, *Ukr. Khim. Zh.* **16**, 383 (1950); *CA* **48**, 1684 (1954).

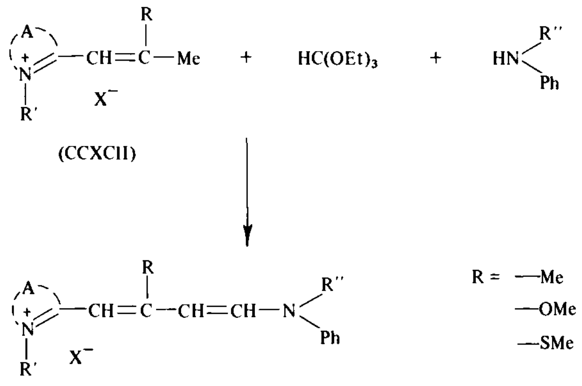
dyes have been described by Baumann and Dehnert,[434] and by Yagupol'skii and Gandel'sman, who have prepared a series of benzothiazole diazastyryls with a variety of fluorine-containing substituents.[435] Sureau has related the lightfastness of diazastyryl dyes to the pK_a of the hydrazones (CCXLIII; R′ = H) from which they can be obtained by oxidative coupling.[436]

C. Hemicyanines

These dyes, exemplified by the anilinovinyl salts (CCXCI; R = Ph), continue to receive a certain amount of attention. Takahashi, for instance, has used conventional synthetic methods[437] to prepare a considerable number of dyes of type (CCXCI) in which R is aryl or pyridyl.[438]



(CCXCI)



(CCXCII)

(CCXCIII)

A variety of new methods have been devised for the synthesis of hemi-

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[434] H. Baumann and J. Dehnert, *Chimia (Aarau)* **15**, 163 (1961).

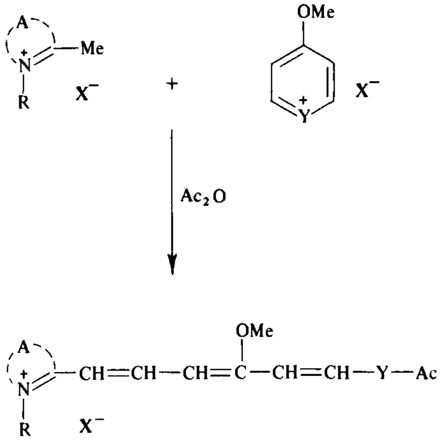
[435] L. M. Yagupol'skii and L. Z. Gandel'sman, *Zh. Obshch. Khim.* **33**, 2301 (1963); *CA* **60**, 692 (1964).

[436] R. Sureau, *Compt. Rend. 36th Congr. Intern. Chim. Ind., Brussels, 1966* Vol. 3; see *Ind. Chim. Belge* **32**, Spec. No., 17 (1967).

[437] Described in F. M. Hamer,[5] Chapter XIII, Sect. 3.

[438] T. Takahashi and M. Hayami, *Yakugaku Zasshi* **80**, 895 (1960); *CA* **54**, 24657 (1960), and earlier papers.

cyanines with substituents on the polymethine chain. Intermediates of type (CCXCII) have proved useful for this purpose, reacting as shown to give (CCXCIII); use of MeOCH=CHCH(OEt)$_2$ in place of ethyl orthoformate gives the higher vinylogs of (CCXCIII).[439] Another method is illustrated by the preparation of (CCXCIV), which on treatment with an amine is converted into a hemicyanine by replacement of the –YAc group.[440]



(CCXCIV)

It has been shown that salts of structure (CCLII) react with methyl heterocyclic quaternary salts to form hemicyanines by elimination of mercaptan (R‴SH).[441] This is, of course, quite analogous to the alkylthio quaternary salt method of preparing monomethinecyanines [Section II,B,2; cf. the analogous preparation of hemioxonols from (CCLII), Section VI,F].

Kiprianov and Slominskii have likewise shown that the quaternary salt (CCXCV), from acetophenone anil and methyl iodide, possesses a reactive methyl group*, and thus undergoes many of the reactions typical of methyl heterocyclic quaternary salts. For instance, ethyl orthoformate gives the symmetrical dye (CCXCVI), *p*-dimethylaminobenzaldehyde forms a styryl derivative, while compounds such as 2-formylmethylene-

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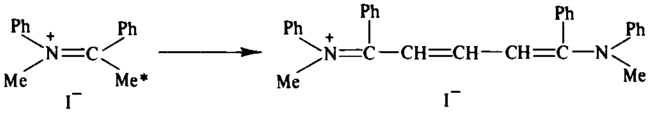
[439] S. A. Kheifets and N. N. Sveshnikov, *Dokl. Akad. Nauk SSSR* **163**, 1177 (1965); *CA* **64**, 843 (1966); see also A. V. Kazymov, E. B. Sumskaya, E. P. Shchelkina, and I. N. Sergeeva, *RP* 195,316; *CA* **68**, 79625 (1968).

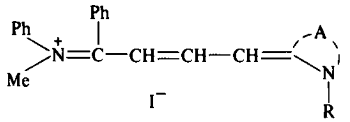
[440] A. I. Tolmachev, *Zh. Obshch. Khim.* 33, 1864 (1963); *CA* **60**, 689 (1964).

[441] N. N. Sveshnikov and N. S. Stokovskaya, *RP* 147,707; 150,960; *CA* **58**, 5818 (1963); **62**, 10577 (1965).

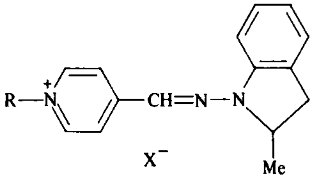
1,3,3-trimethylindoline give the hemicyanines (CCXCVII).[442] Similar reactions, but using the immonium salts from aliphatic and alicyclic ketones, have also been described.[443]



(CCXCV) (CCXCVI)



(CCXCVII)



(CCXCVIII)

Quaternization of the anil formed between a heterocyclic aldehyde and an *N*-aminoindoline, etc., gives an azahemicyanine (CCXCVIII).[444]

D. Open-Chain Dyes

The hemicyanines are intermediate in structure between the true cyanines and the dyes of the present section, in which the terminal nitrogen atoms are attached directly to the ends of the polymethine chain. Such dyes include the well-known Zincke salts (CCXCIX), which have been extensively examined by Grigor'eva[445] among others.

Some considerable interest has been shown in recent years in polymethine dyes in which the terminal nitrogen atoms each carry two small alkyl groups, since it is considered that this represents the cyanine structure in its simplest form. Malhotra and Whiting have prepared the series of dyes (CCC) in which n has the values 0 to 6; apart from the first member ($\lambda_{max} = 224$ nm) the wavelength of maximum absorption increases almost linearly with n from 312.5 nm ($n = 1$) to 848 nm ($n =$

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[442] A. I. Kiprianov and Yu. L. Slominskii, *Zh. Organ. Khim.* 3, 168 (1967); *CA* 66, 86593 (1967).

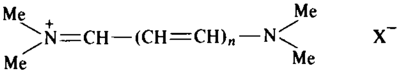
[443] R. A. Jeffreys and Eastman Kodak, *BP* 1,092,252–3; Eastman Kodak, *FP* 1,462,889.

[444] R. Raue, E. H. Rohe, and FBy, *BP* 964,452.

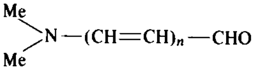
[445] N. E. Grigor'eva, L. I. Shcherbakova, and V. D. Titskaya, *Zh. Organ. Khim.* 3, 1659 (1967); *CA* 68, 12826 (1968), and earlier papers.

$$Ph\overset{+}{N}H{=}CH{-}(CH{=}CH)_2{-}NHPh \qquad X^-$$

(CCXCIX)



(CCC)



(CCCI)

$$O^-{-}(CH{=}CH)_nCHO$$

(CCCII)

6). The same authors have also examined the series (CCCI; $n = 1$–6) and (CCCII; $n = 1$–4), which were considered to represent the merocyanines and oxonols, respectively, in their most fundamental forms.[446]

Improved methods of preparation for dyes of structure (CCC) have been provided by Nikolajewski *et al.*[447]; one of these methods is shown, starting from an unsaturated aldehyde (CCCIII). The same authors have described the cleavage of dyes (CCC) by amines to give similar polymethine dyes with shorter chain lengths, e.g., boiling (CCC; $n = 4$) with ethanolic methylamine for 30 minutes gives (CCC; $n = 3$) in 65% yield; stability decreases as the chain length increases and dyes with $n < 3$ are stable.[448]

Jutz and Müller have described the preparation of dye (CCCIV) by the method shown, also the related dyes with chains of three, five, and nine carbon atoms. These dyes are strongly basic, being protonated in the chain (and hence decolorized) even by water.[449]

Analogs of (CCC) with a bridged chain have been described. Thus, by formylation of cyclopentadiene under the Vilsmeier conditions, Hafner

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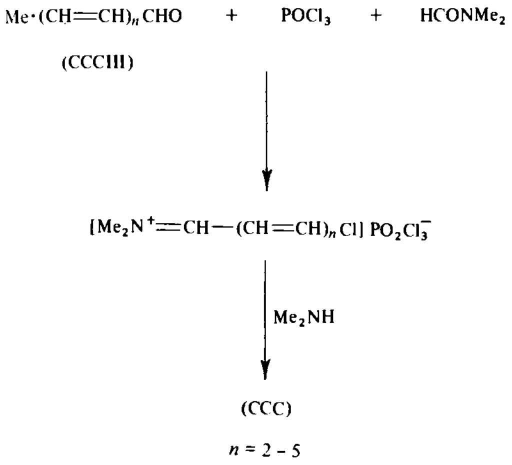
[446] S. S. Malhotra and M. C. Whiting, *J. Chem. Soc.* p. 3812 (1960).

[447] H. E. Nikolajewski, S. Dähne, B. Hirsch, and E. A. Janer, *Chimia* (*Aarau*) **20,** 176 (1966); H. E. Nikolajewski, S. Dähne, and B. Hirsch, *Chem. Ber.* **100,** 2616 (1967); cf. Z. Arnold and A. Holy, *Collection Czech. Chem. Commun.* **30,** 40, 47 (1965).

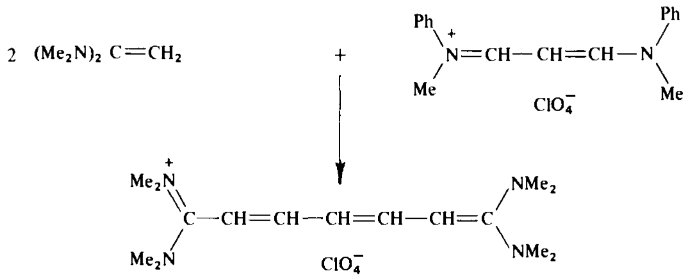
[448] H. E. Nikolajewski and S. Dähne, *Angew. Chem. Intern. Ed. Engl.* **5,** 1044 (1966).

[449] C. Jutz and E. Müller, *Angew. Chem. Intern. Ed. Engl.* **5,** 724 (1966).

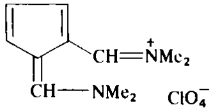


et al.[450] have prepared (CCCV) and some related compounds. More recently, Viehe *et al.*[451] have prepared the compound (CCCVI) which incorporates a cyclobutene ring in the chain.

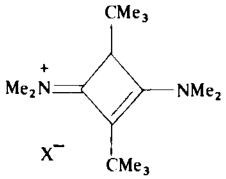
Some further analogs of the bridged trimethines (CCCVI) have been



(CCCIV)



(CCCV)



(CCCVI)

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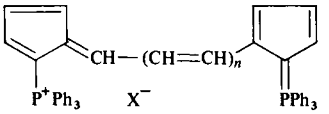
[450] K. Hafner, K. H. Vöpel, G. Ploss, and C. König, *Ann. Chem.* **661,** 52 (1963).

[451] H. G. Viehe, R. Buijle, R. Fuks, R. Merenyi, and J. M. F. Oth, *Angew. Chem. Intern. Ed. Engl.* **6,** 77 (1967).

prepared, but with the CMe_3 groups replaced by $—COR$[451a] or $—CO_2Et$.[451b]

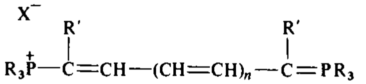
E. Phosphinines

In 1960 van Dormael *et al.* described the preparation and use as photographic sensitizers of a completely new type of polymethine dye in which the conjugated chain was terminated by phosphorus atoms instead of the usual nitrogen. Named "phosphinines," these dyes were of two related types (CCCVII) and (CCCVIII). The same authors also described unsymmetrical dyes (called phosphocyanines) with one phosphorus-containing end group, the other being a conventional nitrogen heterocycle; analogs of merocyanines were also prepared. The synthesis of a typical phosphocyanine (CCCIX) is shown.[452]



n = 0, 1 or 2

(CCCVII)



$$X^- \quad R_3\overset{+}{P}-\overset{R'}{C}=CH-(CH=CH)_n-\overset{R'}{C}=PR_3$$

R = Ph, —CH_2CH_2CN

R′= —CO_2Et, —CN, Bz

(CCCVIII)

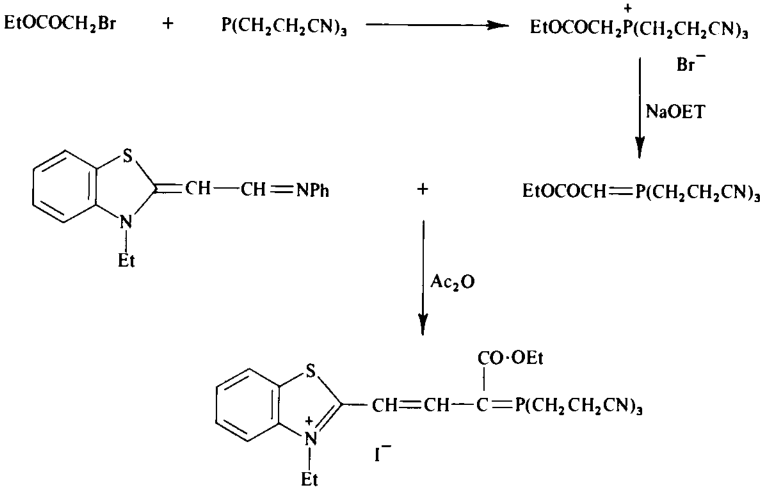
Dyes of similar types have also been prepared independently by Kukhtin *et al.*, who consider that the positive charge is not delocalized over the conjugated chain, but is in all probability localized on one of the terminal groups.[453] The preparation of the first three members (n = 0, 1, and 2) of the simple phosphorus dyes, Ph_3P^+ —$(CH{=}CH)_n$—CH=

[451a] M. Neuenschwander and A. Niederhauser, *Chimia* **22**, 491 (1968).

[451b] R. Gompper and G. Seybold, *Angew. Chem. Intern. Ed. Engl.* **7**, 824 (1968).

[452] A. van Dormael, J. Nys, and H. Depoorter, *J. Wiss. Phot.* **54**, 152 (1960); *J. Phot. Sci.* **9**, 70 (1961); A. van Dormael, *Chimia (Aarau)* **15**, 67 (1961); H. Depoorter, J. Nys, and A. van Dormael, *Tetrahedron Letters* p. 199 (1961); *Bull. Soc. Chim. Belges* **73**, 921 (1964); **74**, 12 (1965); J. Nys, A. van Dormael, and G. Verbeke, *Chimia (Aarau)* **19**, 315 (1965).

[453] V. A. Kukhtin, A. V. Kazymov, and T. N. Voskoboeva, *Dokl. Akad. Nauk SSSR* **140**, 601 (1961); *CA* **56**, 10327 (1962); A. V. Kazymov, T. N. Voskoboeva, and V. A. Kukhtin, *RP* 183,068; *CA* **66**, 19852 (1967); A. V. Kazymov and E. B. Sumskaya, *RP* 186,282; 190,206; *CA* **67**, 3707, 118102 (1967).



(CCCIX)

441 nm

PPh_3, was subsequently described by Ramirez *et al.*[454] and by Märkl[454a]; the electronic structure of these dyes was also discussed (see also ref. 3). Dyes of this type have been reviewed by van Dormael.[454b] The first examples of analogous dyes with arsenic replacing phosphorus, e.g. (CCCIXa) have now been prepared.[454c]

F. Miscellaneous Derivatives of Cyanines

Pokrovskaya *et al.* have studied the known ability of cyanines to form unstable complexes with silver ions in solution, using various merocyanines and rhodacyanines also. In general, complex-forming ability increased with increasing basicity of the heterocyclic rings and with increasing chain length; steric factors were also operative. The ability to form complexes was correlated with the tendency of the dyes to fog a photographic emulsion.[455]

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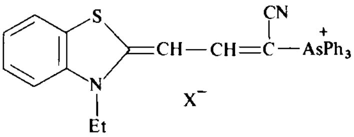
[454] F. Ramirez, N. B. Desai, B. Hansen, and N. McKelvie, *J. Am. Chem. Soc.* **83,** 3539 (1961); see J. S. Driscoll, D. W. Grisley, J. V. Pustinger, J. E. Harris, and C. N. Matthews, *J. Org. Chem.* **29,** 2427 (1964).

[454a] G. Märkl. *Angew. Chem.* **75,** 1121 (1963). For some related bridged dyes see G. Märkl, *Z. Naturforsch.* **18b,** 1136 (1963).

[454b] A. van Dormael, *Ind. Chim. Belge* **33,** 977 (1968).

[451c] J. Nys, *Chimia* Suppl. p. 115 (1968).

[455] K. I. Pokrovskaya, I. I. Levkoev, and S. V. Natanson, *Zh. Fiz. Khim.* **30,** 161 (1956); *CA* **50,** 9926 (1956); K. I. Pokrovskaya, *Zh. Nauchn. i Prikl. Fotogr. i Kinematogr.* **4,** 133 (1959); *CA* **54,** 7385 (1960); *Usp. Nauchn. Fotogr. Akad. Nauk*



(CCCIXa)

The ability of rhodanine and various derivatives to form stable complexes with silver ions is well known (cf. Feigl's reagent, 5-*p*-dimethylaminobenzylidenerhodanine).[456] This property has been used to form water-soluble complexes by reaction of rhodanine merocyanines with silver nitrate, such complexes being more easily incorporated into a photographic emulsion than are the dyes.[457] The gold complexes of merocyanines with an –NR—CS– grouping have been claimed as photographic sensitizers.[344]

The preparation has been described of merocyanines (CCCX) which are derivatives of 8-quinolinol. These dyes show the usual solvatochromism, but the complexes formed with a variety of metal ions are not solvatochromic.[458]

Scheibe *et al.* have discussed the reversible formation of adducts between cationic dyes (including cyanines) and Lewis bases. The adduct from, e.g., pseudocyanine and piperidine is said to have structure (CCCXI); the absorption maximum of the adducts from one particular dye is independent of the nature of the base.[459,459a]

Two groups of workers have examined the formation of charge-transfer complexes between cyanine dyes and various acceptor compounds, e.g., iodine, maleic anhydride, quinones, and tetracyano-*p*-quinodimethane.[460,460a] These complexes were characterized by the appearance of a new absorption band lying at considerably longer wavelength than that of the dye itself; from the position of this new absorption band an estimate of the ionization potential of the dyes was made.[460a]

SSSR, Otd. Khim. Nauk **7**, 191 (1960); *CA* **55**, 26802 (1961); *Tr. Vses. Nauchn.-Issled. Kinofotoinst.* p. 86 (1960); *CA* **57**, 16793 (1962).

[456] *CSD II*, p. 1176; cf. W. I. Stephen and A. Townshend. *J. Chem. Soc.* p. 3738 (1965).

[457] H. D. Hunt and DuP, *USP* 2,993,893.

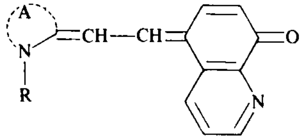
[458] J. W. Faller, A. Mueller, and J. P. Phillips, *J. Org. Chem.* **29**, 3450 (1964).

[459] G. Scheibe, W. Seiffert, H. Wengenmayr, and C. Jutz, *Ber. Bunsenges. Physik. Chem.* **67**, 560 (1963).

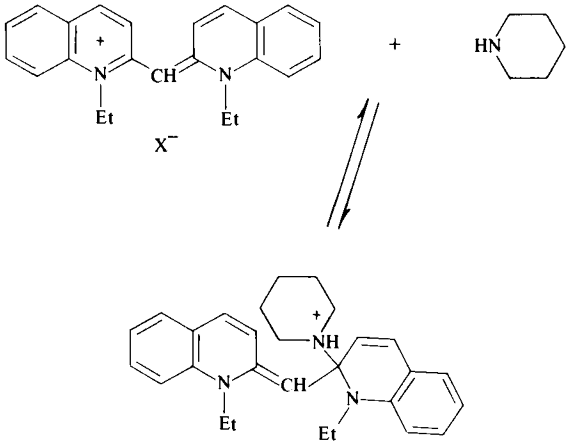
[459a] G. Scheibe, G. Buttgereit, and E. Daltrozzo, *Angew. Chem. Intern. Ed. Engl.* **2**, 737 (1963).

[460] J. E. LuValle, A. Leifer, M. Koral, and M. Collins, *J. Phys. Chem.* **67**, 2635 (1963).

[460a] J. M. Nys and W. van den Heuvel, *Phot. Korr.* **102**, 37 (1966).



(CCCX)



(CCCXI)

Lupinski *et al.* have used the radical-ion from tetracyano-*p*-quinodimethane as the anion of various cyanine dyes, in the hope that these products would show superconductivity (see Section VIID); this was not observed, however.[460b]

Two other groups of workers have prepared cyanines in which the anion is the radical ion from tetracyanoquinodimethane, and have studied the electrical conductivity of the products.[460c,460d]

IX. Some Properties of Cyanine Dyes

This section is concerned with some physicochemical properties of cyanines, particularly those relating to structural problems or to the use

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[460b] J. H. Lupinski, K. R. Walter, and L. H. Vogt, *Mol. Cryst.* **3**, 241 (1967).

[460c] E. Yagubskii, M. L. Khidekel, I. F. Shchegolev, L. I. Buravov, R. B. Lyubovskii, and V. B. Stryukov, *Zh. Obshch. Khim.* **38**, 992 (1968); *CA* **70**, 38879 (1969).

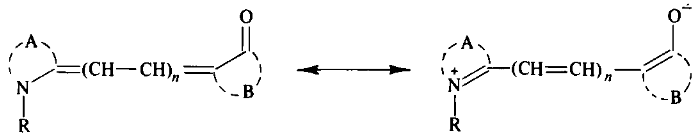
[460d] B. H. Klanderman and D. C. Hoesterey, *J. Chem. Phys.* **51**, 377 (1969).

of these dyes as photographic sensitizers. As the literature on some of these topics is now quite considerable, reference will be made as far as possible to recent review articles; in general only the more interesting work not covered by such reviews will be discussed.

A. Spectroscopic Properties

1. *Ultraviolet and Visible*

Many of the papers referred to in earlier sections include more or less detailed discussions of the effect of structural changes on light absorption. Other recent publications containing more general discussions of this topic (and sometimes the effect of structural changes on other physicochemical properties also) include Kiprianov *et al.*[461–465]



(CCCXIIa) (CCCXIIb)

One particular aspect of the color of cyanines which has received a certain amount of attention recently is that of solvatochromism, reviewed in Kiprianov *et al.*[466–468] This has already been referred to briefly in connection with the merocyanines (Section VI,E); for these dyes the effect is generally attributed to a disturbance in the mesomeric equilibrium (CCCXII a ↔ b) caused by changes in the dielectric constant of the

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[461] A. I. Kiprianov, *Zh. Vses. Khim. Obshchestva im. D. I. Mendeleeva* **7,** 317 (1962); *CA* **58,** 4389 (1963); A. I. Kiprianov, G. G. Dyadyusha, and F. A. Mikhailenko, *Usp. Khim.* **35,** 823 (1966); *CA* **65,** 10698 (1966); A. I. Kiprianov, *Ukr. Khim. Zh.* **33,** 1169 (1967); *CA* **68,** 79620 (1968).

[462] G. Scheibe, *Chimia (Aarau)* **15,** 10 (1961); *Compt. Rend. 36th Congr. Intern. Chim. Ind., Brussels, 1966* Vol. 3; see *Ind. Chim. Belge* **32,** Spec. No., 6 (1967).

[463] L. G. S. Brooker and E. J. VanLare, "Kirk-Othmer," 2nd ed., Vol. 5, p. 763.

[464] O. Riester, *Chimia (Aarau)* **20,** 330 (1966).

[465] S. Dähne and D. Leupold, *Ber. Bunsenges. Physik. Chem.* **70,** 618 (1966); S. Dähne, D. Leupold, H. E. Nikolajewski, S. Kulpe, H. Paul, and R. Radeglia, *Monatsber. Deut. Akad. Wiss. Berlin* **9,** 112 (1967).

[466] A. I. Kiprianov, *Usp. Khim.* **29,** 1336 (1960); *CA* **55,** 7845 (1961).

[467] K. Dimroth, *Chimia (Aarau)* **15,** 80 (1961); also discussion of this paper by L. G. S. Brooker, p. 87.

[468] A. van Dormael, *Ind. Chim. Belge* **31,** 1 (1966).

solvent.[469] Although this view has been questioned by Liptay,[470] it receives confirmation in the work of Dähne *et al.;* they showed that for a simple merocyanine (CCCI; $n = 1$ or 2) varying the solvent causes parallel changes in the light absorption (λ_{max}) and in the electron densities at various points in the chain (the latter being obtained from the chemical shifts in the NMR spectra).[471]

For true cyanines solvatochromic changes are much smaller (apart from those caused by changes in aggregation), and no correlation with dielectric constant is observed. However, the wavelength of maximum absorption for various cyanines correlates well with the refractive index of the solvent.[472]

2. *Infrared*

Among the interesting conclusions drawn from the study of the infrared spectra of cyanines is that of Pestemer, who deduced that only the bond between the two outermost atoms (i.e., –N=C–) at either end of the conjugated chain shows double-bond character.[473]

The detailed interpretation of the IR spectrum of a cyanine is, of course, difficult, due to its complexity, but by examination of several related series Leifer *et al.* have been able to make certain structural assignments.[474] One conclusion was that all of the dyes examined possessed an all-trans arrangement of the conjugated chain, with no evidence for the presence of a cis isomer (see Section IX,B).

Friedrich has investigated the influence of steric effects on the out-of-plane vibration bands for the aromatic hydrogen atoms in various quinoline cyanines.[475]

3. *Nuclear Magnetic Resonance*

Scheibe *et al.*[459,476] and also Dähne and Ranft[477] have used the chemical shifts in the NMR spectra of polymethine dyes to estimate the elec-

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[469] L. G. S. Brooker, G. H. Keyes, R. H. Sprague, R. H. VanDyke, E. VanLare, G. VanZandt, F. L. White, H. W. J. Cressman, and S. G. Dent, *J. Am. Chem. Soc.* **73,** 5332 (1951).

[470] W. Liptay, *Z. Naturforsch.* **20a,** 1441 (1965).

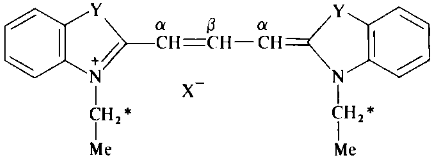
[471] S. Dähne, D. Leupold, H. E. Nikolajewski, and R. Radeglia, *Z. Naturforsch.* **20b,** 1006 (1965); cf. R. Radeglia and S. Dähne, *Ber. Bunsenges. Physik. Chem.* **70,** 745 (1966); R. Radeglia, *Z. Physik. Chem.* (*Leipzig*) **235,** 335 (1967).

[472] W. West and A. L. Geddes, *J. Phys. Chem.* **68,** 837 (1964).

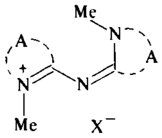
[473] M. Pestemer, *Chimia* (*Aarau*) **15,** 31 (1961).

[474] A. Leifer, M. Boedner, P. H. Dougherty, A. Fusco, M. Koral, and J. E. LuValle, *Appl. Spectry.* **20,** 150 (1966); A. Leifer, D. Bonis, M. Boedner, P. Dougherty, M. Koral, and J. E. LuValle, *ibid.* p. 289; A. Leifer, D. Bonis, M. Boedner, P. Dougherty, A. J. Fusco, M. Koral, and J. E. LuValle, *ibid.* **21,** 71 (1967).

tron densities at various points in the chain. The results confirm theoretical predictions that the electron density would alternate along the chain, and indicate that dyes such as (CCC; $n = 0$, 1, or 2) have the all-trans configuration. In a related group of dyes, consisting of (CCCXIII; Y = O, S, Se, or –CH=CH–) and the tetraethyl analog of (CCC), the τ-values for the methylene groups* decrease regularly with increasing $\lambda_{\max}$ of the visible spectrum; for the α and β-protons, the τ-values decrease less regularly in the same direction.[478]



(CCCXIII)



(CCCXIV)

Examination of a series of azamethinecyanines by NMR spectroscopy has shown, surprisingly, that they all possess the mono-cis arrangement (CCCXIV), even in those cases where the corresponding methinecyanines have the all-trans configuration.[479]

4. *Electron Spin Resonance*

Lu Valle *et al.* have shown that pure crystalline cyanines give no ESR signals, those observed by previous workers being due to impurities.[480] However, ESR signals are given by cyanines adsorbed on silver halides when irradiated by light absorbed either by the dye or by the silver halide.[481]

For a further discussion of the effect of structural changes on the light absorption of dyes, largely of the cyanine and related types, see Scheibe's review.[481a]

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[475] H. J. Friedrich, *Z. Naturforsch.* **18b**, 635 (1963).

[476] G. Scheibe, W. Seiffert, G. Hohlneicher, C. Jutz, and H. J. Springer, *Tetrahedron Letters* p. 5053 (1966).

[477] S. Dähne and J. Ranft, *Z. Physik. Chem. (Leipzig)* **224**, 65 (1963).

[478] S. Dähne and J. Ranft, *Angew. Chem. Intern. Ed. Engl.* **2**, 740 (1963); *Z. Physik. Chem. (Leipzig)* **232**, 259 (1966).

[479] H. J. Friedrich, *Angew. Chem. Intern. Ed. Engl.* **2**, 215 (1963).

[480] J. E. LuValle, A. Leifer, P. H. Dougherty, and M. Koral, *J. Phys. Chem.* **66**, 2403 (1962).

[481] W. C. Needler, R. L. Griffith, and W. West, *Nature* **191**, 902 (1961).

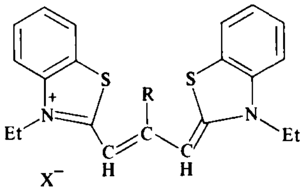
Gasco *et al.* have discussed the light absorption of a series of thiazole and polynuclear thiazole trimethinecyanines in terms of "basicity" and extrachromophoric conjugation.[481b]

Lifshits has studied the solvatochromism of a long series of symmetrical trimethinecyanines derived from 3*H*-indole, benzothiazole, and benzimidazole; the absorption maximum was correlated with the refractive index of the solvent and with the Hammett σ-coefficient of the substituent in the benzene rings.[481c]

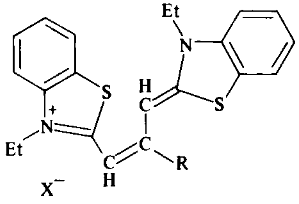
B. STEREOCHEMISTRY

The stereochemical properties of cyanines are of prime importance in relation to their use as photographic sensitizers. In particular, any factors leading to noncoplanarity of the resonating system will cause a drastic reduction in sensitizing power; see the discussions by Brooker *et al.*[2,124] and van Dormael.[482]

Wheatley has shown by X-ray diffraction of dye (CCCXV; R = H) that in the crystalline state it exists as shown in the all-trans configuration (see Sections IX,A,2 and 3).[483] Cyanines in solution are generally considered also to exist largely in the all-trans form, although Brooker *et al.* have interpreted solvatochromic changes in the *meso*-methyl dye (CCCXV; R = Me) in terms of an equilibrium between this all-trans



(CCCXV)



(CCCXVI)

[481a] G. Scheibe, *1964 Opt. Anregung Org. Syst., Int. Farbensymp., 2nd. Schloss Elmau, Ger.* 109 (1966). See also H. D. Försterling, W. Huber, H. Kuhn, H. H. Martin, A. Schweig, F. F. Seelig, and W. Stratmann, *ibid.* p. 55; P. G. Farrell, R. Grinter, and S. F. Mason, *ibid.*, p. 88.

[481b] A. Gasco, E. Barni, and G. Di Modica, *Tetrahedron Letters* p. 5131 (1968).

[481c] E. B. Lifshits, *Dokl. Akad. Nauk SSSR* **179,** 596 (1968); *CA* **69,** 72474 (1968). This work has been reviewed by R. W. Moncrieff, *Textile Mfr.* **94,** 328 (1968).

[482] A. van Dormael, *in* "Photographic Science: Symposium, Paris, 1965" (J. Pouradier ed.), p. 106. Focal Press, London, 1967.

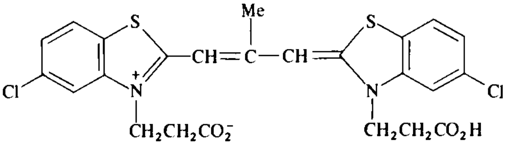
[483] P. J. Wheatley, *J. Chem. Soc.* pp. 3245, 4096 (1959).

form and the mono-cis form (CCCXVI; R = Me).[484] Moreover, West *et al.* have shown that the spectra of various meso-substituted trimethinecyanines are clearly resolved at low temperatures into two bands, attributable to the presence of two stereoisomers.[485]

Some interest has been shown in the changes produced by irradiating a cyanine within its absorption band, such changes generally being attributed to trans → cis rearrangement.[486] This effect has been particularly examined by Scheibe for simple dyes of type (CCC); e.g., irradiation of (CCC; $n = 2$) (all-trans) in its absorption band at 424 nm at —140° gave a new product, λ_{max} 454 nm, to which a mono-cis structure was ascribed.[487] This interpretation has, however, recently been disputed by Leupold *et al.*,[488] who consider that both the 424 and 454 nm species are in fact dimeric.

C. AGGREGATION

The ability of cyanines to form reversible aggregates, with concomitant changes in light absorption, is well known. This subject, which is of the greatest importance in photographic sensitization, has been frequently reviewed, e.g., in Mees and James.[2] An important paper published subsequently to this review dealt with the nature of the H aggregate. Using dye (CCCXVII), which showed an unusually pronounced tendency to form H aggregates, Emerson *et al.* were able to resolve the H band into bands, shifted progressively to shorter wavelength, due to the dimer, trimer, tetramer, and the infinite polymer. Moreover, the highly poly-



(CCCXVII)

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[484] L. G. S. Brooker, D. W. Heseltine, and L. L. Lincoln, *Chimia (Aarau)* **20**, 327 (1966).

[485] W. West, S. Pearce, and F. Grum, *J. Phys. Chem.* **71**, 1316 (1967).

[486] E. Fischer and Y. Frei, *J. Chem. Phys.* **27**, 808 (1957); P. J. McCartin, *ibid.* **48**, 2980 (1965); A. K. Chibisov, *Teoret. i Eksperim. Khim., Akad. Nauk Ukr. SSR* **2**, 825 (1966).

[487] F. Baumgärtner, E. Günther, and G. Scheibe, *Z. Elektrochem.* **60**, 570 (1956); cf. Scheibe.[462]

[488] D. Leupold, H. Kobischke, and U. Geske, *Tetrahedron Letters* p. 3287 (1967).

meric form was so stable that it could be isolated as a solid, and for the first time a cyanine H aggregate could be examined by electron microscopy and X-ray diffraction.[489]

The views of McKay and Hillson, that H-band formation is due to an interaction between the dye cation and a counterion,[490] has found little acceptance, being confuted not only by the above-mentioned paper of Emerson *et al.*, but also by investigations of Padday.[491]

Less controversy surrounds the nature of the J-state, which has always been considered to consist of a highly aggregated form of the dye.[2] A novel helical structure for the J-aggregate of pseudocyanine has been proposed by Mason from a study of the optical rotatory dispersion of the (+)-tartrate of the polymeric cation.[492]

Three important papers from the Polaroid Laboratories are concerned with the structure of cyanine dye aggregates and the mechanism of spectral sensitization and supersensitization.[492a]

D. Acid–Base Properties

Cyanines are reversibly protonated in acid solution with loss of the polymethine mesomerism and hence of the visible light absorption. Various authors have used this property to measure the basicity of cyanines, and have examined the effect of structural variations on the basicity.[61,126,493,494] For instance, Mazzucato *et al.* have found that for a series of symmetrical benzothiazole trimethinecyanines the value of pK_a correlates well with the value of the Hammett σ-coefficient of the substituents in the benzene rings.[493]

Lifshits *et al.* have measured the pK_a values for almost 100 trimethinecyanines of the 3*H*-indole, benzothiazole, quinoline, and benzimidazole

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[489] E. S. Emerson, M. A. Conlin, A. E. Rosenoff, K. S. Norland, H. Rodriguez, D. Chin, and G. R. Bird, *J. Phys. Chem.* **71**, 2396 (1967).

[490] R. B. McKay and P. J. Hillson, *Trans. Faraday Soc.* **63**, 777 (1967), and earlier papers.

[491] J. F. Padday, *J. Phys. Chem.* **72**, 1259 (1968).

[492] S. F. Mason, *Proc. Chem. Soc.* p. 119 (1964).

[492a] A. E. Rosenoff, K. S. Norland, A. E. Ames, V. K. Walworth, and G. R. Bird, *Phot. Sci. Eng.* **12**, 185 (1968). G. R. Bird, K. S. Norland, A. E. Rosenoff, and H. B. Michaud, *ibid.* p. 196. G. R. Bird, B. Zuckerman, and A. E. Ames, *Photochem. Photobiol.* **8**, 393 (1968).

[493] U. Mazzucato, G. Cauzzo, and G. Favaro, *Ric. Sci., Rend.* [2] **A3**, 309 (1963); *CA* **59**, 11694 (1963); U. Mazzucato and N. Mongiat, *Ric. Sci. Rend.* [2] **A3**, 317 (1963); *CA* **59**, 11695 (1963); U. Mazzucato and P. Bassignana, *Ric. Sci., Rend.* [2] **A7**, 215 (1964); *CA* **63**, 4143 (1965).

[494] N. S. Spasokukotskii and E. S. Kozlova, *Tr. Vses. Nauchn.-Issled. Kinofotoinst.* p. 70 (1960); *CA* **57**, 16792 (1962).

series; they confirm the relationship between pK_a and the Hammett σ-coefficient of the substituent in the benzene rings (see ref. 493).[494a]

Feldman *et al.* have used NMR spectroscopy to show that protonation of various methine- and trimethine-cyanines occurs at the α-carbon atom of the chain and not, as might have been expected, at one of the N-atoms.[494b]

E. OTHER PROPERTIES

Various other properties of cyanines, e.g., fluorescence and phosphorescence, adsorption to solid substrates (particularly silver halides), polarographic behavior, and photoconductivity, have been discussed in several recent reviews dealing with photographic sensitization (see Section X,A), and will consequently not be considered here.

X. Some Applications of Cyanine Dyes

A. AS PHOTOGRAPHIC SENSITIZERS

By far the most important use of the cyanines and related dyes is as spectral sensitizers of the photographic process. The literature on the practical and theoretical aspects of this topic is now so extensive that no attempt can be made to summarize it in this chapter. However, several excellent reviews have appeared in recent years, of which those by West and Carroll,[2] Klein and Matejec,[495] Nys,[496] and Meier[497] may be particularly mentioned.

A comparatively recent application of cyanine dyes is in the spectral sensitization of the photoconductivity of, e.g., zinc oxide, which is of importance in electrophotographic reproduction processes. A discussion of this topic is also included in the monograph by Meier.[497]

B. AS LASER Q-SWITCHES

It was discovered in 1964 that solutions of certain reversibly bleachable dyes could be used to produce giant laser pulses by the so-called Q-

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[494a] E. B. Lifshits, N. S. Spasokukotskii, L. M. Yagupol'skii, E. S. Kozlova, D. Y. Naroditskaya, and I. I. Levkoev, *Zh. Obshch. Khim.* **38**, 2025 (1968); *CA* **70**, 19472 (1969).

[494b] L. H. Feldman, A. H. Herz, and T. H. Regan, *J. Phys. Chem.* **72**, 2008 (1968).

[495] E. Klein and R. Matejec, *Phot. Korr.* **101**, 3, 24 (1965).

[496] J. M. Nys, *in* "Photographic Science: Symposium, Paris, 1965" (J. Pouradier, ed.), p. 361. Focal Press, London, 1967. (A summary of the papers on spectral sensitization presented at the symposium.)

[497] H. Meier, "Spectral Sensitization." Focal Press, London, 1968.

switching technique.[498] The first dyes to be so used were metal phthalocyanines, but the use of kryptocyanine (XXXIII) as a Q-switch for the ruby laser was announced very soon afterwards[499]; a benzothiazole pentamethinecyanine could also be used.[500] For the neodymium laser, use of the bridged undecamethinecyanine (CLXXXI) was recommended,[501] but various other long-chain cyanines have also been suggested.[502] A patent claims that tri- and pentamethinecyanines derived from tetrahydrobenzopyrylium salts, e.g., (CXLVIII), or from the thio analogs, are useful as laser Q-switches.[503]

In a more recent development a solution of a pentamethinecyanine was optically pumped by a Q-switched laser. The dye was thereby stimulated to emit fluorescent radiation, so that the solution acted as a new type of liquid laser.[504]

It seems certain that the use of cyanines for these purposes will be developed rapidly in the near future; in fact, there is every likelihood that these uses will come to be second only in importance to the use of cyanines as spectral sensitizers.

A discussion of the use of pyrylium dyes as laser Q-switches, previously reported in a patent,[503] has now been published.[504a]

For further investigations on the use of γ-cyano- or nitropentamethinecyanines as tunable dye lasers (see ref. 504), see Bradley *et al.*[504b] Other dyes which have been used for this purpose include bridged dyes of types (CLXXXVII) and CLXXXIXc).[504c]

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[498] For a discussion of the theory and practice of laser Q-switching, see, for instance, W. V. Smith and P. P. Sorokin, "The Laser," Chapter 4-2. McGraw-Hill, New York, 1966.

[499] P. Kafalas, J. I. Masters, and E. M. E. Murray, *J. Appl. Phys.* **35**, 2349 (1964); B. H. Soffer, *ibid.* p. 2551.

[500] F. P. Schäfer and W. Schmidt, *Z. Naturforsch.* **19a**, 1019 (1964).

[501] B. H. Soffer and R. H. Hoskins, *Nature* **204**, 276 (1964).

[502] O. L. Lebedev, V. N. Gavrilov, Yu. M. Gryaznov, and A. A. Chastov, *Zh. Eksperim. i Teoret. Fiz., Pis'ma v Redaktsiyu* **1**, 14 (1965); *CA* **63**, 12545 (1965); O. L. Lebedev, Yu. M. Gryaznov, A. A. Chastov, and A. V. Kazymov, *Zh. Prikl. Spektroskopii, Akad. Nauk Belorussk. SSR* **6**, 261 (1967); *CA* **67**, 69359 (1967).

[503] Eastman Kodak, *BeP* 687,397.

[504] M. L. Spaeth and D. P. Bortfeld, *Appl. Phys. Letters* **9**, 179 (1966). Similar experiments have also been described by F. P. Schäfer, W. Schmidt, and J. Volze, *ibid.* p. 306; F. P. Schäfer, W. Schmidt, and K. Marth, *Phys. Letters* **24A**, 280 (1967); P. P. Sorokin, W. H. Culver, E. C. Hammond, and J. R. Lankard, *IBM J. Res. Develop.* **10**, 401 (1966); P. P. Sorokin, J. R. Lankard, E. C. Hammond, and V. L. Moruzzi, *ibid.* **11**, 130 (1967); B. H. Soffer and B. B. McFarland, *Appl. Phys. Letters* **10**, 266 (1967).

[504a] J. L. Williams and G. A. Reynolds, *J. Appl. Phys.* **39**, 5327 (1968).

[504b] D. J. Bradley, A. J. F. Durrant, G. M. Gale, M. Moore, and P. D. Smith, *IEEE J. Quantum Electron.* **4**, 707 (1968)

C. IN CHEMICAL ANALYSIS

Cyanine dyes have occasionally been suggested for use as reagents in chemical analysis, e.g., as indicators for acid–base titrations,[505] as adsorption indicators in argentometric titrations,[506] as sensitive reagents for the detection of magnesium,[507] and for the detection of molybdenum.[508]

Of more interest are a number of analytical techniques, mostly due to Sawicki, which depend on the formation of a cyanine or related dye which can be estimated colorimetrically. Thus 3-methyl-2-benzothiazolinone hydrazone (CCCXVIII) was used for the determination of formaldehyde and other aldehydes, based on the formation of a tetrazapentamethinecyanine under oxidizing conditions (see Section V,C,2).[509] An alternative method for formaldehyde involves the formation of a trimethinecyanine by reaction with a quinaldine quaternary salt.[510]

The hydrazone (CCCXVIII) has also proved of value in the detection and determination of azulenes, based on the formation of diazadimethinecyanines of structure (CCCXIX).[511]

The formation of a merocyanine, e.g., (CCCXX), by reaction with a quinaldine quaternary salt under oxidizing conditions was used to determine terminal-ring quinones.[512]

Sawicki *et al.* have also described various methods for the determination of malonaldehyde which depend on the formation of polymethine dyes, e.g., with 1-methylpyrrole, indole, azulene, or 2-thiobarbituric acid. The last of these, which gives the trimethineoxonol (XXXVIII; $n = 1$), was considered to be the most sensitive.[513] A method of determining

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[504c] E. O. Tikhonov and M. T. Shpak, *Ukr. Fiz. Zh.* **12**, 2077 (1967); *CA* **69**, 14508 (1968).

[505] Yu. F. Bydin, *Zh. Fiz. Khim.* **28**, 305 (1954); *CA* **49**, 5174 (1955); R. F. Falcao, *Rev. Port. Farm.* **16**, 81 (1966); *CA* **65**, 14405 (1966).

[506] N. F. Dobrovol'skii, *Tr. Khar'kovsk. Med. Inst.* **15**, 387 (1958); *CA* **53**, 19677 (1959); *Tr. Komis. po Analit. Khim., Akad. Nauk SSSR, Inst. Geokhim. i Analit. Khim.* **11**, 113 (1960); *CA* **55**, 8155 (1961).

[507] A. S. Babenko, *Zh. Analit. Khim.* **13**, 496 (1958); *CA* **53**, 4002 (1959).

[508] A. K. Babko and D. S. Turova, *RP* 190,649; *CA* **67**, 113502 (1967).

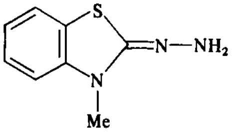
[509] E. Sawicki, T. R. Hauser, T. W. Stanley, and W. Elbert, *Anal. Chem.* **33**, 93 (1961); E. Sawicki, T. R. Hauser, and R. Wilson, *ibid.* **34**, 505 (1962); cf. H. Verachtert and J. Frateur, *Agricultura* (*Louvain*) [2] **14**, 83 (1966); *CA* **65**, 6302 (1966).

[510] E. Sawicki, T. W. Stanley, and J. Pfaff, *Chemist-Analyst* **51**, 9 (1962); *Anal. Chim. Acta* **28**, 156 (1963).

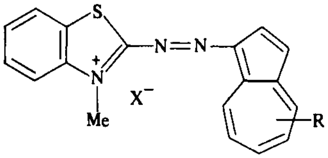
[511] E. Sawicki, T. W. Stanley, and W. Elbert, *Microchem. J.* **5**, 225 (1961).

[512] E. Sawicki, T. W. Stanley, and T. R. Hauser, *Anal. Chim. Acta* **21**, 392 (1959).

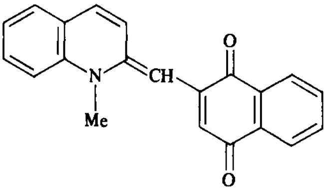
[513] E. Sawicki, T. W. Stanley, and H. Johnson, *Anal. Chem.* **35**, 199 (1963). See Shepherd[55] for a summary of other analytical procedures based on the formation of this dye.



(CCCXVIII)



(CCCXIX)



(CCCXX)

chloropicrin by reaction with pyridine, potassium cyanide, and barbituric acid, also involves the colorimetric determination of the resulting oxonol.[514]

New uses proposed for cyanine dyes include the photometric determination of various organic acids, including nitrophenols,[514a] and of rhenium.[514b]

A method for the colorimetric determination of alkyl halides depends on the quaternization of pyridine, followed by ring-opening with alkali and reaction with aniline to give a Zincke salt (CCXCIX).[514c]

D. Medicinal Uses

In Volume II, reference was made to some cyanines which were said to have therapeutic value, particularly as anthelmintics.[515] These dyes included a series of 3-linked pyrrole cyanines, and one such is in fact in

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[514] E. Asmus and H. Kuchenbecker, *Z. Anal. Chem.* **213**, 266 (1965).

[514a] I. M. Korenman, F. F. Sheyanova, and S. N. Maslennikova, *Tr. Khim. Khim. Tekhnol.* 88, 137 (1966); 105 (1967). I. M. Korenman, F. R. Sheyanova, S. N. Maslennikova, and I. D. Klyukvina, *ibid.* p. 280 (1966); *CA* **67**, 36808, 70371, 82935 (1967); **68**, 111242 (1968).

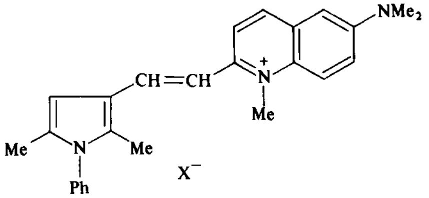
[514b] I. M. Korenman, F. R. Sheyanova, and L. N. Karyakina, *Tr. Khim. Khim. Tekhnol.* p. 109 (1967); *CA* **69**, 15880 (1968).

[514c] A. A. Belyakov, *Zh. Anal. Khim.* **23**, 1729 (1968); *CA* **70**, 74138 (1969).

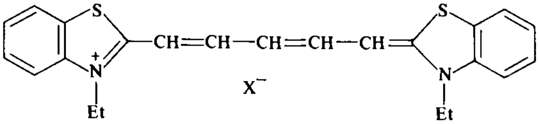
[515] *CSD II*, p. 1185.

use for this purpose, viz., dye (CCCXXI) as the pamoate, known as Pyrvinium.[516]

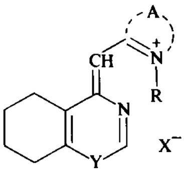
Another cyanine which has likewise found use as an anthelmintic is the pentamethine dye, Dithiazanine (CCCXXII), again preferably as the pamoate.[517] Its use is limited, however, because of its greater toxicity compared with Pyrvinium.[518]



(CCCXXI)



(CCCXXII)



(CCCXXIII)

The tetrahydroquinoxaline dyes (CCCXXIII; Y = NR) have also been examined for possible chemotherapeutic properties; those in which A completes a benzoxazole ring showed the highest antibacterial and anthelmintic activity. One method of preparation involved reaction of the novel tetrahydrobenzoxazine dyes (CCCXXIII; Y = O) with an amine.[519]

Some dyes related to cyanines have been examined for antitumor activity. Such dyes include the merocyanines derived from quinones, (CCCXXIV), etc., the activity of which is rather low, however.[520] Ap-

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[516] J. W. Beck, D. Saavedra, G. J. Antell, and B. Tejeiro, *Am. J. Trop. Med. Hyg.* **8**, 349 (1959).

[517] D. B. Capps and Parke, Davis, *BP* 890,763.

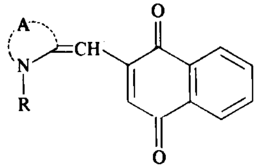
[518] See, for instance, J. E. D. Keeling, *Rept. Progr. Appl. Chem.* **46**, 144 (1961).

[519] R. W. J. Carney, J. Wojtkunski, E. A. Konopka, and G. De Stevens, *J. Med. Chem.* **9**, 758 (1966).

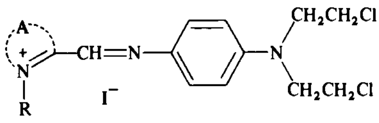
[520] S. Petersen, *Ann. Chem.* **675**, 102 (1964).

parently more active were some azastyryl dyes incorporating a nitrogen mustard grouping (CCCXXV).[521]

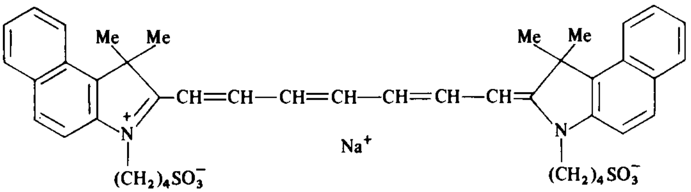
The heptamethinecyanine (CCCXXVI)[522] has achieved some importance, as Indocyanine Green, in the measurement of cardiac output. The determination is based on the strong infrared absorption at ~800 nm, in which region hemoglobin has very little absorption.[523]



(CCCXXIV)



(CCCXXV)



(CCCXXVI)

E. Other Uses

Some interest has been taken in the use of various cyanines as plant growth hormones; although more active than the heterocyclic quaternary salts from which they were prepared, they were less active than heteroauxin.[524] Some cyanines have been recommended as agricultural bactericides, for controlling the leaf blight of rice.[525]

Among the other diverse uses which have been suggested for cyanines,

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[521] W. Schulze, W. Gutsche, and W. Jungstand, *Arzneimittel-Forsch.* **15**, 1235 (1965). For the preparation of related dyes, see also W. Schulze and H. Willitzer, *J. Prakt. Chem.* [4] **31**, 136 (1966), and earlier papers; R. C. Elderfield, I. S. Covey, J. B. Geiduschek, W. L. Meyer, A. B. Ross, and J. H. Ross, *J. Org. Chem.* **23**, 1749 (1958).

[522] D. W. Heseltine, L. G. S. Brooker, and Eastman Kodak, *USP* 2,895,955.

[523] See, for example, F. Begon and C. Bohuon, *Clin. Chim. Acta* **12**, 425 (1965).

[524] T. Ogata, *Rept. Sci. Res. Inst. (Tokyo)* **29**, 507 (1953); *CA* **49**, 12622 (1955); and earlier papers.

[525] I. Ishii and M. Katagiri, *Nippon Nogeikagaku Kaishi* **40**, 437 (1966); *CA* **66**, 92704 (1967).

the following may be mentioned: initiation of the photopolymerization of styrene[526]; increasing the rate of enzymatic production of glucose from starch[527]; enhancement of the production of bright deposits in nickel electroplating.[528]

A number of workers have used the adsorption of a cyanine dye to silver halide as a means of measuring the surface area of the latter.[528a]

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[526] A. Watanabe, *Bull. Chem. Soc. Japan* **32**, 557 (1959): *CA* **54**, 7310 (1960).

[527] I. Hayashibara, *JP* 10,836 (1963); *CA* **59**, 15470 (1963).

[528] R. Fyfe and W. Canning and Co., *BP* 841,372.

[528a] H. J. van de Hul and J. Lyklema, *J. Am. Chem. Soc.* **90**, 3010 (1968). R. Peacock and A. M. Kragh, *J. Phot. Sci.* **16**, 229 (1968). C. H. Giles, *J. Am. Chem. Soc.* **91**, 759 (1969).

Chapter VI

THE PHOTOGRAPHIC COLOR DEVELOPMENT PROCESS

J. Bailey and L. A. Williams

RESEARCH LABORATORIES, KODAK LIMITED, WEALDSTONE, HARROW, MIDDLESEX, ENGLAND

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I. Introduction

Many color prints and transparencies available to the general public contain dyes formed in an exposed film or print by the oxidative coupling of a developer with the nucleophilic species of compounds known as couplers or color formers. Other image-forming systems such as (a) the dye-bleach (Cilchrome), (b) chemical transfer (Polacolor), and (c) dye transfer (Kodak Dye Transfer and Technicolor) are known which employ preformed dyes.

In this review the discussion is limited to the principles and chemistry of the formation of images by oxidative coupling and to an account of the color developers and couplers involved. For accounts of other processes the reader is directed to specific works.[1]

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[1] R. W. G. Hunt, "The Reproduction of Colour." Fountain Press, London, 1957; J. R. Thirtle and D. M. Zwick, *Encyclopedia Chem. Technol.* **5**, 836 (1964); E. C. Gehret, *Brit. J. Phot.* **111**, 480 (1964); J. H. Coote, *Phot. J.* **105**, No. 3, 83 (1965); A. Meyer, *J. Phot. Sci.* **13**, 90 (1965); A. Adams, "Polacolor Film." Morgan and Morgan, New York, 1963; R. M. Schaffert, "Electrophotography." Focal Press, London, 1965; J. Kosar, "Light-Sensitive Systems." Wiley (Interscience), New York, 1965.

Newton showed white light to be a mixture of all the colors of the visible spectrum, and suggested that objects appear white, colored, or black depending on their ability to reflect all, part, or none of the incident light. Young[2] developed the theory of trichromatic vision and postulated the presence of three different types of receptors in the eye, each type being preferentially sensitive to the primary colors violet-blue, green, and red (BGR). An object, therefore, appears blue, green, or red if the light reflected from its surface stimulates only the corresponding receptors of the eye. On the other hand, if the reflected light stimulates the green and red receptors of the eye, the object appears yellow, and by suitable stimulation of the receptors all other colors including cyan (blue-green) and magenta (blue-red) can be matched.

A. Additive Color Systems

Clerk Maxwell[3] demonstrated that this analysis of light into the three primary colors (BGR) could be carried out photographically by taking three separate photographs of an object through blue, green, and red filters. From these negatives, separation positives on glass were prepared, and where light had passed through a filter to give silver density in the negative, the related area in the positive was clear. In this way, Maxwell had a means of modulating the amount of blue, green, and red light reaching the eye, and on projecting in register the positives, using three projectors and the corresponding taking filters, i.e., by adding the green image to the red image and the blue image to the red-green mixed images, the full visible spectral range was restored and an "additive" color reproduction of the original obtained.

Maxwell was fortunate with this demonstration (see Evans[4]), which predated by some twelve years the discovery by Vogel that certain dyes extended the spectral sensitivity of silver halides beyond the blue region of the spectrum (see Chapter V, Vol. IV). Nonetheless this was the first practical demonstration of the feasibility of obtaining color photographs, and systems were devised in which these principles were employed. Separation into the blue, green, and red components of the object was effected in a variety of ways but the most successful was based on the use of a regular mosaic, or screen, of tiny blue, green, and red filters covering the surface of a support. Onto these filters a panchromatic emulsion was applied, and exposure through the support and filters gave differential exposure to the emulsion corresponding to the

[2] T. Young, *Phil. Trans. Roy. Soc. London* **92,** 12 (1802).

[3] J. C. Maxwell, *Proc. Roy. Inst. Gt. Brit.* **3,** 370 (1858–1862).

[4] R. M. Evans, *J. Phot. Sci.* **9,** 243 (1961).

distribution of the blue, green, and red radiations reflected from the subject. First development gave a negative image in silver which was bleached away leaving clear and partially clear areas related to the degree of exposure to the three primary colors (BGR). In addition, silver halide with the distribution necessary to obtain a positive image remained in the emulsion. Reexposure of the material followed by a second development gave a positive image in black opaque silver. This latter modulated the amount of light passing through the filter grid which could reach the eye, and due to the fineness of the mosaic the colors were effectively blended to give full-color reproductions.

B. SUBTRACTIVE COLOR SYSTEMS

In the screen plate described above, the colors of the photographs are obtained by adding the three primary colors (BGR) in order to obtain full spectral coverage. In nature an object appears colored because it absorbs (subtracts) some component from white light. Thus the absorption of the blue component from white light leaves the complementary (minus) color yellow, and removal of the green radiations gives magenta, while subtraction of the red component from white light gives the complementary color cyan.

The use of these subtractive colors yellow, cyan, and magenta for the preparation of color photographs was originally suggested by Ducos du Hauron.[5] He prepared separation negatives by techniques similar to those of Maxwell. From these he prepared positives on transparent supports in the complementary color to that used to obtain the negative. Thus the negative obtained through the red filter was printed in such a manner that the areas of the positive corresponding to the red areas of the subject were clear as in Maxwell's system, but instead of the background being black, du Hauron's separation print was cyan (red-absorbing). Similar positives were prepared for the green and blue areas of the subject with magenta (green-absorbing) and yellow (blue-absorbing) backgrounds, respectively. When laid in register on a white support, or projected in register from a single projector, the clear areas of the cyan print related to the red in the subject were viewed through yellow and magenta filter layers. Since red alone is transmitted by both the filters, the color of the original was restored in the reproduction. The magenta and yellow images functioned similarly to restore the green and blue areas to the print (Fig. 1.)

Photographic reproductions of this type are brighter since instead of employing black opaque silver to modulate the amount of light passing

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[5] L. Ducos du Hauron, *Phot. News* **13,** 319 (1869).

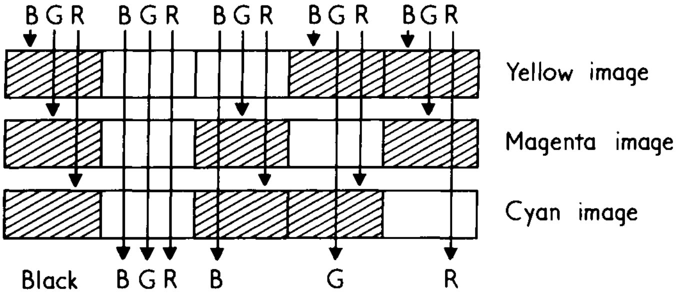

FIG. 1. Diagram illustrating the formation of additive colors by superimposing positives in subtractive colors. The clear areas correspond to emulsion areas affected by blue, green, and red light during the camera exposure.

through a filter grid, which at best transmits only one-third of the available light, the modulation is effected by filters which transmit two-thirds of the incident light. Furthermore, the white areas of the print are whiter than obtainable by light blending in the additive system since the reflected light from white areas is recorded in all three separation negatives which in turn give clear areas in the positive print (Fig. 1).

Du Hauron also suggested that separation negatives could be prepared from a single exposure if three plates were superimposed to give a tripack as shown in Fig. 2. A yellow-colored filter below the blue-sensitive emulsion layer prevents unwanted blue light from reaching the blue plus green and blue plus red sensitive layers below.

In this tripack it was impossible to obtain sharp images in all emulsion layers due to its overall thickness. For acceptable sharp images the three emulsion layers should be in contact to prevent light-scatter at interfaces, and to provide a single plane of focus. A number of tripacks fulfilling these requirements are described in the early photographic literature.

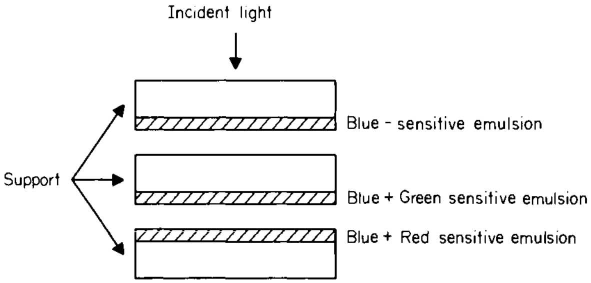

FIG. 2. Du Hauron tripack.

However, it was not until 1912 that Rudolph Fischer[6] described a system which had commercial prospects. In Fischer's integral tripack the three emulsion layers necessary to obtain color separation were coated one on the other on a single support and were inseparable. Of these, the bottom emulsion layer was selectively sensitized to red light, the middle layer sensitized to green light, and the top layer was sensitive only to blue light (Fig. 3). A yellow colored filter below the blue-sensitive emulsion layer prevented blue light reaching the underlying emulsions and by this means separation was automatically achieved on exposure.

Fischer also patented the incorporation of substances (couplers) into the various layers which would on reversal development (see below) react with the oxidized *p*-dialkylaminoaniline developers to give dyes of the complementary color (yellow, cyan, and magenta) to the light, giving rise to the negative image. Since the dye-forming reaction proceeds only in the presence of an oxidizing agent such as exposed silver halide grains, it can, therefore, be directly controlled by the camera exposure via the latent image.

Fisher was unable at that time to interpret his ideas into a practical commercial product, but sometime later, Mannes and Godowsky showed that this dye-forming reaction could be utilized in an integral tripack to

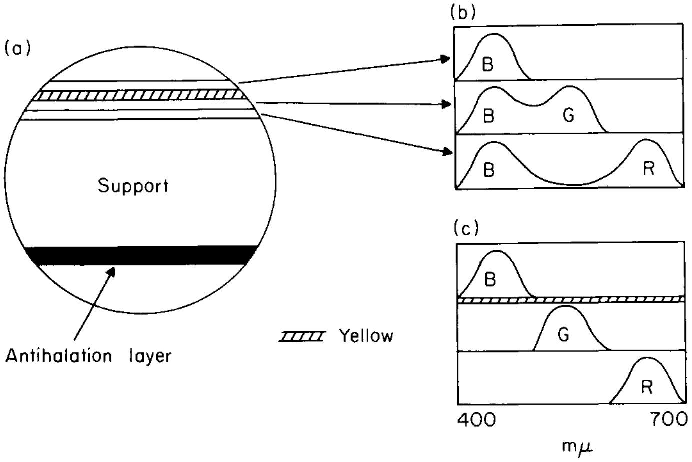

FIG. 3. Integral tripack format. (a) Diagrammatic representation of cross section of integral tripack showing emulsion layers and yellow filter layer. (b) Actual spectral sensitivities of the three emulsion layers. (c) Effective spectral sensitivities of the emulsion layers due to presence of the yellow filter.

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[6] R. Fischer, see *Brit. J. Phot.* **60**, 595 (1913); *BP* 2562.

give dyed positives, by introducing the various couplers into the different layers during a process of selective development. Films based on this suggestion were marketed by the Eastman Kodak Company in 1935 under the name of Kodachrome.[7]

Fischer's original ideas were perfected by the Agfa Company, which later marketed an integral tripack film (Agfacolor) in which appropriate hydrophilic couplers were incorporated into the gelatin phase of the three emulsion layers. A similar product employing the incorporated coupler principle was also marketed by the Eastman Kodak Company under the name of Ektachrome. In this material, instead of the couplers carrying hydrophilic groups to render them gelatin-compatible, a large oleophilic moiety is built into the molecule to impart oil solubility. Solutions of these couplers, the so-called protected couplers, in inert solvents are dispersed in the gelatin phase of the three emulsion layers.

Films of various types based on the above principles are now commercially available from a number of manufacturers, and an account of the major differences in these products is given below.

1. *Reversal Films*

When a film is exposed in a camera and developed in a normal black and white developer, the areas of the film on which light has fallen become developed and silver is deposited. For the purposes of color photography using the integral tripack system it is common practice to process the film which passed through the camera in such a manner that a positive is produced directly. This reversal processing is based on the fact that development of a negative as above, leaves in the emulsion silver halide with the distribution necessary for a positive. Reversal is achieved in a color film, if following the negative development the film is reexposed to fog the remaining halide, which then becomes developable. It is during this second development known as the color development that the dyes used in the positive images are formed.

During any process of development silver ions are reduced to metallic silver, and at the same time the developing agent is itself oxidized. The fate of the oxidation products depends on the system in which they are formed. For example, in conventional black and white photography the oxidized developer reacts with sulfite ions to form a colorless product which is removed from the system and is of no further importance. In color photography the developer oxidation products instead of being allowed to react with sulfite are used in the formation of the dyes which are present in the final color image. This dye-forming reaction produces

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[7] See E. R. Davies, *Phot. J.* **76**, 248 (1936).

dye in proportion to the amount of silver developed, and in the required areas since the dyes when formed are insoluble.

In order to convert the original three light records (BGR) into dye images of the correct color, each layer of the tripack film must, during development, contain only its specific coupler. This can be achieved in two ways, by a selective development process or by the incorporated coupler system.

a. Selective Development Process. The selective development process is used only in reversal systems to give color positives. It involves the successive use of three separate color developers each containing one of the three couplers. After negative processing in a hydroquinone-based developer, the film is exposed to red light through the base of the film (Fig. 4). This produces a latent image in the unexposed areas of the bottom red-sensitive layer, but not in the other two layers which are insensitive to red light. The film is then redeveloped in a solution containing a coupler which reacts with the oxidized color developer to form a cyan image. A further exposure to blue light from above produces a latent image in the top layer only, because the yellow filter absorbs blue

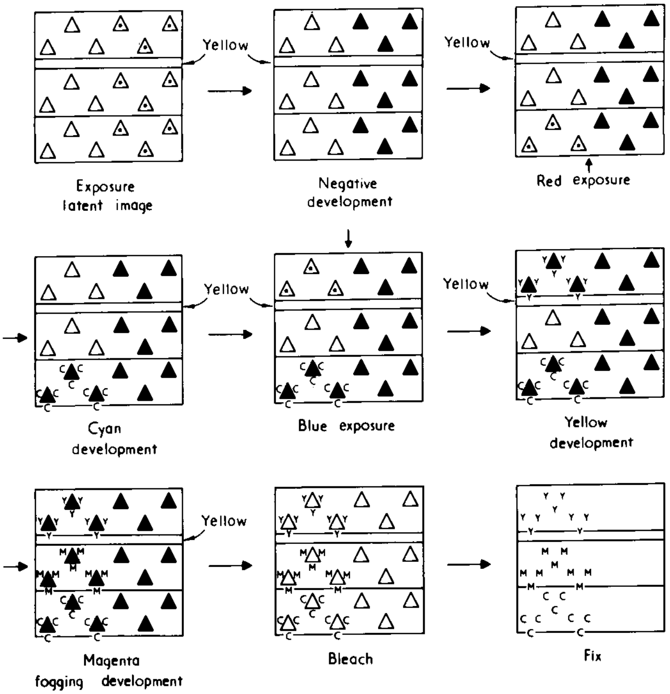

FIG. 4. Schematic selective color processing.

light and protects the middle layer. Color development of this layer gives a yellow image. For the final development the film is passed through a fogging developer which renders the remaining halide developable. This solution also contains a coupler which reacts with oxidized color developer to give the magenta image in the middle layer. Finally the developed silver is converted to silver bromide and removed (fixed) from the layers in a thiosulfate solution.

b. Incorporated Coupler System. In the incorporated coupler system the emulsion layers are arranged on the support in the same order as for selective development. Compared with that system additionally the coupler components of the three dyes are placed in the related emulsion layers during manufacture of the film. After the black and white negative development, a single reexposure and color development suffices to produce the three differently colored dyed images (Fig. 5).

2. *Negative–Positive Color Materials*

Color material designed to produce color negatives from which color prints on paper, or some other opaque support, can be prepared, are now commonplace. In materials for this purpose the incorporated coupler principle is used and the structure of the film and the position of the couplers is the same as for the reversal material. The processing of negative–positive films is much simplified and involves a single development with a color developer, after which the reduced silver is bleached and fixed. Exposure to the color negative, followed by color development of

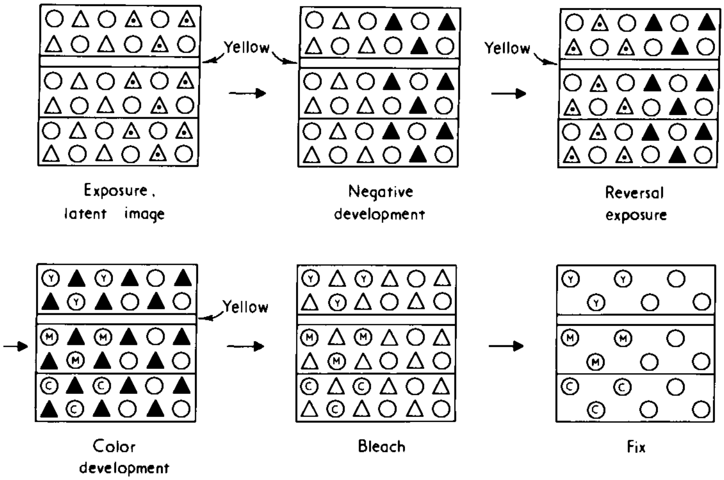

FIG. 5. Schematic processing of reversal film based on the use of incorporated protected couplers.

the color print material, reverses the dye densities and produces the colors of the original (Fig. 6).

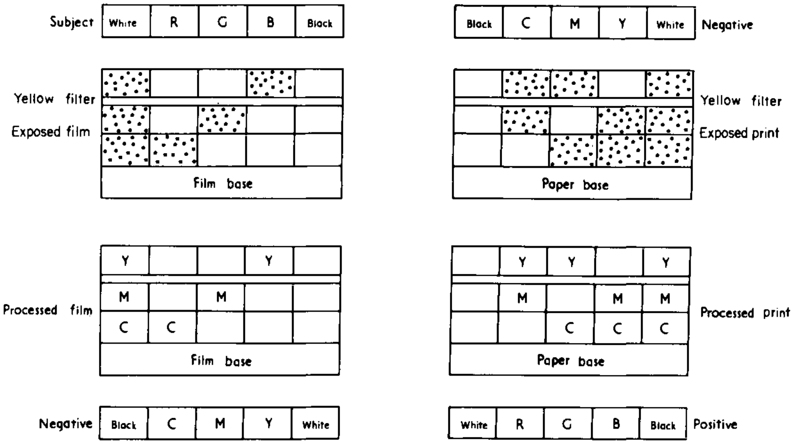

FIG. 6. Schematic processing of negative–positive color material.

II. Formation of Image Dyes by Oxidative Coupling Reactions

It will have been seen that the production of the image dyes in subtractive color photographic processes depends on a photolytic reaction to initiate and control the synthesis of image dyes. The reactions (i) and (ii) proposed by Fischer[6] form the basis upon which a number of modern color photographic products depend, and by suitable choice of the developers and the couplers employed, a range of useful dyes is possible.

(i) Exposed silver halide + Developer → Oxidized developer
(ii) Oxidized developer + Coupler → Dye

Before discussing the variety of dyes available, it would be well to summarize the properties required of dyes of practical value. The image dyes should be stable to light, heat, moisture, and acid, and should be nondiffusing from the layers in which they are formed. Subtractive color photography requires the formation of three dyes—yellow, magenta, and cyan. Each should have maximum absorption in one region of the visible spectrum and transmittance as high as possible in the other two. Thus, suitable yellow dyes have peak absorptions in the blue region of the spectrum (400–500 nm) and high transmittance beyond 500 nm; magenta dyes have absorption maxima in the green (500–600 nm) and high transmittance in the blue and red; cyan dyes have peak absorptions in the

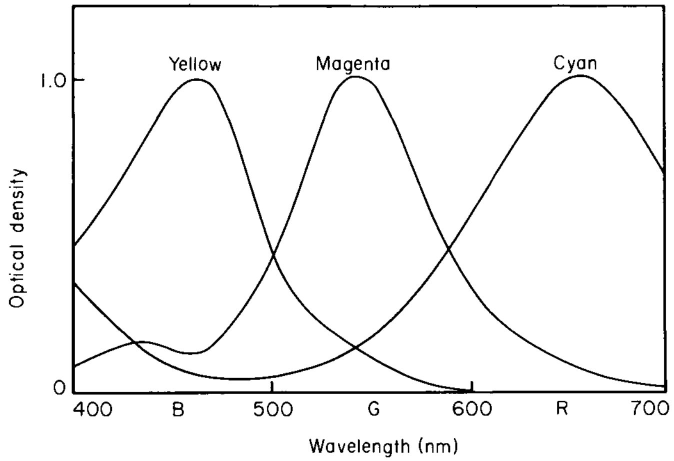

FIG. 7. Absorption curves of dyes for subtractive color photography.

red (600–700 nm) and transmittance as high as possible in the blue and green. Some typical absorption curves are shown in Fig. 7.

The following is an account of the chemistry of a selection of the many dyes, and their corresponding developers and couplers.

A. AZAMETHINE AND INDOANILINE DYES

Oxidized *p*-diethylaminoaniline reacts with benzoylacetanilides, and with pyrazolinones, to give yellow and magenta azamethines, respectively, and with α-naphthols to give cyan-colored indoanilines. Dyes of these classes were known before the advent of the color development process, but, because of their instability, had no application in textiles. On the other hand, these dyes have proved eminently suitable in color photography because it is not difficult to obtain the required range of hues by the chromogenic development process, and because the handling conditions of the resulting photographs are not severe. The dyes are protected in some measure by the gelatin phase in which they are formed, but modifications can be made in the photographic materials to promote dye stability. Furthermore, structural changes in the developers and couplers have led to dyes of improved stability.

The stoichiometry of dye formation is given by Eq. (1), where X and Y are electrophilic groups which activate the methylene group of the coupler molecule.

The mechanism of dye formation has been reviewed.[8] In general,

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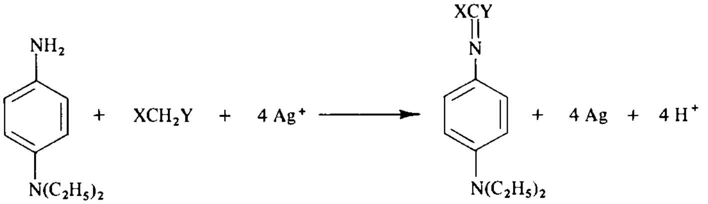
[8] P. W. Vittum and A. Weissberger, *J. Phot. Sci.* **2**, 81 (1954); **6**, 157 (1958); A. Weissberger, *in* "The Theory of the Photographic Process" (C. E. K. Mees and T. H. James, eds.), 3rd ed., Chapter 17, p. 382. Macmillan, New York, 1966.

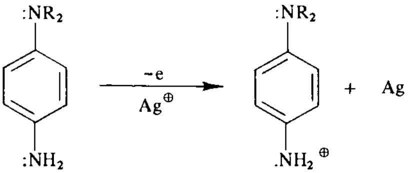


(I) (II) (III)

(1)

couplers react as their anions in alkaline solutions, but the rate of ionization of some is slow and incomplete below pH 11, and so can become rate-determining. Reactivity varies from one coupler to another and depends on the electron density at the nucleophilic carbon atom of the coupler anion.

Oxidation, Eq. (2), of the developer (I) proceeds through the semiquinone cation (IV) which gives the quinone diimine cation (V), either by further oxidation, Eq. (3), or by disproportionation, Eq. (4).

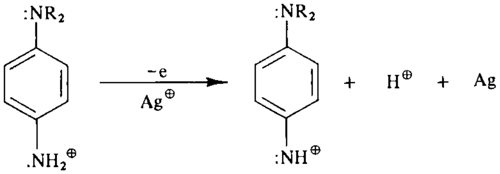


(I) (IV)

(2)

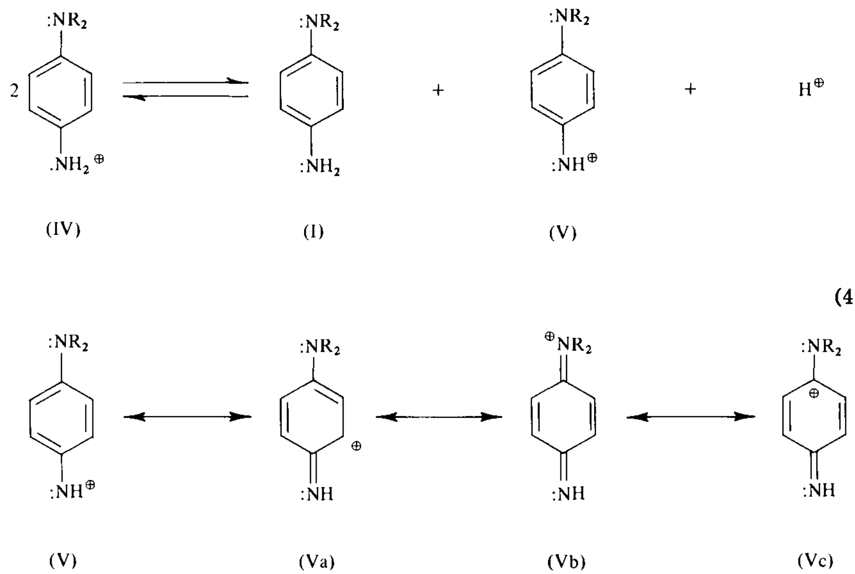
The quinone diimine cation, considerably more stable due to resonance forms (V)–(Vc) than the radical cation (IV), couples according to Eq. (5) with the anion (VI) to give the leuco dye (VII). This is oxidized probably by another quinone diimine cation, to form the dye (III), as represented in Eq. (6).

Although, generally, dye formation is very fast, side reactions can occur in which the quinone diimine cation is attacked, either by alkali to



(IV) (V)

(3)

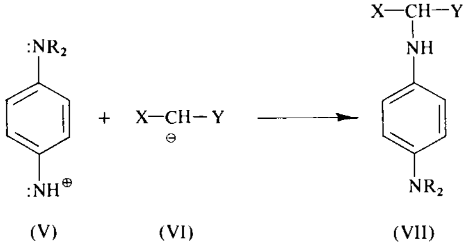


(4)

form the corresponding quinone monoimine, or by sulfite to give the diamine sulfonate.[8a]

1. *Color Developers*

a. p-Phenylenediamines. p-Dialkylaminoanilines can, generally, be prepared by reduction of the corresponding *p*-nitro-, or *p*-nitroso-*N,N*-dialkylanilines, or, in some cases, *p*-(2,5-dichlorophenylazo)-*N,N*-dialkylanilines.[9,10]



(5)

The developing agents, normally used in aqueous alkaline processing

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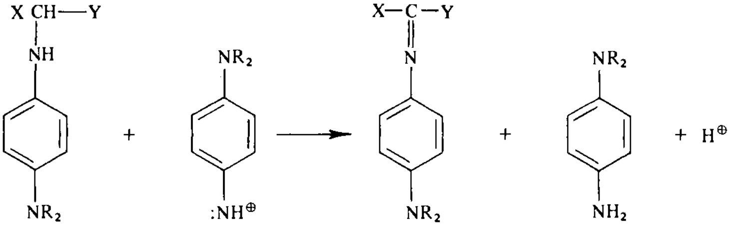
[8a] J. R. Thirtle and D. M. Zwick, *Encyclopedia Chem. Technol.* **5,** 821 (1964).

[9] R. L. Bent, J. C. Desslock, F. C. Duennebier, D. W. Fassett, D. B. Glass, T. H. James, D. B. Julian, W. R. Ruby, J. M. Snell, J. H. Sterner, J. R. Thirtle, P. W. Vittum, and A. Weissberger, *J. Am. Chem. Soc.* **73,** 3100 (1951).

[10] H. Larivé, J. P. Sarrut, and Eastman Kodak, *USP* 2,811,555.



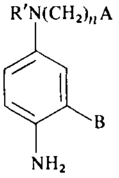
(VII) (V) (III) (I)

(6)

solutions, should be adequately soluble and should react rapidly to give dyes with the required properties. Some *p*-phenylenediamines can cause dermatitis and in order to reduce this toxicity, analogs which contain hydrophilic substituents to lower solubility in skin fats, are available (Table I). Such substituents, attached through polymethylene bridges, have little effect on the absorption characteristics of the resulting dyes.

TABLE I

p-Dialkylaminoaniline Color Developers[a]

	B	*n*	A	*Reference*
	OR	2	$NHSO_2R$	11
(VIII)	CH_3, C_2H_5	2	$NHCOCH_3$	12
	H	2 or more	$C_6H_4SO_3H$	13
	H,R,OR	2-10	$OC_6H_4SO_3H$	14
	H,R,OR	3-4	SO_3H	15
	H,CH_3,C_2H_5	3-12	OSO_3H	16
	$(CH_2)_2NHSO_2R$	2	H	17
	$O(CH_2)_2NHCOR$	2	H	17
	$(CH_2)_2COOH$	0 or more	H	18

[a] R and R′ indicate alkyl groups.

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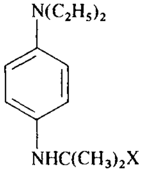
[11] A. Weissberger, D. B. Glass, P. W. Vittum, and Eastman Kodak, *USP* 2,548,574.
[12] A. Weissberger, D. B. Glass, P. W. Vittum, and Eastman Kodak, *USP* 2,592,363.
[13] DuP, *BP* 691,234.
[14] E. L. Martin and DuP, *USP* 2,603,656.
[15] W. Pelz, O. Wahl, and Agfa, *BP* 811,679.
[16] D. W. C. Ramsey and ICI, *BP* 895,422.
[17] A. Weissberger, D. B. Glass, P. W. Vittum, and Eastman Kodak, *BP* 653,284.
[18] M. S. Raasch and DuP, *USP* 2,603,659.

The *p*-diethylaminoaniline derivatives (IX; X = SO_3H,[19] COOH,[20] PO_2H_2[21]) are also claimed to be of low toxicity. Since the parent bases are probably regenerated in alkaline solutions, it is necessary to handle such solutions with care.



(IX)

Similarly, stable water-soluble complexes can be formed by reacting *p*-diethylaminoaniline with sulfur dioxide,[22] and 4-cyclohexylaminoaniline has been reported to be a nonirritant developer of high activity.[23]

Phthalimide[24] and benzylidene[25] derivatives have been proposed for incorporation into the emulsion layers. The parent developers are regenerated, by hydrolysis, on treatment with basic processing solutions.

Substitution in the ring influences the activity of *p*-diethylaminoaniline and for more energetic developers, electron-donating substituents are desirable. Electron-withdrawing substituents on the other hand, lower the activity of the agents. Both the developer reactivity and the position of the absorption maxima of the derived dyes depend on the release of electrons from the *p*-phenylenediamine system. Thus a linear relationship has been established[26] between the frequencies of maximum absorption of the derived dyes and (i) the rates of coupling, and (ii) the rates of deamination of the oxidized developers. The absorption maxima are also closely related to the polarographic half-wave oxidation potentials of the *p*-phenylenediamines. Substituents which contribute to the stability of the polar form of the dyes in the excited state (Xb), cause deepening in color (Table II).

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[19] J. Jaeken, A. E. Van Dormael, and Gevaert Photo-Producten, *BP* 691,815.

[20] J. F. Willems and Gevaert Photo-Producten, *BP* 783,887.

[21] Gevaert Photo-Producten, *BeP* 557,556.

[22] D. H. O. John and May and Baker, *BP* 658,010.

[23] M. S. Raasch and DuP, *USP* 2,612,500.

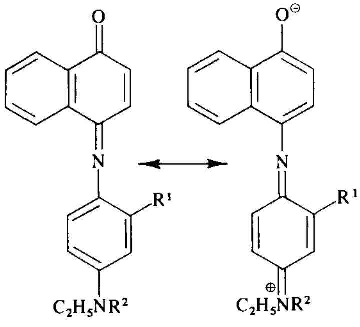
[24] K. O. Ganguin, D. W. C. Ramsey, and ICI, *BP* 803,783; B. Anderson, D. W. C. Ramsey, and ICI, *BP* 1,069,061.

[25] Kodak, *BeP* 681,873.

[26] R. L. Bent, G. H. Brown, M. C. Glessmann, D. P. Harnish, C. G. Tremmel, and A. Weissberger, *Phot. Sci. Eng.* 8, 125 (1964).

TABLE II

ABSORPTION MAXIMA, IN METHANOL, OF INDOANILINES FROM α-NAPHTHOL AND VARIOUS *p*-PHENYLENEDIAMINES

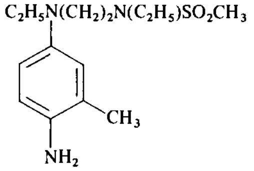


(Xa) (Xb)

Dye (X ; $R^2 = C_2H_5$)		*Dye* (X ; $R^1 = H$)	
R^1	λ_{max}(*nm*)	R^2	λ_{max}(*nm*)
F	592	CH_2CONH_2	570
Cl	596	$(CH_2)_2NHSO_2CH_3$	591
H	605	CH_3	599
$(CH_2)_2NHSO_2CH_3$	622	$(CH_2)_2OH$	598
CH_3	623	C_2H_5	605
C_3H_7	626	C_3H_7	609
$NHCOCH_3$	629		
OC_2H_5	630		
SCH_3	633		
$C(CH_3)_3$	639		

Dyes from the sulfonamide (XI) are less soluble and have higher extinction coefficients than many other *p*-phenylenediamine dyes.[27]

b. Amino-heterocycles. It is claimed that 4-aminopyrazolin-5-ones, such as the pyrazole (XII), and related developers,[28] which contain



(XI)

the grouping $-CH(NH_2)—C{=}O \rightleftharpoons -C(NH_2){=}COH$, couple rapidly to give dyes of greater stability to light and acid than those from *p*-phenylenediamines.

3-Amino-1-*p*-aminophenylpyrazolines[29] (XIII; X = H, Cl, SO_3H, alkyl, alkoxy) couple rapidly, with the usual couplers, to give brilliant

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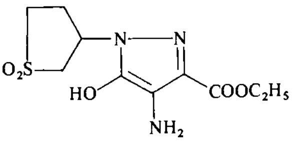
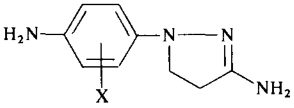
[27] A. Weissberger, D. B. Glass, and Kodak, *BP* 651,909.

[28] W. Pelz, L. Burgardt, O. Wahl, and Agfa, *DBP* 1,002,627.

[29] O. Wahl, R. Mersch, W. Puschel, and Agfa, *BP* 795,476.



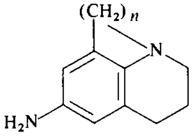
(XII)



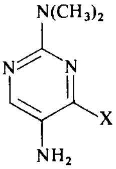
(XIII)

dyes; benzoylacetanilides and pyrazolinones give orange-red and blue dyes, respectively.

The dyes from the developers 8-aminolilolidine (XIV; $n = 2$) and 9-aminojulolidine (XIV; $n = 3$) are deeper in color than those from *p*-phenylenediamines.[30]

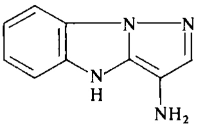


(XIV)

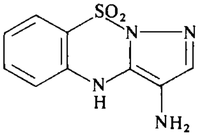


(XV)

5-Amino-2-dimethylaminopyrimidines[31] (XV; X = hydroxy, methoxy, or amino) are color developers of low reactivity. 3-Aminopyrazolo[2,3-*a*]benzimidazole[32] (XVI) and 3-aminopyrazolo[2,3-*b*][1,2,4]benzothiadiazin-dioxide[33] (XVII) have developing properties.



(XVI)



(XVII)

2. *Color Couplers*

Couplers of small molecular size are necessary for processes in which they are dissolved in the developer, because they should have good solubility in the alkaline processing solutions, and should readily penetrate, with the developing agent, into the emulsion vehicle.

Couplers which are incorporated into the emulsion layers during manu-

---

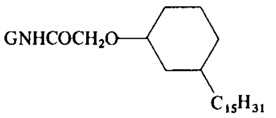
[30] M. S. Raasch and DuP, *USP* 2,707,681.

[31] D. G. Saunders, *J. Chem. Soc.* p. 3232 (1956).

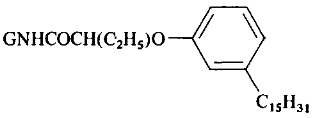
[32] G. Schaum, K. H. Menzel, and Agfa, *DBP* 1,158,836.

[33] K. H. Menzel, H. G. Hanke, G. Wolfrum, R. Putter, and Agfa, *DBP* 1,158,837.

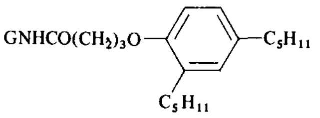
facture should be of sufficient molecular size to prevent migration from their appropriate layer. Large hydrocarbon substituents (ballast groups) impart nondiffusing properties to coupler molecules. The amides (XVIII)–(XXII) (G = coupler residue such as benzoylacetanilide, pyrazolinone, or α-naphthol), prepared by reacting an acid chloride with an amino group present in a coupler,[34] are representative nondiffusing couplers. The oleophilic ballast groups assist the dissolution of the couplers in oils.



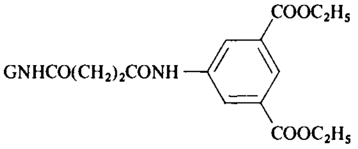
(XVIII)



(XIX)



(XX)



(XXI)

$GNHCO(CH_2)_2N(C_4H_9)CO(CH_2)_6CH_3$

(XXII)

The oil solutions are, with the aid of surfactants, dispersed as minute globules in the silver halide emulsions.

The ballasted couplers (XXIII)–(XXVI) containing hydrophilic groups, prepared by reacting a cyclic anhydride with an amino group present in a coupler,[35] can be dissolved directly in aqueous solutions prior to addition to the emulsion.

Color couplers can be chemically combined with polymeric emulsion vehicles, such as polymeric acetals,[36] esters,[37] and styrene[38] to give non-

---

[34] W. M. Bush, J. R. Thirtle, and Eastman Kodak, *USP* 2,920,961; R. F. Coles and G, *USP* 3,285,747; A. Weissberger, W. M. Bush, I. F. Salminen, and Kodak, *BP* 843,497; F. C. McCrossen, I. F. Salminen, A. Weissberger, and Eastman Kodak, *USP* 2,688,544; S. Kimura, H. One, K. Sano, and Fuji Photo Film, *BP* 1,008,177.

[35] S. Kimura, M. Yoshida, M. Tsuda, and Fuji Photo Film, *BP* 1,045,633; J. Ciernik and J. Aufart, *CzechP* 113,825–827; *CA* 64, 2208 (1966); D. Bellone, A. Guzzi, and Ferrania, *BeP* 656,605; C. W. Greenhalgh and ICI, *BP* 858,482.

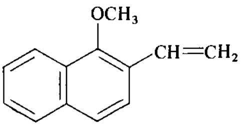
$GNHCOCH(CH_2COOH)CH{=}CHC_{16}H_{33}$ (XXIII)

$GNHCOCH_2N(CH_2COOH)C_{18}H_{37}$ (XXIV)

$GNHCOCH(SCH_2COOH)C_{12}H_{25}$ (XXV)

$GNHCOCH(CH_2COOH)SO_2C_{18}H_{37}$ (XXVI)

diffusing modifications. The conjugating system within the molecule must not be affected, and the coupling position must remain available for oxidative coupling. Likewise, copolymers of vinyl ethers with either ethylene[39] or maleic acid,[40] and of maleic anhydride with either *N*-vinylpyrrolidone[41] or styrene[42] can be utilized. Nonwandering couplers result from the polymerization or copolymerization of the monomers[43] (XXVII)–(XXIX) and from the reaction of gelatin[44] with couplers (XXX)–(XXXII), wherein fragment G incorporates the actual coupling moiety.



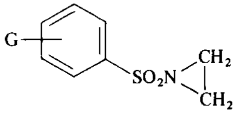
(XXVII)

$CH_3COCH_2CONHCH_2CH{=}CH_2$

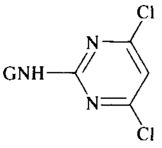
(XXVIII)

$GNHCOCH{=}CH_2$

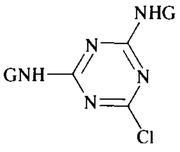
(XXIX)



(XXX)



(XXXI)



(XXXII)

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[36] D. M. McQueen and D. W. Woodward, *J. Am. Chem. Soc.* 73, 4930 (1951).

[37] D. W. Woodward and DuP, *USP* 2,567,750.

[38] B. Gaspar, G. B. Linden, and B. Gaspar, *USP* 2,778,813; L. M. Minsk, F. C. Duennebier, and Kodak, *BP* 754,628.

[39] D. W. Woodward and DuP, *USP* 2,473,403.

[40] DuP, *BP* 995,363.

[41] J. Nogradi, H. Ulrich, W. Pelz, W. Puschel, H. Schellenberger, and Agfa, *DBP* 1,123,913.

[42] K. J. Bannert, E. G. Gazzard, and ICI, *BP* 839,896.

[43] J. L. R. Williams and Eastman Kodak, *USP* 2,739,956; G. D. Jones and G, *USP* 2,561,205; J. C. Firestone and DuP, *USP* 2,976,294.

[44] Fuji Photo Film, *BeP* 656,456; 656,875; 668,303; W. Schindler, H. Pietrzok, and E. M. Marx, *EGP* 46,633.

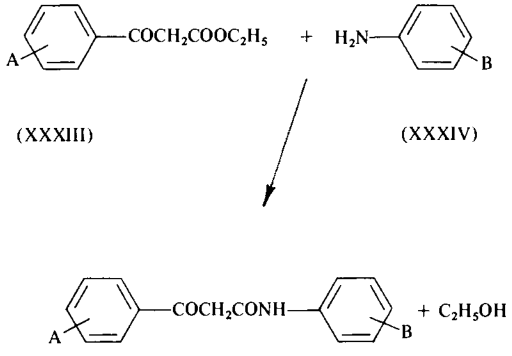
1-Hydroxy-6-mercaptonaphthalene and *p*-benzoylacetamido-thiophenol can be rendered nondiffusing by forming salts with heavy metals.[45]

Couplers, for incorporation into emulsions, should (i) normally be colorless (see Section II,A,2,*h*), (ii) be stable to light, heat, and moisture, (iii) have no adverse photographic activity, such as fogging, desensitizing, or displacing the sensitizing dyes, and (iv) yield dyes with desirable properties at reasonable reaction rates.

A recent review[46] on organic materials for color photography outlines a number of procedures for the syntheses of couplers.

In the following discussion, unless otherwise specified, the dyes reported are from *p*-phenylenediamine developers and absorption maxima quoted are measurements on photographic coatings.

a. N-Substituted 2-Acylacetamides. These compounds are of value as yellow dye forming couplers. The benzoylacetanilides, prepared either by reacting a β-keto ester with an amine,[47] Eq. (7), or by reacting an acetophenone with a urethane,[48] have received much attention. The dye formation is expressed by Eq. (1) with X = C_6H_5CO and Y = C_6H_5NHCO.



(XXXIII) (XXXIV)

(XXXV)

(7)

Benzoylacetanilides containing substituents in one or both phenyl rings have modified properties compared with those of the parent compound. The anilide[49] (XXXV; A = H, B = 5-butylsulfonamido-2-

---

[45] R. V. Young, A. Weissberger, and Eastman Kodak, *USP* 2,596,755.

[46] S. Kimura and M. Yoshida, *Sci. Publ. Fuji Photo Film Co., Ltd.* **13**, 82 (1965).

[47] N. Kunimine, *J. Soc. Sci. Phot. Japan* **14**, 88 (1952); F. C. McCrossen, S. M. Parmerter, A. Weissberger, and Eastman Kodak, *USP* 2,652,329.

[48] G, *BeP* 616,867.

[49] B. H. Tavernier, M. L. Desmit, A. H. de Cat, and Gevaert Photo-Producten, *BP* 848,558.

methoxy), of good solubility in developers, reacts rapidly to give nondiffusible dyes. Ballasted couplers, containing solubilizing functions such as either carboxylic,[50] or sulfonic[51] acid groups directly attached to the phenyl rings, gives dyes many of which possess good stability to light, humidity, and heat. Dyes[52] from coupler (XXXV; A = *p*-carboxy, B = 5-carboxy-2-octyloxy) absorb at 428 nm and are exceedingly stable. Good stabilities to light, heat, and humidity are also claimed for dyes from the couplers (XXXV; A = *o*-halogeno, B = 2-alkoxy-5-carboxy[53]) and (XXXV; A = H, B = 5-*N*-alkyl-*N*-3,5-dicarboxyphenylcarbamoyl-2-octadecyloxy[54]). The diffusion-fast anilides[55] (XXXV; A = H, B = benzimidazol-2-yl) give dye images of very fine grain. Good reactivity has been claimed[56] for the coupler (XXXV; A = H, B = 4-oxodihydroquinoxalin-2-yl).

The relationship between structure and dye absorption has been discussed[57] and shown to depend on the electrophilicity of the substituents in the coupler moieties of the dyes. Thus electron-withdrawing groups cause bathochromic, and electron-donating groups hypsochromic shifts in absorption maxima (Table III).

Azamethine dyes from benzoylacetanilide have some unwanted green absorption. Spectrally improved dyes result from couplers (XXXV; A = H, B = 2-alkoxy-5-carboxy[58]), (XXXV; A = *p*-dialkylamino, B = H[59]), (XXXV; A = 2,3-2′,3′-furan; B = H[60]), and (XXXV; A = ballast group, B = 2-alkoxy[61]).

2.5-Dialkoxybenzoylacetanilides[62] (XXXV; A = 2,5-dialkoxy, B = H) form dyes having relatively high absorption in the ultraviolet, an advantage claimed to be useful in printing negatives.

---

[50] H. Pietrzok, R. Mittag, and VEB Filmfabrik, *DBP* 1,187,479; H. Pietrzok, *EGP* 10,538.

[51] A. H. de Cat, R. K. van Poucke, and Gevaert Photo-Producten, *BP* 808,276; J. Jaeken, A. H. de Cat, R. J. Thiers, and Gevaert Photo-Producten, *BP* 873,124; Gevaert Photo-Producten, *BP* 990,627; 1,039,965; 1,062,203; CIBA, *FP* 1,366,547-548.

[52] W. F. Hoffstadt, A. P. Altavilla, and G, *BP* 934,017.

[53] W. F. Hoffstadt and G, *BP* 894,068.

[54] H. Pietrzok and B. Klimaczewski, *EGP* 30,850.

[55] W. C. Craig and G, *USP* 2,500,487.

[56] A. H. de Cat, B. H. Tavernier, and Gevaert Photo-Producten, *BP* 856,158.

[57] G. H. Brown, J. Figueras, R. J. Gledhill, C. J. Kibler, F. C. McCrossen, S. M. Parmerter, P. W. Vittum, and A. Weissberger, *J. Am. Chem. Soc.* **79**, 2919 (1957).

[58] J. Jaeken, R. L. Jansseune, and Gevaert Photo-Producten, *BP* 857,028.

[59] N. S. Corby, N. H. Haddock, and ICI, *BP* 805,505.

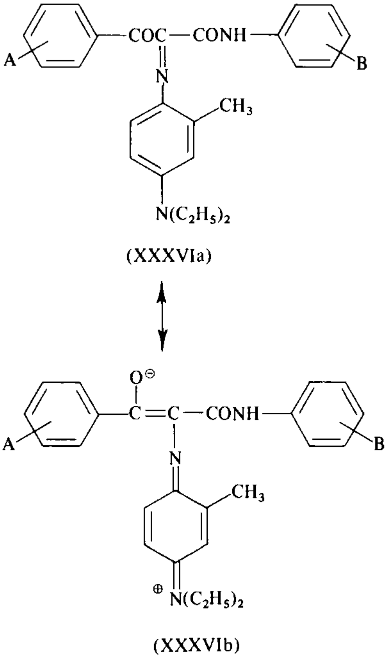
[60] N. S. Corby and ICI, *BP* 819,827.

[61] F. C. McCrossen, P. W. Vittum, A. Weissberger, and Eastman Kodak, *BP* 800,108.

[62] D. J. Fry, D. P. Ayres, and Ilford, *BP* 784,422.

TABLE III

ABSORPTION MAXIMA, IN BUTYL ACETATE, OF AZAMETHINES FROM 4-DIETHYLAMINO-2-METHYLANILINE AND VARIOUS BENZOYLACETANILIDE COUPLERS[a]



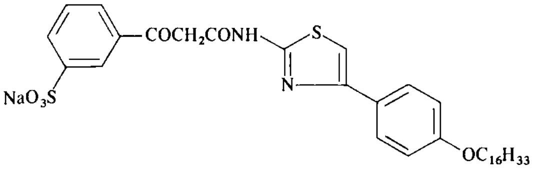
(XXXVIa)

(XXXVIb)

A	B	$\lambda_{max}(nm)$
H	H	433
o-OCH_3	H	420
m-NO_2	H	443
p-NH_2	H	426
H	p-Cl	438
H	p-NO_2	451
H	p-CN	446
H	m-$N(CH_3)_2$	430
H	o-$COOCH_3$	441

[a] Values derived and reprinted from *J. Am. Chem. Soc.* **79**, 2919 (1957). Copyright 1957 by the American Chemical Society. Reprinted by permission of the copyright owners.

Heterocyclic amines, can be reacted with ketoesters to give couplers[63] of high reactivity, such as the amide (XXXVII), which give dyes, λ_{max} 450–460 nm, useful in positive materials.



(XXXVII)

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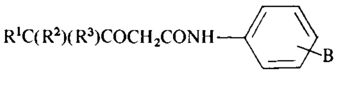
[63] J. Jaeken and Gevaert Photo-Producten, *BP* 873,125; M. H. Verbrugghe, A. H. de Cat, R. A. Roosen, and Gevaert Photo-Producten, *BP* 1,075,084.

An outstanding group of couplers, of high stability to light and heat, which give very stable dyes, λ_{max} at 444–448 nm with low green absorption, are the pivaloylacetanilides[64] (XXXVIII; R^1 = alkyl, substituted alkyl, or alkoxy, R^2, R^3 = alkyl, the total carbon atoms of R^1, R^2, and R^3 being from 3 to 30).



(XXXVIII)

The stabilities of the derived dyes of this class are compared in Table IV.

Complex couplers, for instance, the ether[65] (XL), which contains two reactive centers, have been claimed to be useful in forming yellow image dyes.

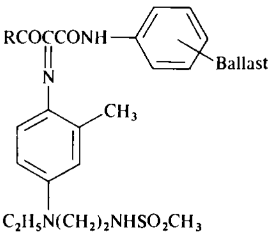
The hydrazones[66] (XLI; R = phenyl, substituted phenyl, or alkyl) have been recommended as color couplers.

b. Cyanoacetic Acid and Acetonitrile Derivatives. Yellow dyes can be obtained by coupling the nitriles (XLII) and (XLIII) with oxidized 4-amino-2-pyrazolin-5-one developers.[67]

The absorptions of the azamethine dyes derived from oxidized *p*-

TABLE IV

LIGHT FADING OF ACYLACETANILIDE AZAMETHINE DYES

	Substituent R	Density unit loss after 30 hr xenon arc exposure
 (XXXIX)	$(CH_3)_3C$-	0.11
	$CH_3CH_2CH(CH_3)$-	0.70
	$(CH_3)_3CCH_2$-	0.45

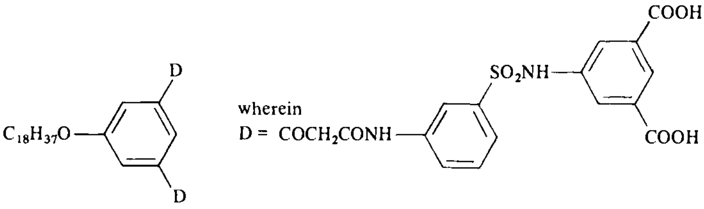
---

[64] A. Weissberger, C. J. Kibler, and Kodak, *BP* 980,507.

[65] H. Pietrzok, R. Mittag, and VEB Filmfabrik, *DBP* 1,187,479; H. Pietrzok, R. Groger, and VEB Filmfabrik, *DBP* 1,049,231; D. E. Tucker and G, *USP* 3,077,403.

[66] P. L. J. R. Merckx and Gevaert Photo-Producten, *BP* 663,550.

[67] L. Burgardt, W. Pelz, O. Wahl, and G, *USP* 3,034,891.

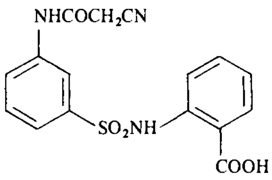


(XL)

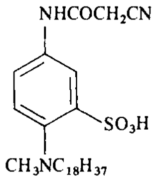
phenylenediamine derivatives and ω-cyanoacetophenone are at too short wavelengths to give good color balance when used in the magenta image of photographic materials. Deeper dyes, absorbing between 510 and 530 nm, result from the related nitriles[68] (XLIV; R = alkoxy, amino, or substituted amino), while dyes absorbing with maxima between 520 and 525 nm can be prepared from the diphenyl ethers[69] (XLV; A = halogeno, B = acylamido, Z = atoms to complete a five-membered heterocycle). Under similar conditions a range of dyes, absorbing between 480 and 550 nm, is obtained from the cyanoacetylhydrazones of various aldehydes and ketones.[70] The azamethines from nitrobenzylcyanides absorb between 505 and 515 nm.[71]

$CH_3C(=NNHCOR)CH_2CONHC_6H_5$

(XLI)



(XLII)



(XLIII)

Other valuable magenta dyes can be prepared from the cyanomethyl-

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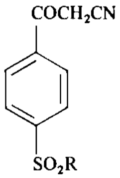
[68] Ferrania, *BP* 1,071,180.

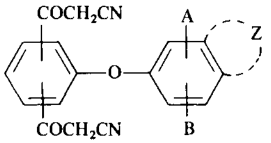
[69] H. Pietrzok, *EGP* 11,521.

[70] P. J. M. Bruylants, P. L. J. R. Merckx, and Gevaert Photo-Producten, *USP* 2,527,476.

[71] M. Kusakabe and I. Yakame, *Rept. Gov. Chem. Ind. Res. Inst. Tokyo* **50,** 172 (1955); *CA* **49,** 15578f (1955).

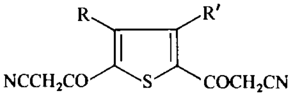


(XLIV)

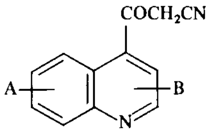


(XLV)

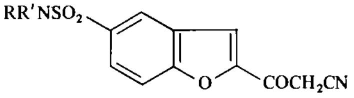
substituted heterocycles (XLVI; R, R′ = alkyl or aryl[72]), (XLVII; A, B = monovalent organic substituents[73]), (XLVIII; R, R′ = solubilizing and ballast groups[74]), and (XLIX; R = alkyl, aryl, or substituted aryl[75]).



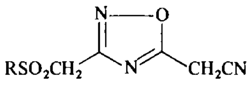
(XLVI)



(XLVII)



(XLVIII)



(XLIX)

c. 2-Pyrazolin-5-ones. These compounds have aroused considerable interest as magenta dye forming couplers because they react rapidly with oxidized *p*-dialkylaminoaniline developers to give stable dyes which have peak absorptions in the green region of the spectrum. The dye formation is expressed in Eq. (1); where X and Y together represent the atoms to complete a pyrazolinone ring system. Examples of couplers that have been claimed are set out in Table V.

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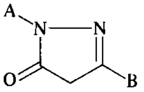
[72] CIBA, *BP* 1,019,117.

[73] CIBA, *BP* 1,042,832.

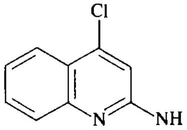
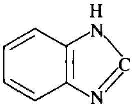
[74] O. Boes, H. Schiller, and Adox Fotowerke, *DBP* 1,077,060.

[75] A. H. de Cat, R. K. van Poucke, and Gevaert Photo-Producten, *BP* 817,286.

TABLE V
2-Pyrazolin-5-one Magenta Couplers



(L)

A	B	*References*
C_6H_5		76
C_6H_5	$C_{15}H_{31}CONH$	77
C_6H_5	$C_6H_5SO_2NH$	78
C_6H_5	$4\text{-}NCC_6H_4NH$	79
$2,4,6\text{-}Cl_3C_6H_2$ $2,6\text{-}Cl_2C_6H_3$	$4\text{-}O_2NC_6H_4NH$	80
$Cl_2C_6H_3$	$C_{11}H_{23}$	81
$4\text{-}C_6H_5COC_6H_4$	CH_3	82
$4\text{-}O_2NC_6H_4$	C_6H_5NH	83
$H(CF_2)_4CH_2$	$C_{15}H_{31}CONH$	84
C_6H_5NHCO	CH_3	85
	C_6H_5	86

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[76] J. J. Jennen and Gevaert Photo-Producten, *BP* 636,988; 681,915.

[77] N. Kunimine, *J. Soc. Sci. Phot. Japan* **14,** 37 (1951); *CA* **47,** 3155 (1953).

[78] N. Kunimine, *J. Soc. Sci. Phot. Japan* **17,** 121 (1955).

[79] C. A. Magguilli, R. E. Paine, and Eastman Kodak, *BP* 1,059, 994.

[80] C. M. Spath and Kodak, *BP* 886,723; Fuji Photo Film, *BeP* 682,384; see also R. J. Tuite and Eastman Kodak, *BP* 1,059,146.

[81] G. Feniak, A. Loria, W. A. Reckhow, and Eastman Kodak, *USP* 2,933,391.

[82] R. Magagnoli and Ferrania, *BeP* 667,399.

[83] Ilford, *Neth. Appl.* 65/08337.

[84] H. A. van den Eynde, R. J. Pollet, A. H. de Cat, and Gevaert-Agfa, *BP* 1,069,533.

[85] D. Bellone, R. Magagnoli, and Ferrania, *DBP* 1,150,577.

[86] D. J. Fry, B. R. D. Whitear, and Ilford, *BP* 813,866.

A review of the chemistry of pyrazolinones has been published.[87] Amino groups in the pyrazole or phenyl or in both rings of 1-phenylpyrazolinones have been used as a means to introduce ballast groups.[88]

Enol esters, formed by *O*-acylation of pyrazolinones, hydrolyze during color development, giving dyes identical to those from the corresponding parent compound.[89]

Pyrazolinones which contain noncoupling phenolic stabilizing groups have recently been disclosed,[90] and the coupler *N*-bis(5-oxo-1-phenylpyrazolin-3-yl)ethylamine is claimed to yield deeper dyes than obtained from the more usual coupler types.[91]

Azamethine dyes from the earlier known pyrazolinones (L; A = phenyl, B = alkyl) have undesirable side absorptions. Although the unwanted blue absorptions are correctable in negative materials by masking techniques they give rise to nonideal color balance in prints and transparencies (see Section II,A,2,*h*). Dyes of lower blue absorption result from couplers in which the substituent, B = alkyl, has been replaced by a substituted amino group, such as phenylureido,[92] alkylamino,[93] guanidino,[94] or benzofuran-2-ylamido.[95] Certain couplers, in which the substituent, A = phenyl, is replaced either by a substituted phenyl group, as for instance 2-monoalkylaminophenyl,[96] 2-hydroxyphenyl[97] 4-ethoxy-3-sulfophenyl,[98] or 4-phenylsulfonylphenyl[99]; or by a heterocycle, such as 2-benzimidazole,[86] also give dyes having lower blue absorptions. The relationship between the high intensity green absorption and the secondary blue absorption bands has been discussed.[100]

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[87] R. H. Wiley and P. Wiley, "Pyrazolones, Pyrazolidones and derivatives." Wiley (Interscience), New York.

[88] A. Loria, E. T. Pesch, and Eastman Kodak, *USP* 2,721,798; 2,772,161; S. P. Popeck, H. Schulze, and G, *USP* 2,829,975; J. A. Sprung, R. M. Lindquist, and G, *USP* 2,902,366; A. Weissberger, A. Loria, I. F. Salminen, and Eastman Kodak, *BP* 904,852; Ilford, *Neth. Appl.* 64/06891–2; 65/02125; B. Graham and Eastman Kodak, *USP* 2,710,871.

[89] DuP, *USP* 2,476,986; 2,575,182; I. F. Salminen and Eastman Kodak, *USP* 2,706,685.

[90] Eastman Kodak, *BeP* 698,354.

[91] B. Graham, A. Weissberger, and Eastman Kodak, *USP* 2,691,659.

[92] D. Bellone, R. Magagnoli, and Ferrania, *DBP* 1,147,483.

[93] C. W. Greenhalgh and ICI, *BP* 737,692.

[94] N. H. Haddock, C. Morris, and ICI, *BP* 737,700.

[95] C. W. Greenhalgh and Ilford, *BP* 890,305.

[96] Agfa, *BP* 892,886.

[97] K. H. Menzel and Agfa, *DBP* 1,231,553.

[98] K. H. Menzel, E. Boeckly, and Agfa, *BP* 1,039,880.

[99] D. Bellone, U. Chittolini, A. Guzzi, and Ferrania, *DBP* 1,190,337.

[100] G. H. Brown, B. Graham, P. W. Vittum, and A. Weissberger, *J. Am. Chem.*

Couplers containing either a 4-cyano group[101] or a multiplicity of chlorine atoms[102] in the phenyl substituent A, and those containing B = perfluoroacylamido,[103] instead of B = acylamido, give dyes which absorb bathochromically compared to the parent dyes.

The relationship between color and dye structure has received attention.[103a] Increased contribution by the polar forms of the dye in the excited state causes a deepening in absorption maximum. Thus, substituents in the coupler moiety of the dye which stabilize the polar forms, such as (LIb), are associated with deepening of absorption. On the other hand, groups which reduce the significance of the polar form cause a hypsochromic shift in the dye absorption (Table VI).

Azamethine dyes from couplers [L; B = acylureido,[104] alkylureido,[105] 2-chloro, 2-nitro or 2-methoxyanilino,[106] 2-(α-sulfostearamido)phenylenesulfenylamino,[107] 2-sulfobenzamido,[108] or 2-thiazolylideneamino[109]] have sharper cuts on the long-wave side of their absorption than those from couplers (L; B = alkyl).

The stereochemistry of azamethine dyes has been investigated by NMR measurements.[110] The *p*-phenylene ring lies in the syn position relative to the carbonyl group of the pyrazolinone in the dye (LI; A = phenyl, B = R = CH_3), whereas, the dye (LI; A = phenyl, B = H, R = CH_3) exists as a mixture of syn and anti forms with the latter predominating. In the dye (LI; A = phenyl, B = R = H) the *p*-phenylene ring flips between two planar conformations.

d. Indazolin-3-ones. These compounds, prepared from 2-hydrazinobenzoic acid derivatives by dehydration,[111] form a unique class of color couplers in that dye formation,[112] Eq. (8), takes place at a reactive

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Soc. **73,** 919 (1951); H. Ono, Y. Tanizaki, and I. Tanaka, *J. Soc. Sci. Phot. Japan* **21,** 115 (1958); W. F. Smith, *J. Phys. Chem.* **68,** 1501 (1964).

[101] A. Weissberger, P. W. Vittum, C. O. Edens, and Eastman Kodak, *USP* 2,511,231.

[102] A. Loria, A. Weissberger, P. W. Vittum, and Eastman Kodak, *USP* 2,600,788.

[103] I. F. Salminen, C. R. Barr, A. Loria, and Eastman Kodak, *USP* 2,895,826.

[103a] G. H. Brown, B. Graham, P. W. Vittum, and A. Weissberger, *J. Am. Chem. Soc.* **73,** 919 (1951).

[104] Gevaert Photo-Producten, *BP* 1,076,544.

[105] M. J. Monbaliu, A. H. de Cat, R. K. van Poucke, and Gevaert Photo-Producten, *BP* 1,007,847; 1,066,334.

[106] C. W. Greenhalgh, K. C. Stone, and Ilford, *BP* 956,261.

[107] A. Klein and Adox Fotowerke, *DBP* 1,103,761.

[108] Gevaert Photo-Producten, *BeP* 654,110.

[109] Gevaert Photo-Producten, *BP* 1,028,619.

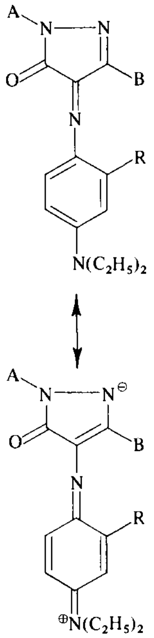
[110] P. J. S. Pauwels, *J. Am. Chem. Soc.* **89,** 580 (1967).

[111] J. J. Jennen and Gevaert Photo-Producten, *BP* 663,190.

[112] J. J. Jennen, *Ind. Chim. Belge* **16,** 472 (1951).

TABLE VI

ABSORPTIVE MAXIMA, IN BUTYL ACETATE, OF AZAMETHINES FROM VARIOUS PYRAZOLINONES AND 2-AMINO-5-DIETHYLAMINOTOLUENE[a]



(LIa)

R = CH_3

(LIb)

A	B	λ_{max}(*nm*)
C_6H_5	H	546
C_6H_5	CH_3	522
C_6H_5	$COOC_2H_5$	557
C_6H_5	$CONH_2$	565
C_6H_5	NH_2	506
C_6H_5	NHC_6H_5	522
4-$O_2NC_6H_4$	CH_3	539
4-$HO_2CC_6H_4$	CH_3	530
4-$H_2NSO_2C_6H_4$	CH_3	532
4-$H_2NC_6H_4$	CH_3	514

[a] Values derived and reprints from *J. Am. Chem. Soc.* **73**, 919 (1951). Copyright 1951 by the American Chemical Society. Reprinted by permission of the copyright owners.

imino group. A possible structure of the reaction product is the zwitterion (LIII).

These magenta dyes have excellent absorption properties, being desirably low in both blue and red absorptions. The parent coupler, however, leaves a yellow stain after the bleaching stage of the photographic processing, a disadvantage not shown by the related acylindazolin-3-ones.[113] Nondiffusing analogs have been reported.[114] Chlorination in the 5- and 6-positions, or nitration in either the 4- or 6-positions of the indazolin-3-one nucleus gives products[115] which are more reactive than the parent compound.

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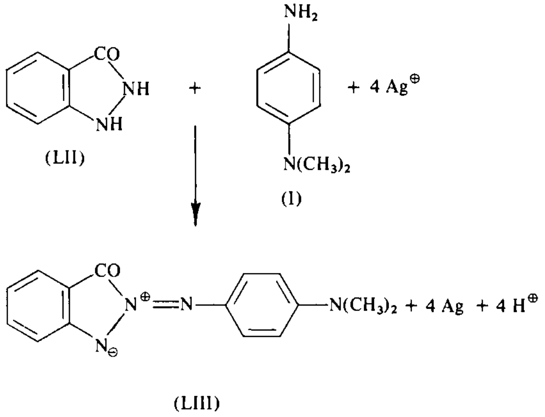
[113] J. J. Jennen, H. P. Eeredkens, and Gevaert Photo-Producten, *BP* 720,284.

[114] G. Koepke, W. Pelz, H. Schellenberger, and Agfa, *DBP* 1,130,287; Ferrania, *BeP* 695,491.

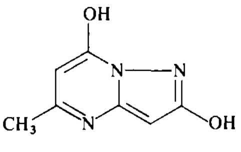
[115] V. D. Chernokal'skii, A. T. Groisberg, Ya. A. Levin, I. I. Levkoev, I. A. Solov'eva, M. I. Barro, and C. A. Kukhtin, *Tr. Vses. Nauchn.-Issled. Kinofotoinst.* **37**, 39 (1960).



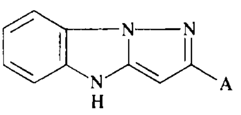
(8)

e. Other Heterocyclic Systems. The azamethine dyes from the pyrazolo[2,3-*a*]pyrimidine[116] (LIV) have absorption maxima at about 550 nm with low blue absorption.

The pyrazolo[2,3-*a*]benzimidazole (LV; A = heptadecyl), prepared either from 1-*o*-aminophenyl-3-heptadecyl-2-pyrazolin-5-one by dehydration,[117] or from 5-amino-1-*o*-aminophenyl-3-heptadecylpyrazole by deamination,[118] couples to give magenta azamethines which have low blue absorption and are stable to dilute acids. Solubilizing groups may be included either in the aromatic ring, or in the ballast side chain.[119] Analogs of higher reactivity have electron-withdrawing substituents at positions 3 and 7.[120]



(LIV)



(LV)

The pyrazolo[3,2-*b*]quinazolinone (LVI; A = methyl, B = Z = hydrogen), prepared from anthranilic acid hydrazide and ethyl acetoacetate couples to give a magenta dye, λ_{max} 550 nm, and its analog (LVI;

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[116] W. Ried and Adox Fotowerke, *DBP* 1,150,872.

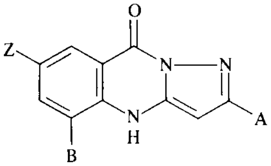
[117] K. H. Menzel, O. Wahl, W. Pelz, and Agfa, *DBP* 1,070,030.

[118] K. Loeffler, K. H. Menzel, and Agfa, *BeP* 621,241.

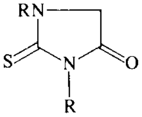
[119] K. H. Menzel, H. Ulrich, and Agfa, *DBP* 1,127,220.

[120] K. H. Menzel, R. Putter, and Agfa, *BP* 1,047,612.

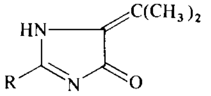
A = methyl, B = stearylamido, Z = sulfonic acid) gives a cyan dye, $\lambda_{\max}$ 650 nm.[121]



(LVI)



(LVII)



(LVIII)

2-Thionoimidazolidin-4-ones[122] (LVII; R = alkyl or aryl) and 5-isopropylideneimidazolin-4-ones[123] (LVIII; R = aryl) give magenta dyes which have lower blue absorption than the corresponding azamethines from pyrazolinones.

f. Phenols and Naphthols. These compounds couple with oxidized developers to give indoanilines, most of which show maximum absorption between 600 and 700 nm. Subsidiary absorptions in the blue and green regions of the spectrum are characteristic of most cyan image dyes. These undesirable side absorptions can be corrected in the color negative by masking techniques (see Section II,A,2,*h*).

Studies[124] on the relationship between color and molecular structure of the indoanilines indicate that structural changes in the coupler moiety which favor charge separation in the dye molecule cause bathochromic shifts in absorption, whereas, changes which inhibit charge separation cause hypsochromic shifts. Hydrogen bonding within the coupler moiety of the dye also influences the position of the absorption maximum (Table VII).

A nonwandering ballasted phenolic coupler (LX; A = hexadecyl) can be prepared from *o*-aminophenol and hexadecylisocyanate.[125]

Indoaniline dyes absorbing with $\lambda_{\max}$ at 668 and 657 nm can be obtained from the ureas (LX; A = *p*-phenylsulfamoylphenylene) and (LX; A = *p*-benzamidophenylene), respectively.[126]

Dyes from 2-*N*-alkylamidophenols are too blue; those from 2-*N*-arylamidophenols too green. Dyes having absorptions between the two, of

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[121] K. H. Menzel, R. Putter, G. Wolfrum, and Agfa, *DBP* 1,111,505.

[122] A. B. Jennings and DuP, *USP* 2,551,134.

[123] D. J. Fry, L. F. A. Mason, B. R. D. Whitear, and Ilford, *BP* 782,545.

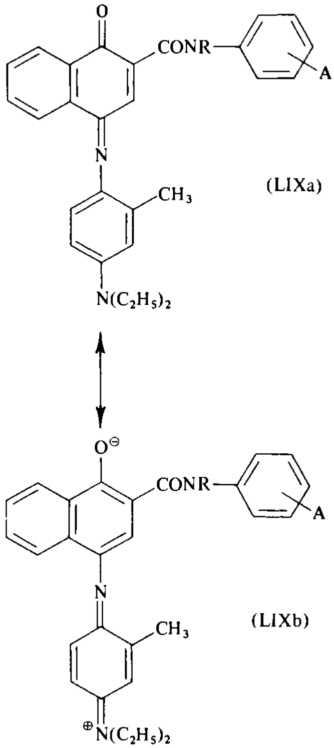
[124] C. R. Barr, G. H. Brown, J. R. Thirtle, and A. Weissberger, *Phot. Sci. Eng.* **5**, 195 (1961); A. P. Lurie, G. H. Brown, J. R. Thirtle, and A. Weissberger, *J. Am. Chem. Soc.* **83**, 5015 (1961).

[125] T. Hoshino and Fuji Photo Film, *Japan Appl.* 6826/51.

[126] R. Magagnoli, E. Coraluppi, and Ferrania, *FP* 1,457,172.

TABLE VII

ABSORPTION MAXIMA, IN BUTYL ACETATE, OF INDOANILINES FROM 4-DIETHYLAMINO-2-METHYLANILINE AND VARIOUS α-NAPHTHOL COUPLERS

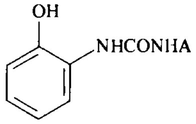

(LIXa)

(LIXb)

R	A	λ max (nm)
H	H	694
CH_3	H	629
C_6H_5	H	628
H	2,4,6-$(CH_3)_3$	681
H	p-$N(CH_3)_2$	687
H	p-OCH_3	689
H	p-Cl	697
H	p-CN	711
H	p-NO_2	713

practical value, are derivable from the bis phenols[127] (LXI; R = alkyl or aryl).

Salicylic acid yields soluble dyes of poor light stability but its derivatives (LXII; A = alkoxy, aryloxy, alkylamino, or arylamino, B = alkoxy, amino, or amido) give useful dyes.[128]


(LX)

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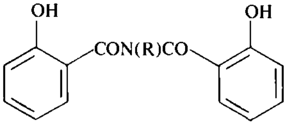
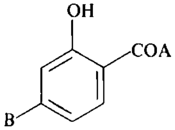
[127] H. T. Thompson and G, *USP* 2,498,466.

[128] I. F. Salminen, A. Weissberger, and Eastman Kodak, *USP* 2,728,660.

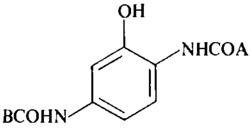


(LXI)



(LXII)

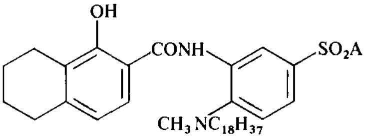
Indoaniline dyes of good heat stability with low blue absorption can be derived from phenols[129] (LXIII; A = alkyl from 4–15 carbon atoms, B = aryloxyalkyl). Dyes from the amides[130] (LXIII; A = ballast, B = thien-2-yl) absorb with maxima between 650 and 660 nm. The related



(LXIII)

sulfonamides have also been described.[131] Dyes from phenols (LXIII; A = perfluoroalkyl, B = alkyl) are deeper in color than the nonfluorinated analogs.[132]

The anilides (LXIV; A = hydroxy, amino, or substituted amino) have good stability and yield cyan dyes of good spectral absorption.[133]



(LXIV)

Phenols and naphthols carrying heterocyclic substituents at the 2-position have been synthesized. Dye images of excellent spectral properties and of fine grain are claimed from the benzimidazoles[134] (LXV). A range of dyes λ_{max} between 596 and 680 nm, of good stability, can be prepared

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[129] I. F. Salminen, C. R. Barr, and Eastman Kodak, *USP* 2,772,162.

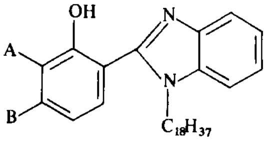
[130] Gevaert Photo-Producten, *BP* 975,773.

[131] J. Jaeken and Gevaert Photo-Producten, *DBP* 1,109,523.

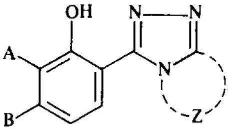
[132] I. F. Salminen, C. R. Barr, A. Loria, and Eastman Kodak, *USP* 2,895,826.

[133] W. Schulte, H. Meckl, and Agfa, *DBP* 1,137,311.

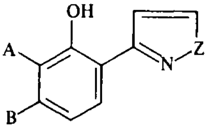
[134] W. C. Craig and G, *BP* 636,996.



(LXV)



(LXVI)

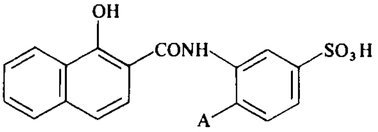


(LXVII)

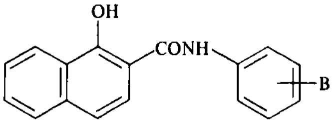
(A, B = H or together complete a phenyl ring).

from the heterocycles[135] (LXVI; Z = atoms to complete a pyridine, quinoline, or benzothiazole ring system). The azoles[136] (LXVII; Z = *O*, or *N*-phenyl) give dyes, fast to heat and light, absorbing with maxima between 652 and 655 nm.

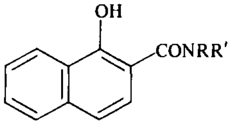
High green transmission has been claimed for indoanilines from naphthols[137] (LXVIII; A = alkoxy, alkylthio, or chloro) and the corresponding sulfonamides.[138] Naphthanilides[139] (LXIX; B = phenylsulfonyl) have been claimed as cyan couplers.



(LXVIII)



(LXIX)



(LXX)

The amides (LXX; R, R′ = alkyl groups in total from 8 to 24 carbon atoms) are oil-soluble nondiffusing couplers.[140] Dyes from the tertiary amide (LXX; R = methyl, R′ = octadecyl) are bluer in shade than those from the secondary amide[141] (LXX; R = H, R′ = octadecyl).

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[135] I. F. Salminen, J. A. VanAllan, and Eastman Kodak, *USP* 2,976,146.

[136] D. Bellone, R. Magagnoli, and Ferrania, *DBP* 1,149,250.

[137] Gevaert Photo-Producten, *BP* 831,731; 975,928; 983,648; see also E. B. Rauch, C. R. Hance, and G, *USP* 3,079,259.

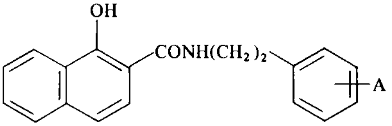
[138] Gevaert-Agfa, *Neth. Appl.* 14,341/66.

[139] D. Bellone, U. Chittolini, and Ferrania, *FP* 1,463,064.

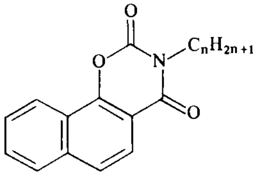
[140] R. F. Coles and G, *USP* 3,005,709.

[141] G. W. Kitchingman and ICI, *BP* 727,693.

The couplers[142] (LXXI; A = 2-acetamido or 2-propionamido), for use in developer solutions, give dye images which have good stability to heat and light, and high green transmittance. These excellent absorption characteristics have been attributed to the fine crystalline form of the dye deposits.



(LXXI)



(LXXII)

Indoanilines from the naphthol[143] (LXXI; A = 4-benzoyl) have $\lambda_{\max}$ at around 675 nm. Sulfonamides[144] (LXXI; A = 4-alkylsulfamoyl) and the naphthalene derivatives[145] (LXXII; n = 12–18) have been claimed as cyan couplers.

g. Couplers Containing a Substituent at the Reactive Position. The coupling reactions previously considered involved the replacement of hydrogen at the reactive center of the coupler molecule. However, certain substituents at this position do not interfere with the coupling reaction and, indeed, many such couplers, have been synthesized. Various beneficial effects can be achieved depending on the type of substituent.

Equation (1) showed that for each molecule of the dye formed, four equivalents of silver are needed. Certain couplers (LXXIII; wherein Z represents a halogen atom[146] or a group such as sulfonic acid,[147] tartronic acid,[148] acyloxy,[149] aryloxy,[150] alkylsulfonyloxy,[151] thiocyanato,[152] or

---

[142] P. W. Vittum, A. Weissberger, and Eastman Kodak, *DBP* 1,096,196; Fuji Photo Film, *BP* 1,062,190; 1,085,437.

[143] R. Magagnoli and Ferrania, *FP* 1,470,880.

[144] R. Magagnoli and Ferrania, *FP* 1,463,231.

[145] Fuji Photo Film, *Japan Appl.* 11303/67.

[146] F. C. McCrossen, P. W. Vittum, A. Weissberger, and Eastman Kodak, *BP* 736,922; A. Loria, I. F. Salminen, A. Weissberger, and Eastman Kodak, *BP* 944,490; A. Loria, W. A. Reckhow, I. F. Salminen, and Eastman Kodak, *USP* 3,006,759; Gevaert-Agfa, *Neth. Appl.* 10,577/66; Fuji Photo Film, *BP* 1,052,488.

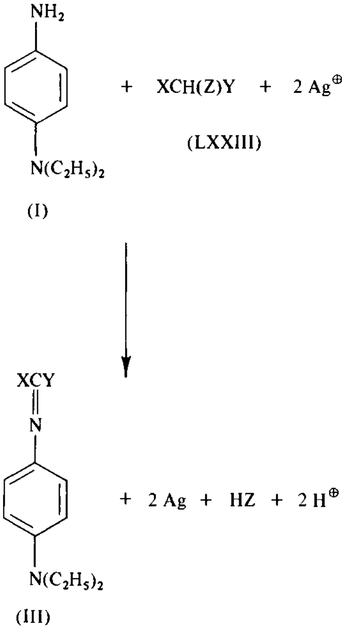
[147] A. H. de Cat, H. R. van den Eynde, and Gevaert Photo-Producten, *BP* 939,030; R. K. van Poucke, A. H. de Cat, M. H. Verbrugghe, and Gevaert Photo-Producten, *DBP* 1,109,522.

[148] E. MacDonald and ICI, *BP* 747,628.

[149] A. Loria and Eastman Kodak, *BP* 1,040,710.

[150] A. Loria and Eastman Kodak, *BP* 1,077,874; 1,084,480; *BeP* 653,722.

alkylaminomethyl[153]) require only two equivalents of silver to produce one molecule of dye, Eq. (9).



(9)

The bis pyrazolinone (LXXIV) splits during chromogenic development and each pyrazolinone nucleus produces an azamethine dye,[154] the reaction rates being approximately equivalent. Such a coupler is useful when broadening of absorption may be required and mixtures of couplers cannot be used because of differences in their rates of reaction.

On the other hand, the mercaptan which is formed when the naphthol (LXXV) reacts with oxidized developer can be used to control image quality.[155]

Similarly, the coupler (LXXVI) with a fluorescent substituent at the reactive position can be incorporated into an emulsion layer. After processing and dye formation, the layer fluoresces only where no develop-

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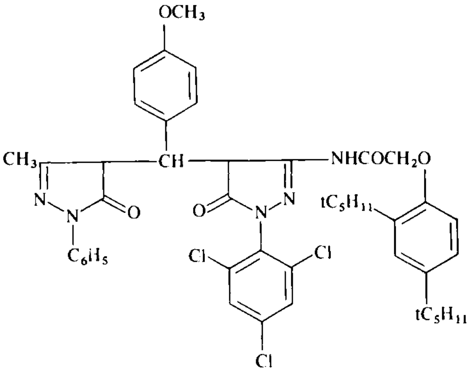
[151] R. F. Porter and Eastman Kodak, *BP* 1,092,506.

[152] A. Loria, I. F. Salminen, and Eastman Kodak, *BP* 977,554; *USP* 3,253,924.

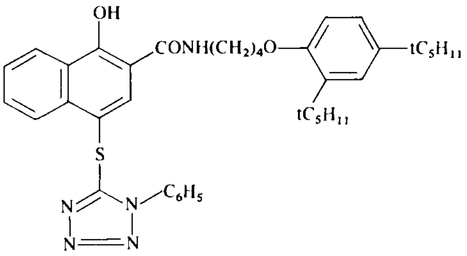
[153] H. W. J. Cressman, J. R. Thirtle, and Eastman Kodak, *FP* 1,478,188.

[154] G. W. Sawdey and Eastman Kodak, *USP* 2,706,683.

[155] C. R. Barr, J. Williams, K. E. Whitmore, and Eastman Kodak, *USP* 3,227,554.



(LXXIV)



(LXXV)

ment has occurred, resulting, when viewed in reflected light, in apparent reduction of density in low density areas.[156]

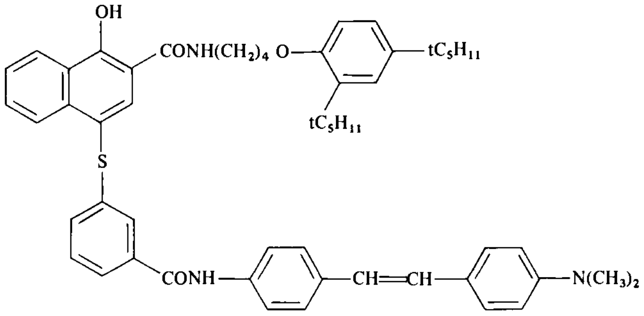
A diffusible indoaniline dye is formed when the nondiffusing naphthol (LXXVII) couples with oxidized developer; the ballast moiety is eliminated during the reaction. The nondiffusing azo dye (LXXVIII) couples with oxidized developer, giving a nonwandering indoaniline dye while releasing a diffusible yellow azo dye [see Eq. (10) for mechanism]. The diffusible dyes formed in these reactions can be transferred to a separate coated layer containing a mordant. Color image transfer processes have been based on such reactions.[157]

The pyrazolinone (LXXIX) reacts with oxidized developer, without loss of the cyanoethyl substituent, to give colorless reaction products.

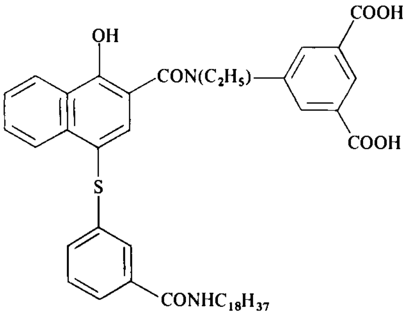
---

[156] J. A. Carter, H. M. Wagner, M. V. Mijovic, and Kodak, *BP* 945,542.

[157] K. E. Whitmore, P. M. Mader, and Kodak, *BP* 904,364; A. Loria, J. Williams, C. R. Barr, and Eastman Kodak, *BP* 1,038,331.



(LXXVI)



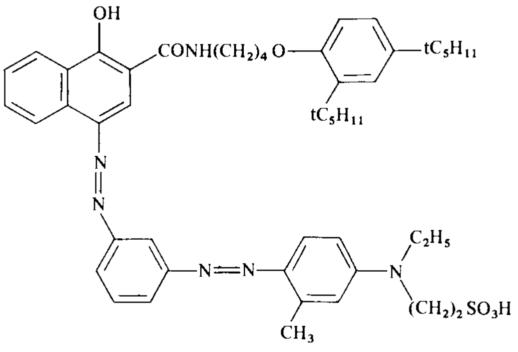
(LXXVII)

It can be used to take up excess oxidation products of the developer, thus eliminating the possibility of unwanted dye formation through autocoupling of the developer.[158] Similarly, 2,6-dihydroxyisonicotinic acid and 3,5-dihydroxybenzoic acid[159] can be used to react with the excess oxidized developer to form soluble dyes which are washed out after development. The effect of either of these techniques is to obtain images of higher color fidelity.

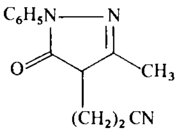
h. Color Masking and Colored Color Couplers. The provision of spectrally improved image dyes has been a contributing factor to advancements in the quality of color reproduction. However, even the best dyes

[158] W. Puschel and Agfa, *BP* 914,145; Ferrania, *BP* 979,654.

[159] I. F. Salminen and Eastman Kodak, *USP* 2,742,832.



(LXXVIII)



(LXXIX)

obtainable have some unwanted subsidiary absorption, so methods have been established to correct these imperfections.

The blue absorption deficiencces of the pyrazolinone azamethines are correctable, in negative materials, by masking techniques which depend on the presence in the nonimage areas of the processed green-sensitive layer, of a dye whose absorption matches as nearly as possible the unwanted absorption of the magenta image dye. This results in a uniform density to blue light throughout the layer. This is optically equivalent to the magenta image dye having no blue light absorption (Fig. 8). To compensate for the overall blue absorption when printing from the negative, it is necessary only to adjust the blue light exposure. In practice, a coupler (LXXX; wherein X and Y are the atoms necessary to complete a pyrazolinone ring system, A is a substituent such as a ballast or solubilizing group), which is colored, is incorporated into the emulsion layer. On development and coupling the chromophoric system responsible for the coupler's color is broken with the simultaneous formation, Eq. (10), of the azamethine image dye (LI). The unchanged dye remaining in the nonimage areas of the negative effectively compensates for the unwanted absorption of the image dye.

Various yellow-colored pyrazolinone azo dyes derived from aromatic[160]

---

[160] B. Graham, P. W. Vittum, A. Weissberger, and Eastman Kodak, *USP* 2,657,134; B. Graham and Kodak, *BP* 737,012; 739,913; J. Williams, and Eastman Kodak, *USP* 2,860,974; L. E. Beavers and Eastman Kodak, *USP* 2,983,608; H. Pietrzok, S. Traue, S. Schmidt, and VEB Filmfabrik, *BP* 1,067,397; A. Guzzi, B. Mariani, E. Tisselli, and Ferrania, *FP* 1,473,581; Fuji Photo Film, *BeP* 664,221; Ilford, *Neth. Appl.* 13,276–7/64.

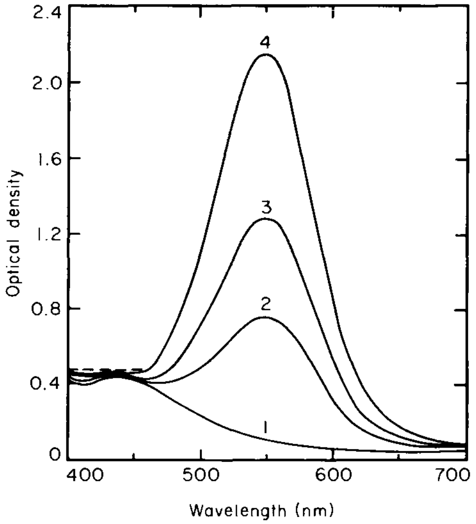
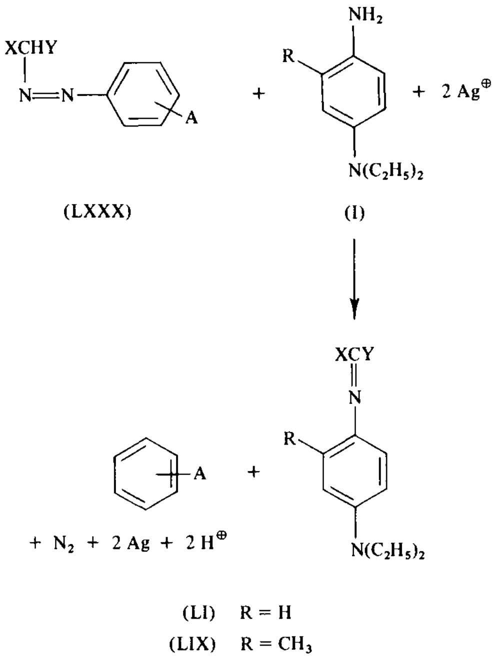
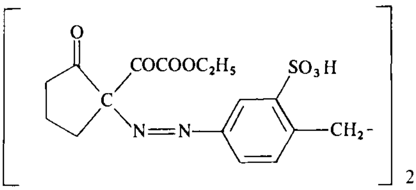


FIG. 8. Curves 2-4 represent the increasing absorption due to the formation of the magenta image dye on development. Curve 1 is that of the blue-absorbing coupler, and the broken abscissa represents the effective zero density of the color negative relative to blue light.



(10)

or heterocyclic amines,[161] and 4-benzylidenepyrazolinones[162] have been used for this purpose. A mixture of a colored and a colorless coupler can be used to control accurately the densities to blue light of the correcting coupler and the image dye. It is claimed that the use of azo bis pyrazolinones,[163] which are less intensely colored than the above simple azo dyes, allows easier color matching. The yellow-colored azo dye (LXXXI) and related compounds couple with oxidized developers to give colorless reaction products and can serve as correcting couplers for pyrazolinone azamethine image dyes.[164]



(LXXXI)

The unwanted side absorptions of the indoanilines can be corrected by the use of colored color couplers derived from α-naphthols. Orange, red, and magenta azo dyes have been claimed to be useful.[165] The formation of the indoaniline image dye (LIX) proceeds according to Eq. (10), wherein X and Y represent the atoms necessary to complete a naphthol coupler system and A is a substituent such as a ballast or solubilizing group.

The color-correcting dyes can be formed in the nonimage areas of a negative by the reaction of the unused couplers, which are present in those areas, with dye-forming compounds. Thus, a yellow-colored mask can be achieved by the reaction of a pyrazolinone with β-furylacrolein[166] or a pyrrole aldehyde.[167] Yellow azo dye masks result from the reaction

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[161] D. G. Saunders, E. B. Knott, and Eastman Kodak, *USP* 3,005.712.

[162] K. O. Ganguin, E. MacDonald, and ICI, *BP* 673,091; R. B. Collins, R. R. Robinson, D. J. Fry, and Ilford, *BP* 674,356; 675,797.

[163] B. Graham and Eastman Kodak, *USP* 2,725,291; see also Agfa, *BP* 800,262.

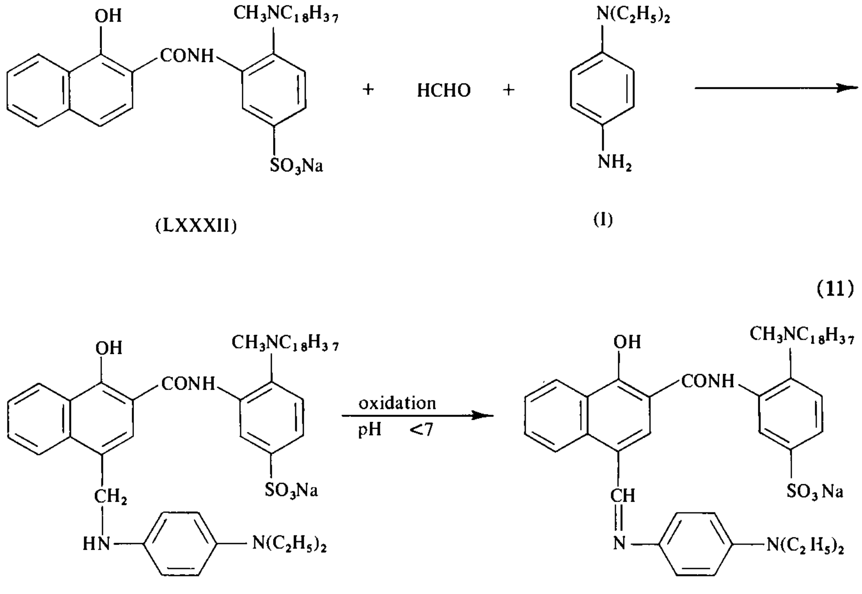
[164] Agfa, *BP* 866,203.

[165] N. Heimbach, H. Morreal, Jr., and G, *BP* 646,367; D. B. Glass, P. W. Vittum, A. Weissberger, and Eastman Kodak, *USP* 2,521,908; B. Graham, J. Williams, and Eastman Kodak, *USP* 2,706,684; K. E. Whitmore and Eastman Kodak, *USP* 2,808,329; K. E. Whitmore, E. T. Pesch, and Eastman Kodak, *USP* 2,860,975; R. J. Gledhill, J. Williams, and Eastman Kodak, *USP* 3,034,892; Fuji Photo Film, *BP* 1,055,617; 1,070,768.

[166] D. Bellone, A. Guzzi, and Ferrania, *DBP* 1,132,799.

[167] Agfa, *BP* 765,280.

of a pyrazolinone with diazonium salts[168] or organic azides[169] and orange-red dyes from α-naphthols with diazonium salts.[168] 2-Quinolone hydrazone can also be used to form azo-masking dyes.[170] Oxidized 4-aminopyrazolin-3-ones[171] give magenta dyes with α-naphthols and a red-colored Schiff base (LXXXIV), used as a mask for the cyan image dye, is obtained by the oxidation of the leuco dye (LXXXIII) formed in the reaction of the naphthol (LXXXII) with formaldehyde and the developer (I)[172] [Eq. (11)].



(LXXXII) (I)

(11)

(LXXXIII) (LXXXIV)

B. AZINE DYES

The possibility of using azines as image dyes is attractive because of their spectral superiority and better stability than the azamethines and indoanilines.[173] They can be formed either by reacting a coupler having an amino substituent ortho to its coupling position, with a conventional

---

[168] DuP, *BP* 665,657; Agfa, *BP* 739,202.

[169] Agfa, *BP* 822,125.

[170] J. Jaeken, R. A. Spriet, H. V. Van Goethem, M. A. Ramaix, and Gevaert Photo-Producten, *BP* 993,749.

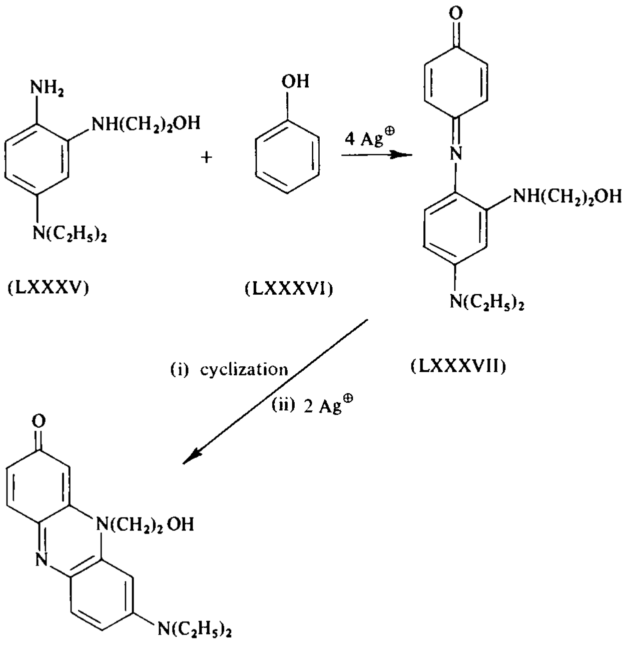
[171] Gevaert Photo-Producten, *BP* 975,930; 975,939.

[172] K. O. Ganguin and E. MacDonald, *J. Phot. Sci.* **14**, 260 (1966).

[173] W. A. Schmidt, V. Tulagin, J. A. Sprung, R. C. Gunther, R. F. Coles, and D. E. Sargent, *Ind. Eng. Chem.* **45**, 1726 (1953).

developer, or by reacting a conventional coupler with a developer which has an amino substituent ortho to its primary amino group.

Oxidative coupling, Eq. (12), gives, firstly, the azamethine (LXXXVII), which after cyclization and further oxidation, yields the azine dye (LXXXVIII).



(LXXXV) (LXXXVI) (LXXXVII) (LXXXVIII)

(12)

The results of early work indicated that precise adjustment of pH was vital to produce a permanent yellow image, and that suitable cyan dyes were difficult to obtain.[173]

1. *Color Developers*

The *o*-phenylenediamines (LXXXIX) and (XC) are further examples of developing agents.[174]

2. *Color Couplers*

5-Amino-1-benzoyl-2-naphthol[175] yields a yellow dye (XCI) with the developer (XC), which is less sensitive to pH changes than the dyes from acetoacetanilide.[173]

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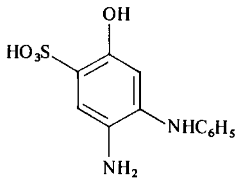
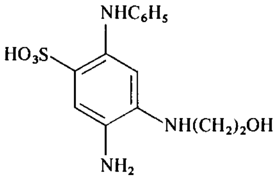
[174] R. C. Gunther and G, *USP* 2,555,127; 2,611,785.

[175] W. F. Hoffstadt and G, *USP* 2,921,851.



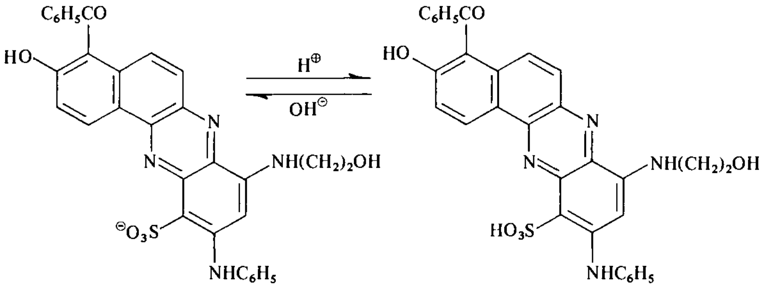
(LXXXIX)



(XC)

The nondiffusing sulfonamide (XCII) has been proposed for use in emulsion layers[176] and the coupler (XCIII) can be used in developer solutions;[177] both give magenta dyes with *p*-phenylenediamines.

The *N*-arylsulfonyl derivatives of *m*-aminophenol and *m*-phenylenediamine are more reactive couplers than the parent compounds; the arylsulfonyl group splits off on azine ring formation.[178]



yellow basic form

magenta acid form pH $<$ 5.

(XCI)

A complex magenta dye (XCIV) is obtained by reacting 2 moles of *p*-diethylaminoaniline with 1 mole of either 6-amino,[179] or 6-chloro-8-hydroxy-2-phenylcinchoninic acid.[180]

The cyan azines derived from 2,4-diaminoaniline developers and the couplers[181] (XCV; Z = benzyl, aryl, or naphthyl) have greater green transmission than the earlier known dyes from *N*-aryl J-acids.[182]

---

[176] A. C. Starke, Jr. and G, *USP* 2,569,906.

[177] B. Gaspar and Minnesota Mining & Manufacturing, *USP* 3,245,795.

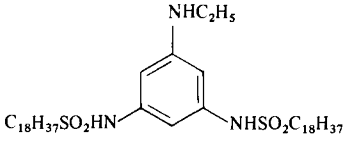
[178] I. V. Aleksandrov, *Zh. Nauchn,. i Prikl. Fotogr. i Kinematogr.* **2**, 191 (1957); *Phot. Abstr.* p. 440 (1958); *ibid.* **2**, 432 (1957); *Phot. Abstr.* p. 1220 (1958).

[179] W. A. Schmidt, R. F. Coles, and G, *USP* 2,886,436.

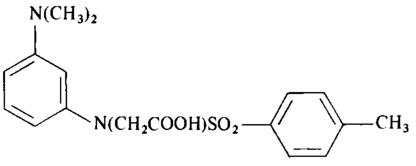
[180] G, *USP* 2,701,766.

[181] R. F. Coles, V. Tulagin, and G, *USP* 2,871,120.

[182] V. Tulagin, W. A. Schmidt, and G, *USP* 2,542,597; V. Tulagin, R. F. Coles, and G, *USP* 2,591,642.

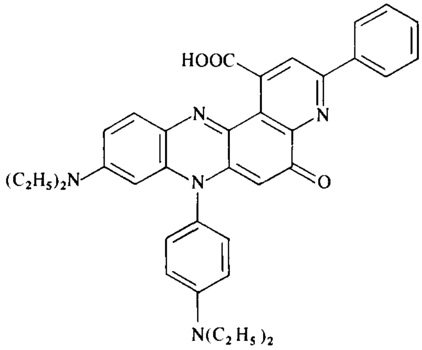


(XCII)

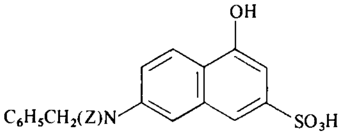


(XCIII)

Benzo[*h*]quinolinols[183] couple with the oxidation products of the developer (XC) to give brilliant dye images with λ_{max} at 650 nm.



(XCIV)



(XCV)

C. Azo Dyes

Azo dyes offer certain advantages, such as better stability to light and enhanced resistance to acids, over the azamethines. Various methods of forming images using azo dyes have been reported. Thus it is possible to produce direct positive images by bleaching the image dyes formed by conventional color development, followed by treatment of the residual couplers, in the nonimage areas, with diazonium salts[184] or heterocyclic hydrazones.[185]

1. *Developers Yielding Azo Dyes*

2-(*o*-Ethoxyphenyl)methylsulfonhydrazide (XCVI) gives under oxidative coupling conditions with a pyrazolinone coupler a yellow azo dye[186] [Eq. (13)]. Similarly, with α-naphthol, a magenta azo dye results.

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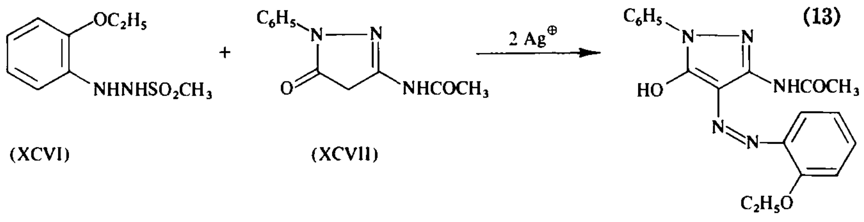
[183] V. Tulagin, R. F. Coles, and G, *USP* 2,717,831.

[184] S. Hünig and H. v. Babo, *BeP* 514,851.

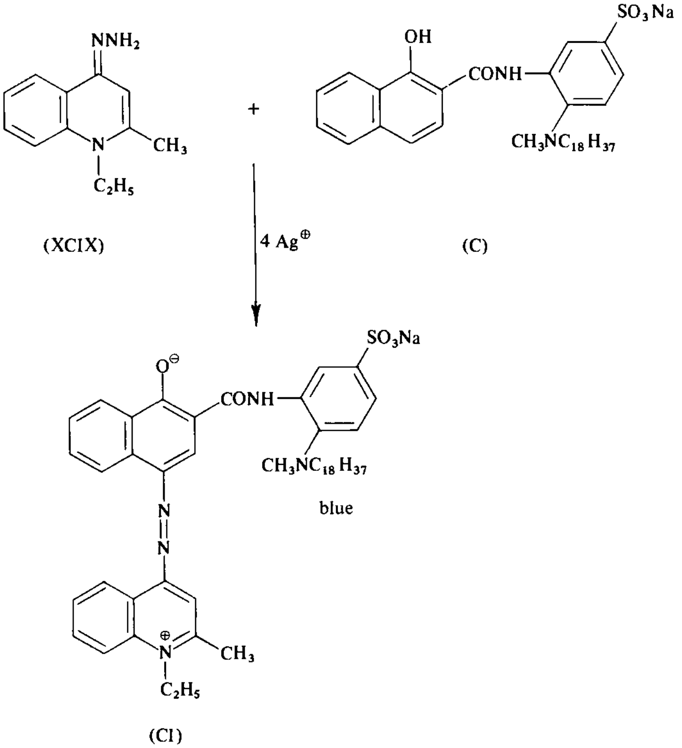
[185] J. Jaeken, M. A. de Ramaix, and Gevaert Photo-Producten, *USP* 3,293,032.

[186] J. A. Sprung, W. A. Schmidt, and G, *USP* 2,708,625.


(XCVI) (XCVII) (XCVIII)

(13)

Azo dyes, also, are formed by oxidative coupling, Eq. (14), of heterocyclic hydrazones with phenols or amines.[187]


(XCIX) (C) (CI)

(14)

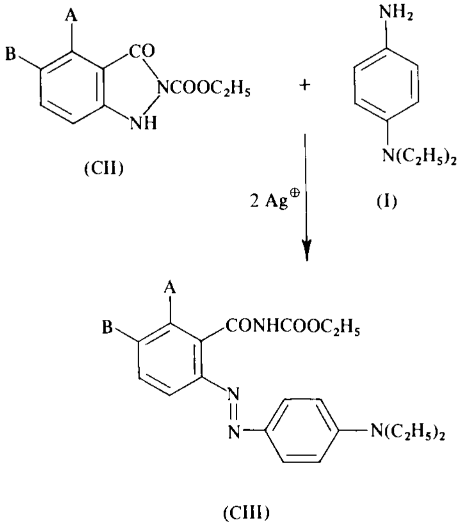
2. *Couplers Yielding Azo Dyes*

2-Ethoxycarbonylindazolin-3-ones[188] (CII) react with oxidized 4-diethylaminoanilines to give azo dyes, Eq. (15), and a range is possible depending on the values of the substituents A and B.

---

[187] S. Hünig and C. Schleussner Fotowerke, *DBP* 963,297; 1,000,689.

[188] J. M. Woolley and ICI, *BP* 722,281; 729,505; E. MacDonald, R. Mirza, J. M. Woolley, and ICI, *BP* 875,470.



(15)

Thus, the dyes (CIII; A = B = H), (CIII; A = methyl or butylcarbamoyl, B = H) and (CIII; A = H, B = sulfamoyl) are orange, yellow, and magenta, respectively. Similarly, the isoxazolinone ring opens on oxidative coupling to give a yellow dye.[189]

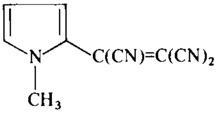
Of interest is the claim that colorless tetrazolium salts are reduced by silver images in potassium cyanide solutions to the corresponding formazans.[190]

D. Dyes Containing Cyanoalkene Substituents

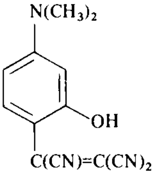
The polycyano developing agents[191] (CIV; where A and B are electron-withdrawing groups, Z = arylene, $n = 0$ or 1) couple under oxidative

$$NCCH(A)(Z)_nCH(B)CN$$

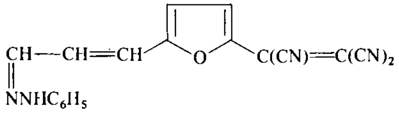
(CIV)



(CV)



(CVI)



(CVII)

conditions with compounds, such as *N*-methylpyrrole, *m*-dimethylaminophenol, and *β*-2-furylacrolein phenylhydrazone to form dyes. The dyes (CV), (CVI), and (CVII) are yellow, magenta, and blue, respectively.

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[189] J. M. Woolley and ICI, *BP* 778,089.
[190] E. MacDonald and Ilford, *BP* 908,299.
[191] T. L. S. Cairns and DuP, *BP* 875,604.

CHAPTER VII

PHOTOCHEMISTRY OF DYES

Hans Meier

STAATLICHES FORSCHUNGSINSTITUT FÜR GEOCHEMIE, BAMBERG, WEST GERMANY

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List of Abbreviations

α	Molar absorption coefficient
C	Concentration (mole/liter or M)
c	Light velocity
[D]	Concentration of a dye (mole/liter)
E	Redox potential of a dyestuff
E_{D}	Activation energy of dark conductivity
$E_{i,j}$	Energy of molecular states

E^0	Standard emf
E_{Ph}	Activation energy of photoconductivity
ϵ	Molar extinction coefficient or molar absorptivity
F	Faraday's constant
ΔG	Free energy change of a reaction
$\Delta G^{\#}$	Free energy of activation
h	Planck's constant (6.625×10^{-27} erg sec)
I_{A}	Absorbed light intensity (einsteins/liter sec)
I_0	Light intensity (quanta/sec)
I'_0	Light intensity (einstein/cm^2 sec)
k	Rate constant
k_{ST}	Rate constant for intersystem crossing of $\mathrm{S}_1 \rightarrow \mathrm{T}_1$
λ	Wavelength
N_{L}	Avogadro number (6.02×10^{23})
ν	Frequency of light (sec^{-1})
$\tilde{\nu}$	Wavenumber
O.D.	Optical density
σ_{D}	Dark conductivity
σ_{Phot}	Photoconductivity
τ	Lifetime
τ_0	Radiative lifetime
φ_i	Primary quantum efficiencies ($\varphi_1, \varphi_2 \ldots$)
$\varphi_{\mathrm{S-T}}$	Quantum efficiency of intersystem crossing
ϕ	Overall quantum yield

Absorption of light by organic dyes is followed by a series of physical and chemical effects. These effects are the result of organic molecules rising by an uptake of light energy to an "excited state" which is more reactive than the normally occupied "ground state."

Exactly speaking, the excited state results from the jumping of an electron from the most populated lowest vibrational energy level of the ground state to a higher energy level. As the raised electron will try to return to the ground state the excitation energy is released in a very short time. Under certain circumstances the energy is dissipated as heat because of radiationless transitions between the energy states. There exists also the possibility of releasing the excitation energy as light, so that fluorescence or phosphorescence is observed. In addition, the excitation energy can be converted into chemical energy by dissociation, intramolecular rearrangement, redox processes with neighbor molecules, or any other photochemical reaction. Moreover, the absorbed energy may be transferred to another molecule which becomes excited by this energy-transfer process and ready for photophysical and photochemical reactions. In such a transfer process the absorbing molecules act as photosensitizers or photocatalysts which displace the action spectrum of a photochemical or photophysical reaction to longer wavelengths, especially to the visible region.

It must be emphasized that many important photoreactions would be impossible without the sensitization effect of organic dyes. For example, a large part of modern photography would be inconceivable, since it is only by the help of the sensitizing action of dyes that silver halide emulsions, which are only sensitive to blue and ultraviolet light, are able to "see" in the same way as the human eye. In addition, sensitization is not limited to spectral shiftings of photoreactions: With sensitizing compounds photoreactions which would not occur without sensitizers can be initiated, or the course of an unsensitized reaction is altered by the action of a sensitizer. These effects are often encountered. As examples there should be mentioned the process of assimilation in plants (photosynthesis), the process of vision in the eye, the biologically important photodynamic and phototropic effect, and the dye-sensitized phototendering of textiles.

From these examples we see that many important processes can be initiated by the illumination of dyes. Therefore, work on the photochemistry of organic dyes is of general interest and takes a large part in the science of fundamental and, especially, organic photochemistry, which has become a field of intense activity in the last decade. The application of new analytical techniques and the results of quantum theory and electronic spectroscopy have led to valuable progress in the understanding of photoreactions in which dyes play a decisive role. In this context it should also be mentioned that many experiments which aimed at photochemical reactions of dyes gave rise to suggestions and statements of general importance. As an example we would cite the question of the relation between color and constitution, the problem of the association of dyes, or the electronic semiconductivity of organic compounds which led to the construction of organic vidicon tubes for television.

In the following sections a summary of the general laws governing the photochemical processes of dyes and of other organic compounds is given first. A report of photochemical reactions of dyes in solution is followed by a survey of light-fading of dyed textiles and other dyed substrates. In the last section the effect of spectral sensitization and special photoreactions of dyes are discussed.

I. The Principles of Photochemical Processes

A. Basic Photochemical Rules

Photochemical reactions are governed by some basic laws:

(1) The law of Grotthus and Draper (1817, 1843) states that only light which is absorbed by a system can produce a photochemical change. This principle of photochemical activation, nowadays a self-evident one, must be strictly observed in studying photochemical reactions. Not only must the emitted wavelength of a used light source coincide with the region of absorption, but care must also be taken to exclude wrongly absorbing glass vessels, filter, etc.

(2) The law of Stark, Einstein, and Bodenstein (1908–1913) states that in the primary step of a photochemical reaction each quantum of light absorbed causes activation of one absorbing molecule.

With this principle the concept of the quantum of energy has been applied to photochemical reactions. But it must be emphasized that only the primary photochemical step and not the overall photochemical process can be generally described by this law because the primary process is often followed by a complex series of reactions. The measured quantum efficiency (or overall quantum yield) ϕ of a photochemical reaction, which may be defined as the number of molecules of reactant or product which are consumed or produced, respectively, per quantum of light absorbed can vary from $\phi = 10^6$ to $\phi < 10^{-5}$.

The principle of the one-quantum activation can be extended by including the fact that excited molecules may be deactivated or destroyed by various radiative, radiationless, and chemical primary processes. As a result of the one-quantum aspect the sum of the different primary quantum efficiencies

$$\varphi_i = \frac{\text{Number of molecules reacting in a special primary process}}{\text{Number of quanta absorbed}} \tag{1}$$

must be unity.[1] For the investigation of the mechanism of photoreactions it is necessary to get detailed information on the quantum efficiencies φ_i of the various primary processes which are immediately following the quantum absorption. For example, a quantum efficiency $\varphi_n = 1$ for radiationless transitions to the ground state observed in a dye would result in lightfastness of the dye molecules concerned. With detailed information on φ_i photoreactions can be interpreted and eventually predicted.

(3) The rule of E. Warburg (1920) states that it is the number of

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[1] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry." Wiley, New York, 1966.

absorbed photons and not their energy content, that is decisive in photochemical reactions. But it must be noted that in systems with several absorbing species and, as a special case, in some special molecules with several active excited states, photochemical reactions may also take a different course depending on the energy (wavelength) of absorbed photons.

(4) The results of modern organic photochemistry have evolved a further important rule, which, formulated by Turro,[2] says: "The lowest singlet and triplet states, which can be populated by a molecule by absorption of each quantum with a certain probability, are the starting points of most organic photochemical processes." The significance of this rule for the explanation of the photochemical behavior of dyes will be seen in the following sections.

B. Fundamental Kinetics of Photochemical Processes

1. *Rules for Absorption of Light*

a. Energetic Relationships. As a consequence of the one-quantum aspect the energy of the absorbed (and emitted) light is equal to the difference in energy between two molecular states E_i, E_j and is described by the equation

$$\Delta E \equiv E_i - E_j = h\nu \tag{2}$$

Where $h = 6.625 \times 10^{-27}$ (erg sec) is Planck's constant; and ν (sec^{-1}) is the frequency of light.

The energy of any transition can be determined from the position of the absorption (or emission) band which is expressed by its wavelength ($\lambda = c/\nu$) or wavenumber ($\tilde{\nu} = 1/\lambda$). For wavelength the units are Angstroms (10^{-8} cm) or nanometers [1 nm = 1 mμ = 10^{-3} μ = 10^{-7} cm = 10 Å] and for wavenumber $\tilde{\nu}$ the reciprocal micron (μm^{-1}) or reciprocal centimeters (cm^{-1}). The energy which is equivalent to the energy of $N_\text{L} = 6.02 \times 10^{23}$ photons (N_L, Avogadro number)

$$E_\text{E} = N_\text{L} h\nu \tag{3}$$

is called one *einstein*. The value of the einstein (in kilocalories) depending on the wavelength can be calculated from the wavelength or wavenumber of any transition by Eq. (4):

$$E\ (\text{kcal/einstein}) = \frac{2.86 \times 10^5}{\lambda(\text{Å})} = 2.86 \times 10^{-3}\, \tilde{\nu}\ (\text{cm}^{-1}) = 28.6\tilde{\nu}\ (\mu\text{m}^{-1}) \tag{4}$$

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[2] N. J. Turro, "Molecular Photochemistry." Benjamin, New York, 1965.

The photochemically interesting spectral region is between 2000 and 7000 Å (respectively, 5.0–1.43 μm^{-1} or 5×10^4–1.43×10^4 cm^{-1}), corresponding to an energy range from $E_{2000} = 143$ kcal to $E_{14000} = 20$ kcal. Solar ultraviolet below 2700 Å, however, never reaches the earth because of the absorption of the shorter rays by ozone and air. Therefore, for photochemical reactions on dyed materials usually visible light between 4000 and 7000 Å and ultraviolet radiation between 3900 and 3500 Å (extreme lower limit about 2700 Å) is active. As the energy necessary for breaking chemical bonds between C and C or C and O amounts to 80 and 88 kcal/mole, respectively, only ultraviolet radiation with an energy higher than these values ($\lambda \leqslant 3250$ Å) can disrupt C—C or C—O bonds in a photolytic reaction. A photolytic cleavage by visible light (for example, with $\lambda = 6000$ Å, $E_{6000} = 45$ kcal) takes place only on rather weak covalent bonds. In discussing photochemical reactions of dyestuffs it must be noted that by the absorption of visible and near ultraviolet light, dye molecules are usually raised to an excited state which is chemically stable.

b. Bougourd-Lambert-Beer Law. Only a part of the incident light intensity I_0 (measured in quanta per second) is usually absorbed in a specimen. With the fraction of the light which is reflected (I_R), scattered (I_S), transmitted (I_T), and absorbed (I_A) the incident light is given by

$$I_0 = I_R + I_S + I_T + I_A \tag{5}$$

Because the fraction reflected and scattered is relatively small the absorbed part can be given by

$$I_A = I_0 - I_T \tag{6}$$

I_T can be expressed by Eq. (7), which is derived in references 3–5.

$$I_T = I_0 \exp(-\alpha C d) = I_0 10^{-\alpha(\log e)Cd} = I_0 10^{-\epsilon C d} \tag{7}$$

where C is concentration in moles per liter; α $(= 2.303\ \epsilon)$ is the molar absorption coefficient; and ϵ $(= 0.43\ \alpha)$ is the molar extinction coefficient or molar absorptivity.

For practical use the Bougourd-Lambert-Beer law is given by the expression

$$\text{O.D.} = \log(I_0/I) = \epsilon C d \tag{8}$$

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[3] M. Pestemer, "Anleitung zum Messen von Absorptionsspektren im Ultraviolett und Sichtbaren." Thieme, Stuttgart, 1964.

[4] C. A. Parker, "Photoluminescence of Solutions." Elsevier, Amsterdam, 1968.

[5] J. Eggert, L. Hock, and G.-M. Schwab, "Lehrbuch der physikalischen Chemie," 9th ed. Hirzel Stuttgart 1968.

The quantity O.D. is known as the optical density. Values of ϵ [dimension, cm^{-1} $(mole/liter)^{-1}$ or cm^2 $mmole^{-1}$] can reach in dyes an order of 10^5.

In systems with a small optical density the expression for the rate of light absorption

$$I_A = I_0\{1 - \exp(-\alpha[D]d)\} \tag{9}$$

can be simplified. By extending the exponential term of Eq. (9) in the order

$$\exp(-\alpha[D]d) = 1 - \alpha[D]d + \frac{(\alpha[D]d)^2}{1 \cdot 2} - \frac{(\alpha[D]d)^3}{1 \cdot 2 \cdot 3} + \cdots \tag{10}$$

and inserting Eq. (10) in Eq. (9) we get

$$I_A = I_0\left(\alpha[D]d - \frac{(\alpha[D]d)^2}{2} + \frac{(\alpha[D]d)^3}{6} - \cdots\right) \tag{11}$$

In the case of small αd the approximation is possible

$$I_A = I_0(\alpha[D]d) \qquad \text{or} \qquad I_A = I_0(2.3\epsilon[D]d) \tag{12}$$

By measuring I_A in einsteins per liter per second and I'_0 in einstein per square centimeter per second the rate of light absorption in the system is given by

$$I_A = 2300\epsilon[D]I'_0 \tag{13}$$

c. Determination of Quantum Efficiency. The relationships given in Eqs. (6) and (7) are helpful for calculating the quantum yield of a series of photochemical reactions of dyes. Because the quantum efficiency ϕ of a photoreaction is given by

$$\phi = \frac{\text{Moles decomposed, etc.}}{\text{Moles of quanta (einsteins) absorbed}} \tag{14}$$

it follows that the rate of any photoreaction (and also the rate of fluorescence and phosphorescence) is equal to the rate of light absorption I_A multiplied by the quantum efficiency ϕ of the considered photoreaction

$$\pm\frac{d[D]}{dt} = I_A\phi \tag{15}$$

where [D] is the concentration of dye D moles per liter; t is (usually) in seconds; and I_A is in einsteins per liter per second. For example, in the photobleaching of a dyestuff by decomposition, photoreduction, etc., we have by substituting Eqs. (6) and (7) into Eq. (15)

$$-\frac{d[D]}{dt} = (I_0 - I_T)\phi = I_0\{1 - \exp(-\alpha[D]d)\}\phi \tag{16}$$

Expressing I_0, the intensity of the exciting light, instead of in the unit einsteins per liter per second, in einsteins per square centimeter per second (I'_0) we have

$$-\frac{d[\mathrm{D}]}{dt} = \frac{10^3 \cdot I'_0 B}{d}\{1 - \exp(-\alpha[\mathrm{D}]d)\} \tag{17}$$

For consideration of the mechanism of dye fading it is important to know that a dye usually fades according to a first-order law if the dye is illuminated in a state in which every molecule is reached with the same probability both by photons and by any reactive species (electron-donating molecules, etc.), i.e., in solutions, true dispersions, or monolayers.[6,7] In the case of such unimolecular or pseudo-unimolecular photoreactions the fading rate of the dye is simply proportional to the rate of the absorption of light corresponding to Eq. (15), so that the proportion decomposed or bleached over a fixed time is independent of the initial concentration of the dye. Therefore, the rate of fading decreases exponentially with time and by plotting the dye concentration (for example, expressed in percentage of the initial concentration) against the time of illumination one gets an exponential curve, or by plotting the logarithm of the dye concentration against the time a straight line is observed.

By integrating Eq. (16) we see that first-order photoreactions can be experimentally recognized from a linear relation between $\ln\{\exp(\alpha[\mathrm{D}]d) - 1\}$ or $\log[(I_0/I_\mathrm{T}) - 1]$ and time.[6-9] One obtains

$$-I_0\phi_\mathrm{B}t = \frac{1}{\alpha d}\ln\{\exp(\alpha[\mathrm{D}]d) - 1\} + C \tag{18}$$

and with $[\mathrm{D}] = [\mathrm{D}]_0$ at $t = 0$ it follows that

$$\ln\{\exp(\alpha[\mathrm{D}]d) - 1\} = -\alpha d I_0 \phi t + \ln\{\exp(\alpha[\mathrm{D}]_0 d) - 1\} \tag{19}$$

In the decadic form we obtain by multiplying with 2.3 and substituting $\alpha = 2.3\,\epsilon$ and $I_0/I_\mathrm{T} = \exp(\alpha[\mathrm{D}]d)$ in Eq. (14)

$$\log\left(\frac{I_0}{I_\mathrm{T}} - 1\right)_t = -\epsilon d I_0 \phi t + \log\left(\frac{I_0}{I_\mathrm{T}} - 1\right)_{t=0} \tag{20}$$

As can be seen from Eq. (20), the quantum efficiency ϕ can be calculated from the slope $\tan\alpha = \epsilon\, d\phi\, I_0$ (or $\tan\alpha = 1000\,\epsilon\, I'_0\,\phi$) of the linearly plot of $\log[(I_0/I_\mathrm{T}) - 1]$ against time.

With this method the quantum efficiency of the photoreduction of

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[6] H. Meier, "Die Photochemie der organischen Farbstoffe." Springer, Berlin, 1963.

[7] G. Baxter, C. H. Giles, and W. J. Levington, *J. Soc. Dyers Colourists* **73**, 386 (1957).

[8] M. Pestemer, *Z. Elektrochem.* **58**, 121 (1954).

[9] N. Kosui, K. Uchida, and M. Koizumi, *Bull. Chem. Soc. Japan* **38**, 1958 (1965).

methylene blue ($1 \times 10^{-6}\,M$) by allylthiourea ($2.0 \times 10^{-3}\,M$, pH = 7.2) has been determined to be on the order of $\phi = 10^{-3}$ [9] and for photoreduction of thionine by anethole ($2 \times 10^{-4}\,M$) ϕ between 0.1 and 0.27 has been measured.[8]

2. *Rates of Photochemical Reactions*

a. Fundamental Relationship. With a knowledge of the reaction kinetics of photochemical processes important information can be obtained on the mechanisms of photoreactions. Generally, the rate of any dark reaction between n_A, n_B, etc., molecules of type A, B, etc., is described by

$$-\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^{n_A}[\mathrm{B}]^{n_B} \cdots \tag{21}$$

The magnitude k, the reaction rate constant, of the order $(\text{time})^{-1}(\text{concentration})^{1-n}$, is characteristic for the reaction. The exponents n_A, n_B define the reaction order, which is said to be zero, first, or second with respect to the reactant A in the case of $n = 0, 1, 2$. The molecularity which is given by the number of really reacting molecules for forming the activated complex is usually equal to the total order $n = n_A + n_B + \cdots$. In the case of $n_A = 1$, $n_B = 1$ we have a bimolecular and a second-order reaction.

There exist significant differences between thermal and photochemical reactions, which must be taken into account by discussing the total rate of dark and photochemical reactions. In *dark reactions* the energy necessary for activation and for forming transition states, respectively, comes from the kinetic energy of the reactants. The velocity of the reaction is dependent on the number of collisions between the molecules and becomes at any time proportional to the concentration of the reacting molecules. In *photochemical processes*, however, the energy of the radiation absorbed by the reactants is decisive for the course of the reaction. As a consequence, the number of molecules which are formed or decomposed in a time interval must be in relation to the number of the quanta absorbed in the same time.

Therefore, the total rate of a photochemical reaction is given by Eq. (22), formulated by Plotnikow,[10]

$$-\frac{d[\mathrm{D}]}{dt} = k_L I_A \tag{22}$$

in which $-d[D]/dt$, the rate at which molecules are photochemically transformed and I_A, the rate at which quanta of light are being absorbed, are connected by help of the specific photochemical total rate factor k_L;

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[10] J. Plotnikow, "Allgemeine Photochemie." de Gruyter, Berlin, 1936.

k_L includes—contrary to Eq. (21)—reactant concentrations, extinction coefficients, and other terms.

The total reaction order of photochemical reactions can be zero, first, and second, and often there is a switchover from one order to another in the course of illumination. Because of differences between photochemically and thermally activated species there can be differences between the orders of dark reactions and photoreactions. In discussing rates of photochemical reactions one must also note that there are differences possible between local and measured total rates in systems which do not allow a uniform absorption of light in the reaction volume.

b. The Total Orders of Photochemical Reactions. Dyes present in a substrate fade according to an approximately *first-order* law, as discussed above, or according to an approximately *zero-order* law.[6,7] These fading rates are in agreement with the order of photochemical reactions which can be expected in ideal systems. Often the rate of fading of dyed fabrics is *between* these extreme cases. This can be derived by inserting Eq. (16) in Eq. (22) and expressing the intensity of the exciting light in einsteins per square centimeter per second:

$$-\frac{d[\mathrm{D}]}{dt} = k_L \frac{10^3 I'_0}{d}\{1 - \exp(-\alpha[\mathrm{D}]d)\} \tag{23}$$

Taking the concentration at the beginning of the reaction as $[\mathrm{D}]_0$ and the change of the concentration per time t as $x = [\mathrm{D}]_0 - [\mathrm{D}]$, one obtains

$$-\frac{d([\mathrm{D}]_0 - x)}{dt} = k_L \frac{10^3 I'_0}{d}[1 - \exp\{-\alpha([\mathrm{D}]_0 - x)d\}] \tag{24}$$

By integrating it follows that

$$\alpha 10^3 I'_0 k_L = \alpha d x + \ln \frac{1 - \exp(-\alpha[\mathrm{D}]_0 d)}{1 - \exp\{-\alpha([\mathrm{D}]_0 - x)d\}} \Big/ t \tag{25}$$

With the help of this equation the change of x and $[\mathrm{D}]$, respectively, with time t of exposure can be calculated. The first-order and zero-order rate can be taken from Eq. (25) as limits.

i. Zero-order reaction. This order can be given as an approximation in cases in which as a result of thick layers or/and high extinction coefficients the absorption of light is large, i.e., (αd) large, so that $\exp(-\alpha x d) \rightarrow 0$. With this condition it follows that $x = (10^3\ I'_0/d)k_L t = [\mathrm{D}]_0 - [\mathrm{D}]$ and

$$[\mathrm{D}] = [\mathrm{D}]_0 - \left(\frac{10^3 I'_0}{d} k_L\right) t \qquad \text{or} \qquad [\mathrm{D}] = [\mathrm{D}]_0 - k_{L,0} t \tag{26}$$

By plotting the concentration of dye present—or the optical density O.D. $= (\epsilon d)c$ which is proportional to c—against time we get a straight line with a slope given by the zero-order rate constant $k_{\mathrm{L},0} = (10^3 I'_0/d)\ k_\mathrm{L}$. In this case the rate of fading is constant and the amount of dye which is lost over a fixed time is the same.

ii. First-order reaction. The first-order law of photochemical change is often observed in dye solutions and monolayers in which every molecule is illuminated and attacked by other reactive compounds with the same probability. Because of the smallness of (αd) the exponential term $\exp(-\alpha[\mathrm{D}]_0 d)$ of Eq. (25) can be approximated corresponding to Eqs. (10)–(12) in $(1 - \alpha[\mathrm{D}]_0 d)$, so that

$$\ln \frac{[\mathrm{D}]_0}{[\mathrm{D}]_0 - x} = (10^3 I_0 \alpha k_\mathrm{L})t \qquad \text{or} \qquad \ln \frac{[\mathrm{D}]_0}{[\mathrm{D}]} = k'_{\mathrm{L,I}}t \tag{27}$$

By plotting log[D], or log(optical density), against time t we get a straight line

$$\log[\mathrm{D}] = \log[\mathrm{D}]_0 - k_{\mathrm{L,I}}t \tag{28}$$

the slope of which gives the first-order or pseudo-first-order rate constant $k_{\mathrm{L,I}} = 1000\ I'_0\ \epsilon\ k_\mathrm{L}$.

The first-order rate decreases exponentially with time and the proportion of the dye which is decomposed during a fixed period of time is independent of the concentration.

In Fig. 1 the two reaction orders often observed by exposing to light are shown in a scheme. We see that the order of any photochemical process can be determined by plotting log(O.D.) or O.D. against time of exposure.

iii. Second-order reaction. In several cases plots of 1/[D] or 1/(O.D.) against time of exposure show linearity. This proves a second order of the photoreaction with regard to the dye because the second-order law is given by

$$\frac{1}{[\mathrm{D}]} - \frac{1}{[\mathrm{D}]_0} = k_{\mathrm{L,II}}t \qquad \text{or} \qquad \frac{1}{(\mathrm{O.D.})} - \frac{1}{(\mathrm{O.D.})_0} = \frac{k_{\mathrm{L,II}}}{\epsilon d}\,t \tag{29}$$

3. *Steady-State Treatment*

For the theoretical evaluation of rate laws determined from kinetic experiments reactive intermediates of excited states are treated as if they were in a steady state. It is assumed that the reactive intermediates, like radicals, excited states, and other reactive species, are produced very quickly to an immeasurably low, but constant concentration. As a consequence of this steady-state approximation the rate of the reaction of intermediates equals the rate of their formation.[1,11,12] Hence, the steady-

[11] M. Bodenstein, *Z. Physik. Chem.* **85**, 329 (1913).

[12] O. K. Rice, *J. Phys. Chem.* **64**, 1851 (1960).

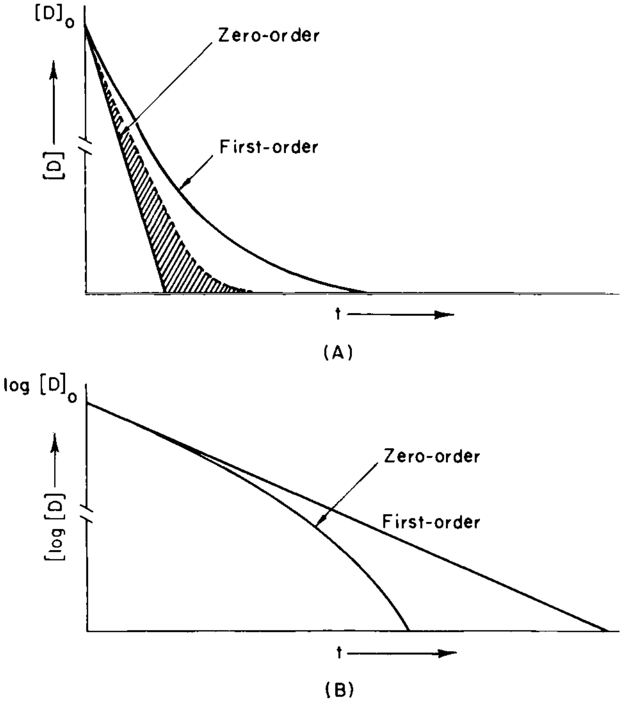

Fig. 1. Scheme of fading-rate curves: (A) [D] or O.D. against time; (B) log[D] or log(O.D.) against time.

state concentration [D*] of any reactive species is constant during a uniform excitation:

$$\frac{d[D^*]}{dt} = 0 \tag{30}$$

With this assumption the derivation of a theoretical rate law is possible with the help of a special kinetic scheme and a knowledge of the different reactions (with specific rate constants) which are active in the formation and disappearance of the reactive intermediates. It should be noted that in many cases the rate of formation of the reactive species is equal to the rate of light absorption, eventually multiplied by the quantum efficiency, corresponding to Eq. (1) and Eq. (9).

For demonstrating the importance of the last approximation we shall discuss the bimolecular deactivation of any excited state D* which is normally deactivated by a radiative or a radiationless process. With I_F as the rate of fluorescence (einsteins/sec) or as the rate of any photodecomposition of the dye ($-d[\mathrm{D}]/dt$ in mole/sec) and Q as any quenching substance we obtain

$$
\begin{array}{lll}
 & \text{Rate} & \\
\mathrm{D} + h\nu = \mathrm{D}^* & I_\mathrm{A}\ \text{(einsteins/liter sec)} & \text{(31a)} \\
\mathrm{D}^* = \mathrm{D} + h\nu & k_\mathrm{f}[\mathrm{D}^*] = I_\mathrm{F} = -d[\mathrm{D}^*]/dt & \text{(31b)} \\
\text{or}\quad \mathrm{D}^* \rightarrow \text{Products} & & \\
\mathrm{D}^* + \mathrm{Q} = \mathrm{D} + \mathrm{Q} & k_\mathrm{q}[\mathrm{D}^*][\mathrm{Q}] & \text{(31c)} \\
\mathrm{D}^* = \mathrm{D} + \text{heat} & k_\mathrm{n}[\mathrm{D}^*] & \text{(31d)}
\end{array}
$$

For formation and disappearance of D* we have

$$\frac{d[\mathrm{D}^*]}{dt} = I_\mathrm{A} - k_\mathrm{f}[\mathrm{D}^*] - k_\mathrm{q}[\mathrm{D}^*][\mathrm{Q}] - k_\mathrm{n}[\mathrm{D}^*] \tag{31e}$$

and with the steady-state assumption $d[\mathrm{D}^*]/dt = 0$

$$I_\mathrm{A} = k_\mathrm{f}[\mathrm{D}^*] + k_\mathrm{q}[\mathrm{D}^*][\mathrm{Q}] + k_\mathrm{n}[\mathrm{D}^*] \tag{31f}$$

Because the quantum efficiency is given by $\phi = I_\mathrm{F}/I_\mathrm{A}$ [Eq. (14)] we have with a quencher concentration of 0 and [Q], respectively,

$$\phi_0 = \frac{k_\mathrm{f}[\mathrm{D}^*]}{I_\mathrm{A}} = \frac{k_\mathrm{f}}{k_\mathrm{f} + k_\mathrm{n}} \quad \text{and} \quad \phi_\mathrm{Q} = \frac{k_\mathrm{f}[\mathrm{D}^*]}{I_\mathrm{A}} = \frac{k_\mathrm{f}}{k_\mathrm{f} + k_\mathrm{n} + k_\mathrm{q}[\mathrm{Q}]} \tag{31g}$$

From Eq. (31g) the *Stern-Volmer relation*[13,14] can be derived

$$\frac{\phi_0}{\phi_\mathrm{Q}} = \frac{k_\mathrm{f} + k_\mathrm{n} + k_\mathrm{q}[\mathrm{Q}]}{k_\mathrm{f} + k_\mathrm{n}} = 1 + \frac{k_\mathrm{q}}{k_\mathrm{f} + k_\mathrm{n}}[\mathrm{Q}] = 1 + K[\mathrm{Q}] \tag{32}$$

Plotting ϕ_0/ϕ_Q against concentration of quenching molecules results in a straight line, the slope of which gives the Stern-Volmer quenching constant K ($= k_\mathrm{q}\tau$).

4. *Lifetime of Excited Species*

The lifetime of an excited state or of a reactive species is one of the main factors governing the course of a photoreaction. States characterized by a relatively long lifetime have a great chance to react in a photochemical process instead of being deactivated by a return to the ground state involving emission of light or radiationless processes. Generally, the unimolecular lifetime τ of an excited state or a reactive species is defined as the time in seconds in which the concentration of the excited species decays to $1/e$ of the initial value.

In the case of a radiationless and radiative deactivation of the excited

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[13] O. Stern and M. Volmer, *Physik. Z.* **20,** 183 (1919).

[14] T. Förster, "Fluoreszenz organischer Verbindungen." Vandenhoeck & Ruprecht, Göttingen, 1951.

molecule D^* $[D^* = D + h\nu\ (k_f)$ and $D^* = D + \text{heat}\ (k_n)]$ we have with the rates $k_f[D^*]$ and $k_n[D^*]$

$$-\frac{d[D^*]}{dt} = (k_f + k_n)[D^*] \tag{33a}$$

and by integration with $[D^*]_0$ at $t = 0$ and $[D^*]_t$ at time t

$$\ln\frac{[D^*]_t}{[D^*]_0} = -(k_f + k_n)t \tag{33b}$$

With the definition of $\tau([D^*]_t \rightarrow 1/e\ [D^*]_0)$ we obtain

$$\tau = \frac{1}{k_f + k_n} \tag{34}$$

From Eq. (34) we see that the lifetime τ is given by the reciprocal sum of the first-order and pseudo-first-order rate constants of the different deactivation processes. Only in the special case of deactivation without any radiationless process does the measured emission lifetime τ equal the true radiative lifetime τ_0 which can be calculated using the approximation[1,4]

$$\frac{1}{\tau_0} \sim 10^4 \cdot \epsilon_{\max} \tag{35}$$

C. Excited Electronic States and Photochemistry

1. *Electronic Transitions*

a. Formation of the Lowest Excited State. By the absorption of a quantum of light a molecule is raised from a low energy level to a higher one by displacing an electron. Because of the connection of this quantized electronic transition with quantized rotational and vibrational motions, the absorbed energy is divided between different degrees of freedom. The size of the quanta necessary for displacing electrons from an occupied orbital into a higher orbital is larger than the size of vibrational or rotational quanta. Therefore, in general the transitions in a molecule can be described with a simple energy-level diagram (see Fig. 2) in which, without any indication of rotational levels, the vibrational levels are only outlined. Such diagrams give a good picture for describing intramolecular transitions because higher vibrational and rotational levels of an electronic state are deactivated very rapidly by *intrastate conversion* to the lowest levels.

In this connection it should be mentioned that an electron can also be raised into relatively high orbitals by the absorption of corresponding energetic light quanta. But in such excited states of high energy mol-

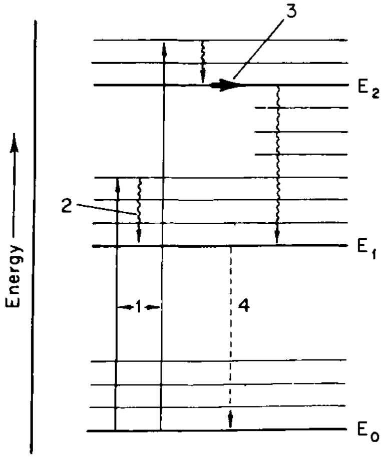

FIG. 2. Energy-level diagram with important transitions: 1, absorption; 2, intrastate conversion; 3, internal conversion (isoenergetic transition); 4, radiative transition (fluorescence).

ecules are converted by an *internal conversion* process after an extremely rapid loss of vibrational energy because of a crossing of potential energy surfaces of the different electronic states to a high vibrational level of the lower state. As a result, by absorption of light the lowest vibrational level of the first excited state is usually reached in about 10^{-12} seconds.

Since only some very rapid photochemical processes (photodissociation, etc.) can start from the short-lived upper states, the lowest vibrational level of the lowest excited state must be taken generally as the reactive state for photoreactions. This results from the relatively long lifetime of the lowest electronically excited state. The rapid deactivation of the upper states is slowed down after reaching this lowest excited state, which can be explained by help of quantum mechanical formulations of the Franck-Condon principle.[4,15,16] Above all in organic molecules with rigid cyclic structures or in long conjugated systems the radiationless conversion from $S_1 \rightarrow S_0$ (and $T_1 \rightarrow S_0$) is difficult.

b. Deactivation of the Lowest Excited State. Before discussing the possibility of starting a chemical reaction from an excited molecule one must consider the transitions by which a molecule in the first excited electronic state can lose its energy.

i. Radiationless transitions. In radiationless transitions, which can

[15] M. R. Wright, R. P. Frosch, and G. W. Robinson, *J. Chem. Phys.* 33, 934 (1960); 38, 1187 (1963).

[16] G. Herzberg, "Molecular Spectra and Molecular Structure: Spectra of Diatomic Molecules," I, 2nd ed., p. 560. Van Nostrand, Princeton, New Jersey, 1950.

occur as intra- and intermolecular processes, an electronic state is converted to another without any absorption or emission of light. As special transitions we have the *internal conversion* mentioned above, in which there is an intramolecular radiationless transition between states of like multiplicity, and the *intersystem crossing* as an intramolecular transition between singlet and triplet states. These transitions occur isoenergetically because of the necessary crossing of the potential energy surfaces of the different states. The crossing can be illustrated with the help of a potential energy diagram of a diatomic molecule (Fig. 3). This diagram approximates the multidimensional surface which exactly represents the potential energy of a polyatomic molecule as a function of its nuclear configuration.

Besides these intramolecular transitions, in photochemical reactions intermolecular radiationless energy transitions can be of great importance. By these processes, the energy of an excited state is transferred to another molecule. For example, catalytic fading may be the result of such a reaction.

ii. Formation of triplet states by intersystem crossing. In discussing the different radiationless transitions it is necessary to remark that the usually antiparallel oriented spins of electrons are not changed at excitation. The resultant spin angular momentum S remains zero, and the number of ways (multiplicity) in which this spin momentum can combine

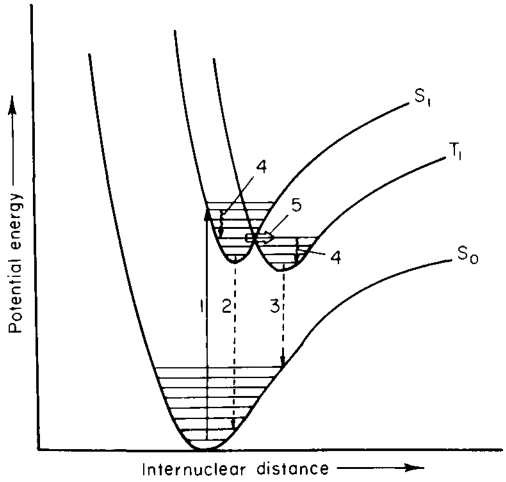

FIG. 3. Potential energy diagram of a diatomic molecule: S_0, ground state; S_1, singlet state; T_1, triplet state; 1, excitation; 2, fluorescence; 3, phosphorescence; 4, internal conversion of the vibrational states of S_1, T_1; 5, isoenergetic intersystem crossing.

with the magnetic momentum of the electron orbital motion is $2S + 1 = 1$, so that ground state and excited state are usually singlet states. By changing the direction of the spin magnetic momentum of one electron the electron pair in the ground and excited state is characterized by parallel spins. As resultant momentum or spin quantum number one obtains $S = \frac{1}{2} + \frac{1}{2} = 1$, and because of the combination multiplicity of $2S + 1 = 3$ such levels are called triplet states. Transitions between singlet and triplet states are spin-forbidden. Therefore triplet states are populated only with low probability by direct singlet–triplet excitation, which results in a low extinction coefficient of singlet–triplet absorption bands. As a consequence triplet states are also emptied very slowly and therefore characterized by a long radiative lifetime τ_0 [Eq. (35)].

For photochemical reactions it is very important that triplet states with a long radiative lifetime can be produced easily by intersystem crossing, i.e., by an indirect excitation process from the corresponding singlet state. We shall see that the order of the rate constant for intersystem crossing from the lowest excited singlet state to the triplet state is of great influence on the photochemical reactivity of an excited molecule.

iii. Radiative transitions. In radiative transitions a molecule emits light by returning to the ground state. *Fluorescence* is observed by deactivation of an excited singlet state ($S_1 \rightarrow S_0$) and phosphorescence by a radiative triplet–singlet ($T_1 \rightarrow S_0$) transition. Because of the difference in radiative lifetimes between singlet and triplet states, which vary from 10^{-9} to 10^{-6} seconds for the singlet state and from 10^{-3} to 10 seconds for the triplet state, *prompt fluorescence* has a very short lifetime compared to the long-lived phosphorescence emission. Since triplet levels have a lower energy than the corresponding singlet levels, phosphorescence spectra ($T_1 \rightarrow S_0$) are situated at the long-wavelength side of the fluorescence. This fact can be used for the determination of energy values for triplet states. It should be noticed that fluorescence emission corresponding to the $S_1 \rightarrow S_0$ transition can also be observed with a lifetime longer than the radiative lifetime of the singlet state. Such *delayed fluorescence* is the result of an intermediate formation of a triplet state followed by an intra- or intermolecular energy transfer which again brings about an excited lowest singlet state. In addition to this E-(or eosin-)type[17] and P-type[18,19] delayed fluorescence a *recombination de-*

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[17] C. A. Parker and C. G. Hatchard, *Trans. Faraday Soc.* **59,** 284 (1963).

[18] C. A. Parker and C. G. Hatchard, *Proc. Chem. Soc.* p. 147 (1962); *Proc. Roy. Soc.* **A269,** 574 (1962).

[19] C. A. Parker, *Chem. Brit.* **2,** 160 (1966).

layed fluorescence and phosphorescence[20–22] can be emitted in solids by excited molecules which are formed by a recombination of photochemically originated fragments.

It should be mentioned that these radiative processes are of great importance for understanding mechanisms of photochemical reactions. For example, many years ago the observation of phosphorescence pointed to the existence of a long-lived intermediate state in excited molecules.[23,24] In a variety of experiments (triplet–triplet energy transfer in EPA glass at —180°, photomagnetism of fluorescein, electron spin resonance, etc.) by Lewis, Kasha, Evans, Terenin, and others[25–35] not only the "triplet nature" of this state could be proved, it could also be shown that triplet states are formed in fluid solutions in an unexpectedly high yield by intersystem crossing.[36–42] For example, for chlorophyll a and b triplet yields are 0.64 and 0.88, respectively, in ether solutions.[41] Experiments on delayed fluorescence, moreover, gave indications of a triplet–triplet annihilation and of an efficient triplet–triplet transfer process. The last-mentioned process has become a valuable tool for populating triplet

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[20] P. Debye and J. O. Edwards, *J. Chem. Phys.* **20,** 236 (1952).

[21] H. Linschitz, M. G. Berry, and D. Schweitzer, *J. Am. Chem. Soc.* **76,** 5833 (1954).

[22] W. M. McClain and A. C. Albrecht, *J. Chem. Phys.* **43,** 465 (1965).

[23] E. Weidemann and G. Schmidt, *Ann. Physik* [3] **56,** 201 (1895).

[24] A. Jablonski, *Z. Physik* **94,** 38 (1935) ; *Nature* **131,** 839 (1933).

[25] G. N. Lewis, D. Lipkin, and T. T. Magel, *J. Am. Chem. Soc.* **63,** 3005 (1941).

[26] A. Terenin, *Acta Physicochim. USSR* **18,** 210 (1943).

[27] G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.* **66,** 2100 (1944) ; **67,** 994 (1945).

[28] G. N. Lewis and M. Calvin, *J. Am. Chem. Soc.* **67,** 1232 (1945).

[29] G. N. Lewis, M. Calvin, and M. Kasha, *J. Chem. Phys.* **17,** 804 (1949).

[30] D. F. Evans, *Nature* **176,** 777 (1955).

[31] C. A. Hutchison and B. W. Mangum, *J. Chem. Phys.* **29,** 952 (1958) ; **34,** 908 (1961).

[32] L. H. Piette, J. H. Sharp, T. Kuwana, and J. N. Pitts, *J. Chem. Phys.* **36,** 3094 (1962).

[33] C. A. Hutchison, *J. Phys. Chem.* **7,** 203 (1967).

[34] R. G. Shulman and R. O. Rahn, *J. Chem. Phys.* **45,** 2940 (1966).

[35] T. Shiga and L. H. Piette, *Photochem. Photobiol.* **3,** 223 (1964).

[36] S. Boudin, *J. Chim. Phys.* **27,** 285 (1930).

[37] H. Kautsky, *Chem. Ber.* **68,** 152 (1935).

[38] H. L. Bäckström and K. Sandros, *Acta Chem. Scand.* **12,** 823 (1958).

[39] G. S. Hammond, *in* "Reactivity of the Photoexcited Organic Molecule," pp. 119–144. Wiley (Interscience), New York, 1967.

[40] R. Livingston, *Quart. Rev. (London)* **14,** 174 (1960).

[41] P. G. Bowers and G. Porter, *Proc. Roy. Soc.* **A296,** 435 (1967).

[42] S. K. Lower and M. A. El-Sayed, *Chem. Rev.* **66,** 199 (1966).

states and starting protochemical reactions[39-41,43-45] in molecules with low triplet yields. Fading of dyes may be the result of such a process in a series of systems.

iv. Correlation between photochemical reactivity and lifetime of an excited state. With these results it becomes evident that organic molecules can be excited into a long-lived state which has enough time for starting any photochemical reactions. The importance of a long lifetime of an electronically excited state results from the fact as mentioned above that the time scale for photochemical reactions is fixed by the rate of prompt radiative transition or radiationless transition from the excited state to the ground state. No photochemical process can start from a molecule excited in the singlet or triplet state if the time necessary for the primary photochemical reaction is longer than the lifetime of these excited states.

For example, the high lightfastness of nonfluorescent dyes in relation to fluorescent dyes may often be explained by an extremely rapid radiationless transition $S_1 \rightarrow S_0$ which is of much shorter duration than the spontaneous fluorescence time, which usually is of the order of 10^{-8} seconds. Therefore, the relatively slow fading process can no longer compete with the deactivation. But it is also possible that fluorescence is very weak because of a high rate of intersystem crossing to a reactive triplet state.

2. *Electronically Excited States*

For starting a photochemical reaction the formation of an electronically excited state in a molecule is decisive. It must be emphasized that such an *excited molecule* can be regarded as a *new species* which is characterized by other properties than the same molecule in the ground state. Besides its characteristic lifetime the excited molecule has a definite energy and a changed electron distribution which is responsible for a specific chemical reactivity compared to the ground state.[46]

a. Photochemically Important Molecular Orbitals. In photochemistry one-electron transitions between different orbitals are considered. In this connection, it should be remembered that atomic and molecular orbitals are illustrated as the space in which electrons can be found with a high

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[43] R. O. Kan, "Organic Photochemistry." McGraw-Hill, New York, 1966.

[44] R. Steinmetz, *Fortschr. Chem. Forsch.* 7, 445 (1967).

[45] P. C. Neckers, "Mechanistic Organic Photochemistry." Reinhold, New York, 1967.

[46] G. Porter, *in* "Reactivity of the Photoexcited Organic Molecule," pp. 79–110. Wiley (Interscience), New York, 1967.

probability. For example, bonding orbitals are characterized by a high electron density between the adjacent atoms.

In molecules especially, there are orbitals of a bonding, antibonding, and nonbonding character which are characterized by a lower, higher, or equal energy compared to the energy of the combined atomic orbitals. Corresponding to the spatial distribution the following types of orbitals must be taken into account when discussing photochemical reactions.

The σ *(bonding) orbitals*, in which the atomic orbitals overlap along the bond axis.

The σ^* *(antibonding) orbitals* which have a nodal plane at right angles to the bond direction. Because of a repulsive interaction between the atoms these orbitals are antibonding.

The π *(bonding) orbitals* which are formed in multiple bonds as a result of a combination of p (or d) orbitals. These orbitals are antisymmetric relative to the nodal in the plane of the molecule. In the case of conjugated double bands the electron charge is delocalized over the conjugated atoms.

The π^* *(antibonding) orbitals* have an additional nodal plane at right angles to the bond direction. The repulsive force is only weak.

The n *(nonbonding) orbitals* which are filled with a lone pair of electrons at heteratoms (O, N) and which have the same shape and energy as the atomic orbitals. For example, the n orbital of a carbonyl group is the $2p_y$ orbital of oxygen, and in pyridine the n orbital is located at the sp^2 hybrid of nitrogen.

In conjugated systems in which the lone-pair electrons on the heteroatom can conjugate with the π-electrons of the ring, we do not have a nonbonding n orbital at the heteroatom. Such orbitals, e.g., characteristic for pyrrole, furan, or aniline, can be described as l (lone-pair) orbitals.

b. Photochemically Important Excited States

i. Classification of electronic states. In photochemistry the excited states are classified by the orbitals which are concerned in the one-electron transitions.[1,47] For example, the transition of an electron in an occupied π-orbital into a π^*-orbital is defined as a π–π^* transition, which will be written for absorption as $\pi^* \leftarrow \pi$ and for emission as $\pi^* \rightarrow \pi$. The resulting electronically excited state with one electron (and a hole) in the π-orbital and one electron in the antibonding π^*-orbital is called a π, π^* state.

Because of the large energy necessary for σ–σ^* and n–σ^* transitions

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[47] M. Kasha, *Discussions Faraday Soc.* **9**, 14 (1950).

($\lambda \leqslant 200$ nm) σ, σ^* and n, σ^* states need not be considered in photochemical reactions of dyestuffs. In general, the following states and transitions are possible:

π, π^* states: These states are the results of π–π^* transitions in olefinic, aromatic, and other π-electron systems. In extended π-electron systems the difference between the energy of the ground state and the energy of the π, π^* state is relatively small so that π–π^* transitions can occur in the near ultraviolet and the visible region. The π–π^* transitions are characterized by an intense absorption with $\epsilon_{\max} > 10^3$ and a transition moment parallel to the molecular plane. Corresponding to Eq. (35) π, π^* states have a radiative lifetime of 10^{-9} to 10^{-7} seconds. As the electron charge distribution is more extended and more polarizable in the π, π^* state than in the ground state, polar solvents decrease the energy of the excited state more than that of the ground state. Therefore, the π–π^* absorption bands are shifted to longer wavelengths by changing from a nonpolar to a polar solvent. By the substitution of a π-electron system with strongly electron-releasing groups a shifting of the π–π^* transition to longer wavelengths corresponding to a decrease of the energy of the π, π state can be observed. This shifting is the reason for differences in the photochemical behavior of different substituted dyestuffs, e.g., of the anthraquinoid type.

n, π^* states: These states are the results of n–π^* transitions in which nonbonding (n) electrons, principally from nitrogen, oxygen, or sulfur, are raised into an antibonding π^*-orbital, e.g., observed in C=O, =N—, or NO_2 groups. Because of the relatively large energy of the n electrons n–π^* transitions are often localized at the long-wavelength side of the π–π^* transition bands. The probability of the n–π^* transition which is characterized by a transition moment perpendicular to the molecular plane is low, with $\epsilon_{\max} < 10^3$ and a long radiative lifetime of $\tau > 10^{-6}$ seconds. In acid media and in polar solvents the n–π^* transition bands are shifted to shorter wavelengths as a consequence of a hydrogen bond at the n electron site and the solvent in the ground state.

CT states: These states, which result from an intramolecular charge transfer, can be observed in π-electron systems R with both electron-donor substituents D (NH_2, OH, etc.) and electron-acceptor substituents A (C=O, NO_2, etc.). The CT transition can be represented according to Porter[46,48] as D^+R^-A, DR^+A^-, D^+RA^-, and DR^*A. They are characterized by an intense absorption band ($\epsilon_{\max} > 10^4$) situated at a greater wavelength compared with that of molecules with D or A substituents alone. The red shift observed on changing the solvent polarity (e.g.,

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[48] G. Porter and P. Suppan, *Trans. Faraday Soc.* **61**, 1664 (1965).

hydrocarbon to alcohol) is larger than the corresponding shift of π–π^* transitions because of a very strong reduction of the energy of the CT state which is characterized by high permanent dipole moments. It must be taken into account that the appearance of an absorption band at long wavelengths by substitution in the molecule can be a hint at the formation of a low-lying CT state with different reactivity than n, π^* or π, π^* states.

ii. Survey of the electronically excited states in dyes. The electronically excited states classified in the last section must be divided according to the resultant spin momentum of the orbitally unpaired electrons in singlet and triplet states. Because of the different reactivity of singlets and triplets one has to discuss six types of excited states in photochemical reactions of dyestuffs. The significance of these states is given by the fact that each state is characterized by a definite energy, lifetime, and electron density distribution. In many cases the excess electronic energy of an excited state can be the only reason for a special course of a photochemical reaction. But there may also be a considerable changing of bonds between atoms which results in a different behavior of ground and excited states. For example, in carbonyl groups the shift of one n electron from oxygen into the π^*-state results in an increased electrophilic character of the carbonyl oxygen relative to the unexcited C=O group. Moreover, triplets are often particularly qualified for photochemical reactions because of their long lifetime.

As discussed in Section I,C,1,b transitions between the different states are possible by internal conversion and intersystem crossing. The probability of such transitions can be high in the case of a small difference between the energies of the electronic states. Therefore, the mutual position of the different states has a great influence on the reactivity of an excited molecule. As mentioned above, also intercombinational transitions between singlet and triplet states may be very rapid. For such processes a spin–orbital coupling for mixing singlet and triplet states is necessary, so that the rate constant for intersystem crossing can be approximated by the expression

$$k_{\mathrm{ST}} \propto \frac{\zeta}{|E_{\mathrm{S}_1} - E_{\mathrm{T}_1}|} \tag{36}$$

Spin–orbital coupling may be enhanced by internal and external perturbations,[49] e.g., by a paramagnetic species[50,51] (e.g., O_2, NO) or a heavy

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[49] M. A. El-Sayed, *Accounts Chem. Res.* **1**, 8 (1968).

[50] C. Dijkgraaf and G. J. Hoijtink, *Tetrahedron* **19**, 179 (1963).

[51] D. F. Evans, *J. Chem. Soc.* p. 2753 (1959).

atom (characterized by a term ζ) fixed in the molecule itself or in a neighbor molecule.[15,52-57] Furthermore, small energy differences between the lowest excited singlet state (E_{S_1}) and the corresponding triplet state (E_{T_1}) enhance spin-orbital coupling and the probability of intersystem crossing (given by k_{ST}).

Because the magnitude of the singlet–triplet split depends on the spatial overlapping between the orbitals ψ_1, ψ_2 which are involved in the transition[58-60] π, π^* states have a larger singlet–triplet energy difference than the small overlapping n, π^* states. According to Eq. (37)

$$\Delta E(S_1 \rightarrow T_1) = \int \psi_2\psi_1 \frac{[e^2]}{|r_{12}|}\, d\tau \tag{37}$$

the singlet–triplet split for related orbital excitations (e.g., π–π^*) decreases with an increase of $|r_{12}|$, i.e., with an increase of the space available to the electrons and an increase in the size of the molecules, respectively. In conformity with Eq. (37) we see that the energy differences $\Delta E(S_1 \rightarrow T_1)$ between the lowest excited (π, π^*) singlet and triplet states in naphthalene[61] are in the order of 30 kcal/mole (13,300 cm^{-1}) compared with 5 kcal/mole ($\sim$2000 cm^{-1}) for the corresponding (n, π^*) states of benzophenone.[62]

The $\Delta E(S_1 \rightarrow T_1)$ split of the lowest energy n_N–π^* transition of azaromatics (e.g., pyridine) is about twice that of the n_O–π^* transitions of molecules with carbonyl groups.[59] Moreover, in polymethines the singlet–triplet splitting of the lowest energy π–π^* transitions is of the order of 10,000 cm^{-1}, decreasing with increasing number of methine groups, and in large cyanine dyes (e.g., pinacyanol) the singlet–triplet splitting of the lowest π–π^* transition diminishes to a value of the order of 4 kcal/mole ($\sim$2150 cm^{-1}).

In connection with nonradiative transitions symmetry rules must also

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[52] M. Kasha, *J. Chem. Phys.* **20,** 71 (1952).

[53] S. P. McGlynn, J. Diagre, and F. J. Smith, *J. Chem. Phys.* **39,** 675 (1963).

[54] S. Siegel and H. S. Judeikis, *J. Chem. Phys.* **42,** 3060 (1965).

[55] T. Medinger and F. Wilkinson, *Trans. Faraday Soc.* **61,** 620 (1965).

[56] M. Zander, *Z. Anal. Chem.* **226,** 251 (1967).

[57] R. F. Borkman and D. R. Kearns, *J. Chem. Phys.* **46,** 2333 (1967).

[58] M. A. El-Sayed and G. W. Robinson, *J. Chem. Phys.* **34,** 1840 (1961); **35,** 1896 (1961).

[59] S. P. McGlynn and F. J. Smith, *in* "Modern Quantum Chemistry" (O. Sinanoğlu, ed.), Part III, pp. 67–80. Academic Press, New York, 1965.

[60] H. A. Staab, "Einführung in die theoretische organische Chemie," 3rd ed. Verlag Chemie, Weinheim, 1962.

[61] H. B. Klevens and J. R. Platt, *J. Chem. Phys.* **17,** 470 (1949).

[62] D. S. McClure and P. L. Hanst, *J. Chem. Phys.* **23,** 1772 (1955).

be taken into account: $S_1 \rightarrow T_1$ nonradiative transitions are more rapid than the corresponding nonradiative transitions to the ground state. Moreover, transitions between the singlet and triplet states of the same electronic configuration have a lower probability than analogous transitions between different configurations,[63] e.g.,

$$^1(\pi,\pi^*) \rightarrow {}^3(\text{n},\pi^*) \text{ or } {}^1(\text{n},\pi^*) \rightarrow {}^3(\pi,\pi^*) > {}^1(\pi,\pi^*) \rightarrow {}^3(\pi,\pi^*)$$

But in discussing the last-mentioned correlation it must be noted that, for example, in a carbonyl compound, intercombinational transitions are very quick because the n orbital is located at the "heavy" oxygen atom.

In conclusion, the following states are important for the photochemical behavior of an organic dye:

$^1(\pi,\pi^*)$ and $^3(\pi,\pi^*)$ states: While the radiative lifetime of $^1(\pi,\pi^*)$ is in the order of 10^{-9}–10^{-7} seconds with a quantum efficiency of fluorescence $\phi_f \sim 0.5$–0.05 the corresponding lifetime of $^3(\pi,\pi^*)$ is about 0.1–10 seconds with $\phi_p \sim 0.5$–0.05. The singlet–triplet splitting, usually high in organic molecules, can reach small values in dye molecules because of the great delocalization of the orbitals. Therefore, corresponding to Eq. (36), in dye molecules high rate constants for intersystem crossing to a triplet state are possible. Moreover, additional n,π^* states, as, e.g., in anthraquinoid systems, may increase the intercombinational transitions so that quantum yields of triplet formation of the order of one can be observed.

$^1(n,\pi^*)$ and $^3(n,\pi^*)$ states: The mean radiative lifetime of an $^1(\text{n},\pi^*)$ state is relatively long ($\tau_f > 10^{-6}$ seconds) because of the weak absorption to that state. Furthermore, as a result of a small spatial overlapping between the n orbital and the π^*-orbital there exists only a small energy difference between $^1(\text{n},\pi^*)$ and $^3(\text{n},\pi^*)$ states which usually give a high rate of intersystem crossing. Therefore, the quantum efficiency of fluorescence is very small ($\phi_f < 0.01$). The quantum efficiency of phosphorescence which is emitted from the $^3(\text{n},\pi^*)$ state characterized by a long radiative lifetime of $\tau_p \sim 10^{-3}$ seconds is of the order of $\phi_p \sim 0.5$–0.05. The $^3(\text{n},\pi^*)$ state is a very reactive one, not only because of its long lifetime, but also—analogous to the $^1(\text{n},\pi^*)$ state—by its highly localized unpaired electrons which may react similarly to free radicals. Therefore, in dyes with the $^3(\text{n},\pi^*)$ state as the lowest state a different course of a photochemical reaction may occur than in similar dyes with the $^3(\pi,\pi^*)$ state as the lowest. As the mutual position of n,π^* and π,π^* states can be influenced by the environment or substituents the photochemical behavior may be changed dramatically by small variations of solvents or structure. In this context it must also be taken into

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[63] M. A. El-Sayed, *J. Chem. Phys.* **38,** 2834 (1963).

account that by insertion of an n,π^* state between $^1(\pi,\pi^*)$ and $^3(\pi,\pi^*)$ the singlet–triplet transition probability from $^1(\pi,\pi^*)$ and $^3(\pi,\pi^*)$ may be increased.

^{1}*(CT) and* ^{3}*(CT) states:* Charge-transfer states must be considered in the presence of strong electron-donating groups and electron-accepting groups attached to a π-electron system. The intense absorption band of such systems is situated at longer wavelengths than in corresponding systems with only a donating or an accepting group. The energy difference between the ^{1}(CT) and ^{3}(CT) states is similar to that of n,π^* states. Contrary to hypsochromic-shifted n,π^* states, CT transitions are shifted to long wavelengths by changing from nonpolar to polar solvents. By this effect the course of a photochemical reaction may be influenced by changing the solvent since the reactivity of CT states can strongly differ from that of n,π^* states. For example, the hydrogen-transfer reaction of carbonyl compounds resulting from the reactivity of electrophilic n,π^* states may be suppressed if the lowest triplet becomes a CT state which is characterized by an opposite electron distribution of the carbonyl group.[48]

c. *Energy-Level Diagrams.* For discussing photoreactivity of a compound it is necessary to have detailed information on the energies, lifetimes, and generation of the different states. As seen above, important data can be obtained from absorption spectra (e.g., lifetime τ_0 from $\epsilon_{\max}$ [Eq. (35)], energy of a singlet state from the 0–0 band in the absorption spectrum or information of reactive n,π^*, π,π^*, or CT states by solvent shifting effects), from fluorescence and from phosphorescence spectra (e.g., energies of triplet states), from spectra of polarized luminescence,[64–67] or by measurement of the quantum yield of fluorescence (e.g., quantum efficiency of triplet population by the approximation $\phi_T \sim 1 - \phi_f$ in several compounds[68]). As a valuable tool for the direct observation of triplet states in solution, flash spectroscopy (or flash photolysis) is of great importance. In this method (see Fig. 4), first used by Norrish and Porter,[69–71] a large number of molecules is excited with an intense flash to upper singlet states, and as a consequence of intersystem crossing also

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[64] F. Dörr, *Angew. Chem.* **78,** 457 (1966).

[65] F. Dörr, *in* "Optische Anregung organischer Systeme. 2nd Internationales Farbensymposium" (W. Foerst, ed.), pp. 566–585. Verlag Chemie, Weinheim, 1966.

[66] W. Körber and V. Zanker, *Z. Angew. Phys.* **17,** 398 (1964).

[67] C. Dijkgraaf, *Spectrochim. Acta* **A23,** 365 (1967).

[68] A. R. Horrocks and F. Wilkinson, *Proc. Roy. Soc.* **A306,** 257 (1968).

[69] R. G. W. Norrish and G. Porter, *Nature* **164,** 658 (1949).

[70] G. Porter, *Proc. Roy Soc.* **A200,** 284 (1950).

[71] G. Porter and A. D. Osborne, *in* "Optische Anregung organischer Systeme. 2nd Internationales Farbensymposium" (W. Foerst, ed.), pp. 553–565. Verlag Chemie, Weinheim, 1966.

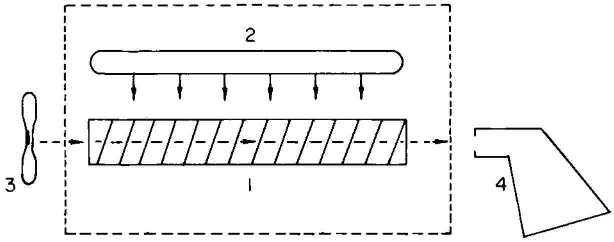

FIG. 4. Scheme of the flash photolysis apparatus: 1, reaction vessel; 2, photolysis flash lamp; 3, spectroscopic flash or continuous light source; 4, spectrograph.

to the lowest triplet state. Since triplet–triplet transitions are characterized by high intensity, triplet spectra can be measured in the absence of disturbing photolysis products by help of a spectroscopic flash of low intensity which is triggered about 10^{-5} seconds after photolytic flash. By registration of the decreasing optical density O.D. of the triplet–triplet absorption with time, the kinetics of the triplet decay (e.g., triplet lifetime[72]) and the influence of quenching species [Q] can be measured. In first-order kinetics log(O.D.)–time plots yield absolute rate constants [see Eq. (28)], and in second-order decay the 1/O.D.–time plots give relative rate constants k/ϵ [see Eq. (29)]. In fluid solutions triplet states are usually radiationless, and are deactivated (i.e., without phosphorescence emission) by a pseudo-first-order quenching[46,73] and by a bimolecular diffusion-controlled impurity quenching process which is given by

$$-\frac{d[\mathrm{T}_1]}{dt} = k_1[\mathrm{T}_1] + k_\mathrm{q}[\mathrm{T}_1][\mathrm{Q}] \tag{38}$$

The rate constant for a diffusion-controlled encounter reaction $k_\mathrm{q} = 8RT/3000\eta$ liters mole^{-1} sec^{-1}, where R is the molar gas constant; T, the absolute temperature, and η, viscosity in poises, is over large ranges of viscosity of the order of 10^9–10^{10} liters mole^{-1} sec^{-1}. Therefore, by inserting k_q in the second-order rate constant (k/ϵ) measured by the flash method the molar extinction coefficient of triplet–triplet transitions may be determined. Moreover, with a simultaneous measurement of the depletion of S_0 an estimation of the concentration of triplets is possible.[71,74–76] In combination with a Q-switched laser the triplet lifetime

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[72] G. Porter and M. W. Windsor, *Proc. Roy. Soc.* **A245**, 238 (1958).

[73] G. Jackson, R. Livingston, and A. C. Pugh, *Trans. Faraday Soc.* **56**, 1635 (1960).

[74] D. P. Craig and I. G. Ross, *J. Chem. Soc.* p. 1589 (1954).

[75] G. Porter and M. W. Windsor, *Discussions Faraday Soc.* **17**, 178 (1954).

[76] R. Livingston and W. R. Ware, *J. Chem. Phys.* **39**, 2539 (1963).

of metal-free phthalocyanine has been found to be of the order of 10^{-6} seconds at room temperature.[77]

It would be beyond the scope of this chapter to give a more detailed survey of all measurements from which data for the construction of a state diagram can be taken; see, e.g., Turro and others.[2,4,76,78-83] Some special problems will be discussed in the next sections. In Fig. 5 only a scheme of such a diagram is given.

In state diagrams the energy of the lowest vibrational level of an electronically excited state is represented by horizontal lines relative to the energy of the lowest vibrational level of the ground state. The energy of the ground state is arbitrarily given as zero. Singlet and triplet states are shown separately with eventually known data of the rate constants (or lifetime [Eq. (34)]) for radiative and radiationless transitions, and with data on the relative population of the different states. With the help of such data it is possible to predict from which state a photochemical reaction may eventually start, or an explanation can be given of why under certain circumstances any photoreaction is favored. For photochemical work a compilation of such data for all interesting substances

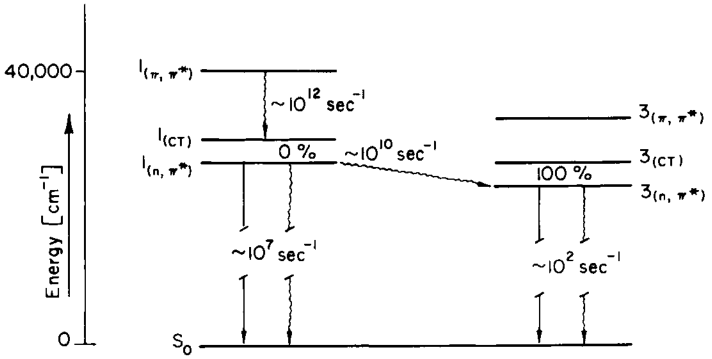

FIG. 5. Energy-state diagram; e.g., for *p*-aminobenzophenone in cyclohexane.

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[77] W. F. Kosonocky, S. E. Harrison, and R. Standner, *J. Chem. Phys.* **43**, 831 (1965).

[78] M. Kasha, *Radiation Res.* Suppl. 2, 243 (1960).

[79] M. Kasha, *in* "Comparative Effects of Radiation" (M. Burton, J. S. Kirby-Smith, and J. L. Magee, eds.), p. 72. Wiley, New York, 1960.

[80] B. Holmström, *Arkiv Kemi* **22**, 329 (1964).

[81] R. P. Bauman, "Absorption Spectroscopy." Wiley, New York, 1962.

[82] H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy." Wiley, New York, 1962.

[83] T. Förster, *in* "Optische Anregung organischer Systeme. 2nd Internationales Farbensymposium" (W. Foerst, ed.), pp. 509–552. Verlag Chemie, Weinheim, 1966.

is of the greatest importance. Therefore, the aim of many photochemical studies on dyes in solution consists in finding valuable information on energies, lifetimes, and populations of the electronically excited states with the help of the different methods mentioned above.

II. Photochemical Reactions of Dyes in Solution

A. PHOTOFADING MODEL SYSTEMS

The search for methods for preventing the damaging action of light on dyes and dyed substrates calls for a thorough understanding of the photochemical behavior of dyestuffs themselves. Since the first exact investigations on the phototendering of dyed materials, 150 years ago by Bancroft,[84] many valuable results on the conditions of fading, the influence of the nature of the substrate, the dependence on the dye structure, etc., have been obtained.[6,85-90] But it should not be overlooked that the complexity of the systems and the different variables affecting the fading process have brought about many difficulties for the elucidation of a detailed mechanism of the photochemical reactions of dyes. Only by a simplification of the conditions can an exact study of the different photoreactions be successful. Therefore, a great deal of our knowledge on the photochemical behavior of dyes and dyed materials is the result of studying the photoreactions of simple model systems.

In such systems simple dyes are chosen as models for complex dyestuffs, e.g., benzophenone and simple anthraquinones for the vat dyes.[91-95] Furthermore, these dyes are dissolved in model organic solvents, which are characterized by chemical properties similar to those of the fiber. With such model substrates the difficulties in studying solid-state reactions can be reduced. There is no doubt that in some cases dyes in model

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[84] E. Bancroft, "Experimental Researches Concerning the Philosophy of Permanent Colours." Cadell & Davies, London, 1813.

[85] K. Venkataraman, "The Chemistry of Synthetic Dyes," Vol. II, Chapter 40. Academic Press, New York, 1952.

[86] K. McLaren, *J. Soc. Dyers Colourists* **72**, 527 (1956).

[87] K. McLaren, *J. Soc. Cosmetic Chemists* **18**, 245 (1967).

[88] A. Landolt, *J. Soc. Dyers Colourists* **65**, 659 (1949).

[89] C. H. Giles and R. B. McKay, *Textile Res. J.* 33, 527 (1963).

[90] M. Pestemer, *in* "Optische Anregung organischer Systeme. 2nd Internationales Farbensymposium" (W. Foerst, ed.), pp. 475–508. Verlag Chemie, Weinheim, 1966.

[91] N. K. Bridge and W. M. McClean, *J. Soc. Dyers Colourists* **75**, 147 (1959).

[92] N. K. Bridge, *Trans. Faraday Soc.* **56**, 1001 (1960).

[93] J. L. Bolland and H. R. Cooper, *Nature* **172**, 413 (1953); *Proc. Roy. Soc.* **A225**, 405 (1954).

[94] H. S. A. Gilmour, *Phys. Chem. Org. Solid State* **1**, 358 (1963).

[95] F. Dörr, *Chimia* (*Aarau*) **15**, 63 (1961).

organic solvents and on a practically used substrate behave differently. For example, measurements have shown no exact resemblance between the photochemical behavior of aminoanthraquinone compounds in solution in ethyl acetate or dyed on cellulose acetate films,[96-98] and the question has been raised if cellulose could really be replaced by ethanol as a model substance in photochemical systems containing vat dyes.[99] Nevertheless, it must be emphasized that by the study of the photochemistry of dyes in solution our knowledge of the photochemical behavior of dyes has greatly increased. By these studies valuable data on the mechanism of fading of dyed textiles and on correlations between the structure of dyes and their activity for phototendering has been obtained.

Above all, Oster and co-workers[100-103] during their studies on the photobleaching of dyes in solution got convincing hints that the chemically reactive state in many photochemical reactions of dyes is a long-lived triplet state. Nowadays, there is no doubt of the reality of this conclusion, because the epoch-making flash photolysis technique of Norrish and Porter has given direct evidence of the production of triplet states of dyes in solution by observation of triplet–triplet absorptions. As a result of their flash photolytic studies of organic molecules in ordinary fluid solutions Porter and Windsor[75,104,105] (1954) postulated the triplet state formation as "a phenomenon of very general occurrence in a wide variety of compounds." Since then it has been possible to prove, in a series of studies, that in many photochemical reactions of organic compounds and dyestuffs in solution the formation of the triplet state with a lifetime of about a tenth of a millisecond is decisive. For example, in aromatic hydrocarbons,[72] chlorophyll,[106,107] fluorescein,[108-110] eosine,[111]

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[96] G. S. Egerton, J. M. Gleadle, and A. G. Roach, *J. Soc. Dyers Colourists* **82,** 369 (1966).

[97] G. S. Egerton, N. E. N. Assaad, and N. D. Uffindell, *J. Soc. Dyers Colourists* **83,** 45 (1967).

[98] G. S. Egerton and N. E. N. Assaad, *J. Soc. Dyers Colourists* **83,** 85 (1967).

[99] G. S. Egerton, N. E. N. Assaad, and N. D. Uffindell, *J. Soc. Dyers Colourists* **84,** 220 (1968).

[100] G. Oster and A. H. Adelman, *J. Am. Chem. Soc.* **78,** 913 (1956).

[101] G. Oster and N. Wotherspoon, *J. Am. Chem. Soc.* **79,** 4836 (1957).

[102] G. K. Oster, G. Oster, and G. Prati, *J. Am. Chem. Soc.* **79,** 595 (1957).

[103] G. Oster, *Sci. Am.* **219,** 158 (1968).

[104] G. Porter and M. W. Windsor, *Nature* **180,** 187 (1957).

[105] G. Porter, *Chimia (Aarau)* **15,** 63 (1961).

[106] R. Livingston, *J. Am. Chem. Soc.* **77,** 2179 (1955).

[107] S. Claesson, L. Lindqvist, and B. Holmström, *Nature* **183,** 661 (1959).

[108] L. Lindqvist, *Arkiv Kemi* **16,** 79 (1960).

[109] L. Lindqvist, *J. Phys. Chem.* **67,** 1701 (1963).

[110] V. Kasche and L. Lindqvist, *J. Phys. Chem.* **68,** 817 (1964).

[111] A. Kira and S. Kato, *Sci. Rept. Tohoku Univ. First ser.* **48,** 142 (1965).

lumiflavine,[112] and retinene[113] triplets could be detected in solutions with photoflash studies. In a large variety of experiments it has been shown that photochemical reactions, e.g., the photoreduction of riboflavin or the photoreactions in solutions of ketones and quinones, proceed via triplet states.[80,114–120]

There seems to be no doubt that the results on the photochemical behavior of dyes in solutions can be transferred in principle to more complex systems. In many cases the reactions taking place on light absorption by the dye should be similar both in model systems and in dyed fibers. Therefore, the results of model systems can give valuable hints at methods for retarding photofading and phototendering. As a simple example for the retardation of photofading by certain compounds the decrease of anaerobic photobleaching of riboflavin in aqueous solutions by KI, which is the consequence of the effective quenching of the triplet intermediate, should be mentioned.[119] In other cases photofading could be retarded by the formation of a charge-transfer complex between dye and an added compound.[120] Or, by a knowledge of the type of the reactive state, the phototendering action of a dye could be stopped by substituents which change the relative positions of, e.g., $^3(\pi, \pi^*)$ and $^3(n, \pi^*)$ states.[121] That is, in cases of known mechanisms of photobleaching or phototendering there exists the possibility that systematic studies can lead to methods for changing the course of a photoreaction and for preventing or diminishing photofading. And it is important that an understanding of the mechanisms of photochemical reactions results principally from studies of the photochemistry of dyes in solution.

It should be noted that there had been relatively little work on the subject—see, e.g., Venkataraman and Rabinovitch[85,122]—until Oster and his co-workers[123–126] started extensive research on the photochemistry

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[112] L. Tegnér and B. Holmström, *Photochem. Photobiol.* **4**, 505 (1965).

[113] K. H. Grellmann, R. Memming, and R. Livingston, *J. Am. Chem. Soc.* **84**, 546 (1962).

[114] G. Oster, J. Bellin, and B. Holmström, *Experientia* **18**, 249 (1962).

[115] F. Millich and G. Oster, *J. Am. Chem. Soc.* **81**, 1357 (1959).

[116] K. Kikuchi and M. Koizumi, *Bull. Chem. Soc. Japan* **40**, 736 (1967).

[117] B. Holmström, *Arkiv Kemi* **22**, 281 (1964).

[118] M. Green and G. Tollin, *Photochem. Photobiol.* **7**, 129 (1968).

[119] B. Holmström and G. Oster, *J. Am. Chem. Soc.* **83**, 1867 (1961).

[120] W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.* **83**, 2789 (1961).

[121] F. Dörr, *Z. Elektrochem.* **64**, 580 (1960).

[122] E. Rabinovitch, "Photosynthesis and Related Processes," Vol. I, Chapters 4 and 18. Wiley (Interscience), New York, 1945.

[123] G. Oster and A. D. McLaren, *J. Gen. Physiol.* **33**, 215 (1950).

[124] G. Oster, *Trans. Faraday Soc.* **47**, 660 (1951).

of dyes in solution in the early 1950s. Up to now these studies have given valuable insight into the main mechanisms of the photoreactions of dyes. Moreover, in the course of these studies important problems have attracted attention. Besides questions of biological interest the dye-sensitized photopolymerization[127–130] and the possibility of production of three-dimensional topographical maps in plastics with the help of the photochemical reactivity of dyes have been recognized.[103]

B. TYPES OF PHOTOCHEMICAL REACTIONS OF DYESTUFFS

There is a series of basic photochemical reactions which may lead to the decomposition of a dye; see, e.g., the reviews of this topic in references 131 and 87. As under practical conditions dye molecules usually are in contact with other substances, not only the photobleaching of a dye itself but also above all the possibility of reactions with other substances present in the system must be considered. These chemical reactions may involve reduction, oxidation, the creation of free radicals, etc. The starting point may be the first n, π^* or π, π^* excited singlet and triplet states, respectively. In this context it is interesting to note that as early as 1814 Bancroft[84] concluded from experiments that oxidation or reduction processes are responsible for photofading. Nowadays, when considering photofading it must also be taken into account that not only the absorption of light by the dye but also photoexcitation of other substances present in the system can lead to photodecomposition of dyestuffs. Therefore, the following types of photoreactions must be discussed.

1. *Intramolecular Photoreaction*

In this type of reaction, formulated by Eq. (39),

$$D + h\nu \rightarrow D^*; \qquad D^* \rightarrow \text{Products} \tag{39}$$

there is no necessity for an interaction with any other substance for the photoprocess. Photodecomposition as the result of an instability of the excited dye molecules is not the common route to photofading of dyestuffs adsorbed on fibers, etc.

In the case of *diazo compounds*, however, this photoprocess is very intense and has found widespread application as the basis of image-

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[125] G. Oster, *J. Polymer Sci.* **9**, 553 (1952).

[126] G. Oster, *Phot. Sci. Eng.* **4**, 173 (1956).

[127] G. Oster, *Phot. Sci. Eng.* **4**, 237 (1960).

[128] G. Oster, *J. Polymer Sci.* **B2**, 1181 (1964).

[129] G. A. Delzenne, *Ind. Chim. Belge* **30**, 679 (1965).

[130] G. Oster, *J. Polymer Sci.* **C12**, 63 (1966).

forming systems.[131–139,139a] When diazonium salts absorb light the yellow diazo color disappears, nitrogen is evolved, and colorless decomposition products, which have been investigated in solutions,[140] are formed. The concentration of the diazo compound decreases according to a first-order law so that the photodecomposition can be described by Eq. (15) and Eq. (20). The quantum yield, e.g., measured by Eggert,[141] is independent of the concentration of the diazo compound and varies between 0.2 and unity. In the presence of moisture irradiation leads to a phenolic decomposition product according to

$$RC_6H_4N = NCl + H_2O \xrightarrow{h\nu} RC_6H_4OH + N_2 + HCl$$

In practice the image formation is the result of a coupling between this phenolic or an added phenolic component and the unchanged diazo compound.

As another example of the general type of intramolecular reactions photochemical *cis–trans isomerization* should be mentioned. The characteristic fact of this molecular rearrangement, in which the triplet state is involved, is the loosening of a π-bond in the molecule and a rotation on the σ-bond without any discontinuity in the electron distribution. As examples, the cis–trans isomerization of indigo, azo compounds[134,142–145] or cyanin dyes at low temperatures[146] should be mentioned. This change from the cis configuration to the trans form by visible light is of great importance in nature. The excitation of the light-sensitive vision chro-

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[131] H. C. A. van Beek and P. M. Heertjes, *Studies Conserv.* **11,** 123 (1966).

[132] R. Landau, P. Pinot de Moira, and A. S. Tanenbaum, *J. Phot. Sci.* **13,** 144 (1965).

[133] R. Landau, *J. Phot. Sci.* **10,** 32 (1962).

[134] H. Zollinger, "Diazo and Azo Chemistry," Chapter 4.1. Wiley (Interscience), New York, 1961.

[135] R. Moraw and J. Munder, *Phot. Sci., 8th Symp., Zürich, 1961* pp. 390–399. Focal Press, London, 1963.

[136] S. Kikuchi and M. Sukigara, *Intern. Congr. Phot. Sci., Tokyo, 1967* Sect. V.

[137] T. Tsunoda and T. Yamaoka, *Intern. Congr. Phot. Sci., Tokyo, 1967* Sect. V.

[138] J. Kosar, "Light-Sensitive Systems," p. 194. Wiley, New York, 1965.

[139] K. H. Saunders, "The Aromatic Diazo-Compounds," 2nd ed., Chapter X. Arnold, London, 1949.

[139a] K. Venkataraman, "The Chemistry of Synthetic Dyes," Vol. I, pp. 233–239, Academic Press, New York, 1952.

[140] J. de Jonge and R. Dijkstra, *Rec. Trav. Chim.* **67,** 328 (1948).

[141] J. Eggert, *Z. Elektrochem.* **34,** 602 (1928); *Phot. J.* **76,** 17 (1936).

[142] G. M. Wyman, *Chem. Rev.* **55,** 625 (1955).

[143] G. Gabor and E. Fischer, *J. Phys. Chem.* **66,** 2478 (1962).

[144] S. Malkin and E. Fischer, *J. Phys. Chem.* **66,** 2482 (1962).

[145] G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.* **85,** 2515 (1963).

[146] F. Baumgärtner, E. Günther, and G. Scheibe, *Z. Elektrochem.* **60,** 570 (1956).

mophore molecule *11-cis-retinal* (vitamin A aldehyde) which, by association with fatty proteins (opsin), forms the visual pigment rhodopsin or iodopsin results in a cis–trans isomerization (see Fig. 6) to the all-*trans*-retinal, i.e., rhodopsin is converted into prelumirhodopsin with an all-trans chromophore. This primary process is followed by a series of reactions which lead to a separation of the chromophore from the protein; see Wald[147–149] and the reviews in references 6 and 150–152.

In this context it should be mentioned that in plant photoperiodism a similar intramolecular reaction is decisive. The periodism chromophore *phytochrome* (which is chemically related to the greenish yellow pigments of human bile) is changed by absorption of red light ($\lambda_{\max} =$ 664 nm) to a far-red-absorbing molecule ($\lambda_{\max} = 724$ nm). According to Hendricks[153] the reversible far-red phytochrome formation is the result

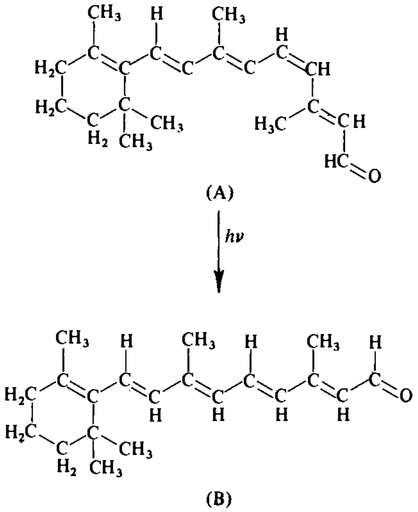

FIG. 6. Cis–trans isomerization of 11-*cis*-retinal (A) to all-*trans*-retinal (B).

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[147] G. Wald, *in* "Light and Life" (W. D. McElroy and B. Glass eds.), pp. 724–749. Johns Hopkins Press, Baltimore, Maryland, 1961.

[148] R. Hubbard and G. Wald, *Proc. Natl. Acad. Sci. U. S.* **37**, 69 (1951).

[149] R. Hubbard and G. Wald, *J. Gen. Physiol.* **36**, 269 (1952–1953).

[150] H. H. Seliger and W. D. McElroy, "Light: Physical and Biological Action," pp. 305-312. Academic Press, New York, 1965.

[151] R. A. Weale, *in* "Photophysiology" (A. C. Giese, ed.), Vol. 4, pp. 1–45. Academic Press, New York, 1968.

[152] J. B. Thomas, "Einführung in die Photobiologie," pp. 151–198. Thieme, Stuttgart, 1968.

[153] S. B. Hendricks, *Sci. Am.* **219**, 174 (1968).

of a photochemical shifting of two hydrogen atoms such as demonstrated in Fig. 7. It should, however, be noted that besides this reversible tautomerization a *cis–trans* isomerization of the chromophore or a reversible oxidation–reduction reaction has been suggested.[154-157] An internal oxidation–reduction process seems unlikely[158] because of the small differences in the absorption spectrum. However, the *cis–trans* isomerization similar to the rhodopsin systems must be discussed under the different possibilities. Kinetic experiments hint at a formal analogy

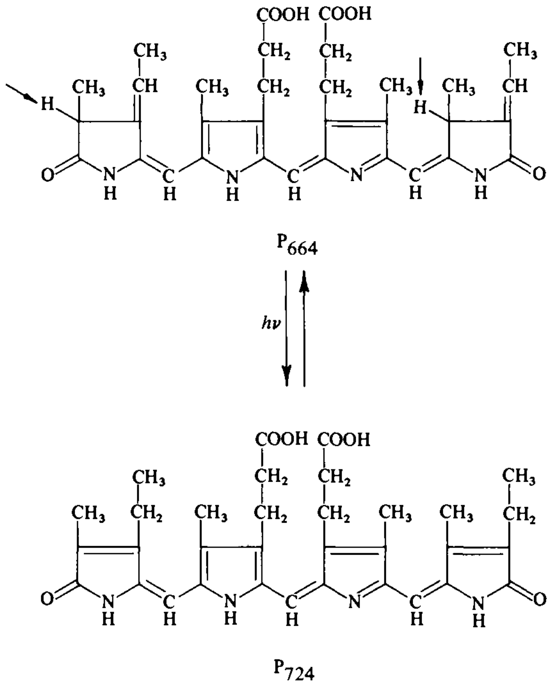

FIG. 7. Possible photochemical reaction $P_{664} \underset{724\,\mathrm{nm}}{\overset{664\,\mathrm{nm}}{\rightleftarrows}} P_{724}$ of the photoperiodism chromophore phytochrome (according to Hendricks[153]).

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[154] S. B. Hendricks, H. A. Borthwick, and R. J. Down, *Proc. Natl. Acad. Sci. U. S.* **42**, 19 (1956).

[155] H. W. Siegelman and W. L. Butler, *Ann. Rev. Plant Physiol.* **16**, 383 (1965).

[156] H. W. Siegelman and S. B. Hendricks, *Federation Proc.* **24**, 863 (1965).

[157] S. B. Hendricks, *in* "Photophysiology" (A. C. Giese, ed.), Vol. 1, Chapter 10, pp. 305–331. Academic Press, New York, 1964.

[158] R. M. Klein and P. C. Edsall, *Plant Physiol.* **41**, 949 (1966).

between phytochrome and rhodopsin systems[159,160] and there seems to be no doubt that the phytochrome conversion is coupled with alterations in the molecular form of the associated protein, which can be reversed by absorption of far-red light.

As a consequence of the phytochrome photoprocess a number of important photomorphogenetic effects in plants, e.g., flowering and seed germination, are started and enzymatically controlled by the presence of the far-red phytochrome; see Hendricks and others.[157,161–168] Likewise, according to Haupt[169–171] the dim-light phobophototaxis of *Mougeotia* chloroplasts is a result of the phytochrome activity.

Measurements of the action spectra of phototactic[172] and phototropic effects[163] showed that also *riboflavin* (I) can function as a phototactic and a phototropic pigment. This biologically important vitamin (synonyms: lactoflavin and vitamin B_2), which is characterized by a reversible reduction and reoxidation and an interesting photochemical reactivity, fades during irradiation in oxygen-free aqueous solutions without any agents[119,173,174] by the reduction of the isoalloxazine nucleus. On aeration the yellow color returns, indicating a reoxidation of the dihydroisoalloxazine group. With this photoreaction the question arises whether the equivalent of two hydrogen atoms producing dihydroriboflavin comes from the cleavage of water.[175–177] Holmström and Oster[119] argued against

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[159] H. Linschitz, V. Kasche, W. L. Butler, and H. W. Siegelman, *J. Biol. Chem.* **241,** 3395 (1966).

[160] H. Linschitz and V. Kasche, *Proc. Natl. Acad. Sci. U. S.* **58,** 1059 (1967).

[161] H. A. Borthwick and S. B. Hendricks, *in* "Handbuch der Pflanzenphysiologie" (W. Ruhland, ed.), Vol. 16, pp. 299–330. Springer, Berlin, 1961.

[162] S. B. Hendricks, W. L. Butler, and H. W. Siegelman, *J. Phys. Chem.* **66,** 2550 (1962).

[163] J. B. Thomas, "Primary Photoprocesses in Biology." North-Holland Publ., Amsterdam, 1965.

[164] W. L. Butler and R. J. Down, *Sci. Am.* **203,** 56 (1960).

[165] G. Blauw-Jansen, *Rec. Trav. Botan. Neerl.* **8,** 1 (1959).

[166] P. Schopfer, *Planta* **69,** 158 (1966).

[167] R. M. Klein, *Physiol. Plantarum* **18,** 1026 (1965).

[168] G. Oster, *in* "Photoperiodism and Related Phenomena in Plants and Animals," Publ. No. 55, pp. 3–14. Am. Asso. Advance Sci., Washington, D. C., 1959.

[169] W. Haupt, *Planta Deut. Botan. Ges.* [N.S.] **55,** 465 (1960); *Vortr. Gesamtgebiet Botan.* **1,** 116 (1962).

[170] W. Haupt and G. Bock, *Planta* **59,** 38 (1962).

[171] W. Haupt and E. Schönbohm, *Naturwissenschaften* **49,** 42 (1962).

[172] W. Haupt and I. Schönfeld, *Ber. Deut. Botan. Ges.* **75,** 14 (1962).

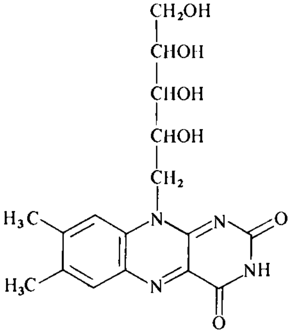
[173] R. Kuhn, H. Rudy, and T. Wagner-Jauregg, *Chem. Ber.* **66,** 1950 (1933).

[174] O. Warburg and W. Christian, *Biochem. Z.* **266,** 377 (1933).

[175] J. R. Merkel and W. J. Nickerson, *Biochim. Biophys. Acta* **14,** 303 (1954).

[176] G. Strauss and W. J. Nickerson, *J. Am. Chem. Soc.* **83,** 3187 (1961).

[177] L. P. Vernon, *Biochim. Biophys. Acta* **36,** 177 (1959).



(I)

this mechanism because of energetic considerations and postulated that fading of riboflavin results from photooxidation of its own ribityl side chain. Up to now in a series of kinetic, polarographic, and flash photolytic studies considerable evidence for the intramolecular photobleaching could be given,[80,114,178-182] and a good insight into the mechanism of the cleavage reactions in the side chain could be obtained.[179,183-187] According to Song and Metzler[188] the cleavage may be regarded as a case of photoelimination[1] which is a characteristic reaction of aldehydes and ketones containing a γ-hydrogen atom and also of amides (Norrish Type II Split). This reaction may also occur through a six-membered ring "intermediate" (II), and result in an enol (1-deoxyribulose) (IV) and lumichrome (III). By replacing the two hydrogen atoms in the 2′-position of the side chain by deuterium the rate of photolysis was remarkably reduced, in agreement with this mechanism.

Moreover, by quenching experiments with KI and flash work it could be shown that the long-lived lowest triplet excited state is the photoreactive species in the anaerobic photobleaching of riboflavin and flavin mononucleotide.[80,119,188-190] The fractional quenching of fluorescence by

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[178] E. C. Smith and D. E. Metzler, *J. Am. Chem. Soc.* **85**, 3285 (1963).

[179] W. M. Moore, J. T. Spence, F. A. Raymond, and S. D. Colson, *J. Am. Chem. Soc.* **85**, 3367 (1963).

[180] P. Song, E. C. Smith, and D. E. Metzler, *J. Am. Chem. Soc.* **87**, 4181 (1965).

[181] G. K. Radda and M. Calvin, *Biochemistry* **3**, 384 (1964).

[182] G. R. Penzer and G. K. Radda, *Quart. Rev. (London)* **21**, 43 (1967).

[183] M. M. McBride and D. E. Metzler, *Photochem. Photobiol.* **6**, 113 (1967).

[184] P. Karrer and F. N. Meerwein, *Helv. Chim. Acta* **18**, 1126 (1935).

[185] M. Halwer, *J. Am. Chem. Soc.* **73**, 4870 (1951).

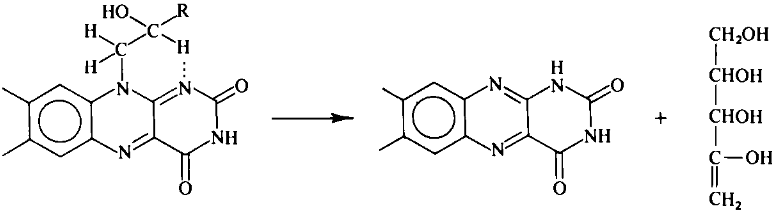
[186] C. S. Yang and D. B. McCormick, *J. Am. Chem. Soc.* **87**, 5763 (1965).

[187] M. M. McBridge and W. M. Moore, *Photochem. Photobiol.* **6**, 103 (1967).

[188] P. Song and D. E. Metzler, *Photochem. Photobiol.* **6**, 691 (1967).

[189] B. Holmström, *Bull. Soc. Chim. Belges* **71**, 869 (1962).

[190] M. Green and G. Tollin, *Photochem. Photobiol.* **7**, 145 (1968).



(II) (III) (IV)

KI and phenol is significantly smaller than the fractional decrease in the rate of anaerobic bleaching. Because of a similar order of fractional inhibition of photobleaching rates and of fluorescence in ethanol solutions, Song and Metzler,[188] however, concluded that the singlet state of riboflavin may also be active in photolysis under special conditions, i.e., that two pathways of the photofading may exist with a singlet state as an intermediate in ethanol and a triplet state as an intermediate in water. Further work on this problem seems to be necessary.

Evidently the reversible photobleaching of methylene blue in phosphate- and borate-buffered solutions without any reducing agents belongs to a photodecomposition reaction similar to that observed with riboflavin. Perhaps the tertiary amine groups act as the electron donors in the reaction, analogous to the ribityl group.[191-193]

To the reactions that have been discussed in this section phototropic color changes of dyes should be added. These reactions, defined by the term phototropism or (more clearly) *photochromism* are characterized by a light- or UV-induced reversible color change of a dye. According to Luck[194] it is decisive for photochromism that light-induced reversible transitions lead to states with quantum-mechanical stability but thermodynamic instability. This process, described by Eq. (40), is schematically given in Fig. 8.

$$D \overset{h\nu}{\rightleftarrows} S(\rightleftarrows T) \rightleftarrows X \rightarrow Y \tag{40}$$

Often the reversible process is partly followed by an irreversible reaction which gives a thermodynamically stable product Y. Because of the slowness of the reverse process a dye with photochromic color change has poor lightfastness. On the other hand, in cases of a rapid reaction from the photochromic species X to D there exists the possibility of an

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[191] Y. Usui, H. Obata, and M. Koizumi, *Bull. Chem. Soc. Japan* **34**, 1049 (1961).

[192] H. Obata, *Bull. Chem. Soc. Japan* **34**, 1057 (1961).

[193] Y. Usui and M. Koizumi, *Bull. Chem. Soc. Japan* **34**, 1651 (1961).

[194] W. Luck, *in* "Optische Anregung organischer Systeme. 2nd Internationales Farbensymposium" (W. Foerst, ed.), pp. 666–697. Verlag Chemie, Weinheim, 1966.

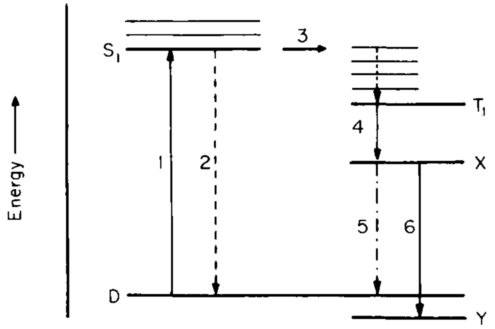
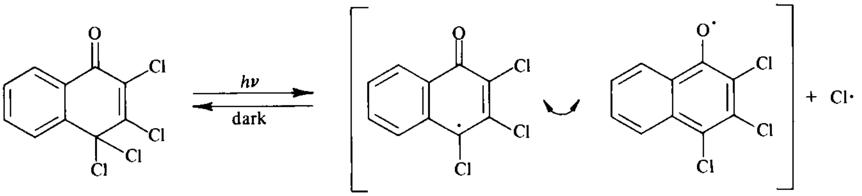


FIG. 8. Simple state diagram for illustrating photochromic transitions: 1, excitation (to S_1); 2, radiative and/or radiationless deactivation; 3, intersystem crossing $S_1 \rightarrow T_1$; 4, transition to the photochromic species X; 5, transition from X to D; 6, irreversible transition to Y.

enhancement of lightfastness. This effect may occur above all in compounds in which there is such a rapid deactivation either of the excited singlet or the triplet state by quick transition to the phototropic species that the starting of any other photochemical reaction from the excited state is not probable (see Section I,C,1,b,*iv*). Photochromism in solution and in the solid state, first observed in 1899 by Marckwald,[195] can be the result of intramolecular changes, e.g., tautomerism, ring opening, cis–trans isomerization, or free radical formation, and stereoisomeric



(V)

transitions, formation of aggregations, and other reactions; see the reviews in references 94, 194, 196, and 197.

As examples of a free radical formation the photochromism of cooled solid solutions of tetrachloro-1-oxodihydronaphthalene (V)[198] or of

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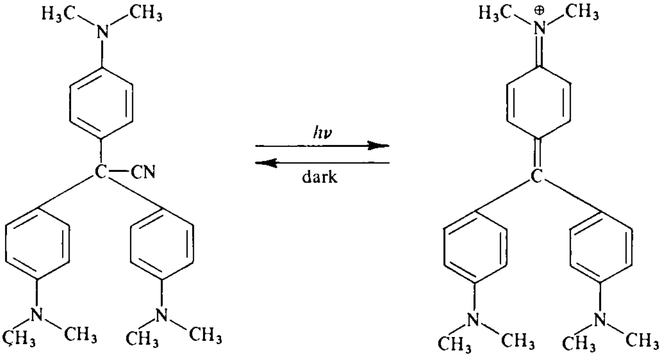
[195] W. Marckwald, *Z. Physik. Chem.* **30**, 140 (1899).

[196] G. H. Brown and W. G. Shaw, *Rev. Pure Appl. Chem.* **11**, 2 (1961).

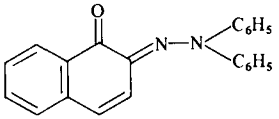
[197] R. Dessauer and J. P. Paris, *Advan. Photochem.* **1**, 275–321 (1963).

[198] F. Feichtmayr and G. Scheibe, *Z. Naturforsch.* **13b**, 51 (1958); *J. Phys. Chem.* **66**, 2449 (1962).

methanolic solutions of chlorophyll[199-201] should be mentioned. The photochromism of methanol–ethanol solutions of triphenylmethane dyes, such as malachite green and crystal violet (VI),[202] can be explained by the mechanism given below. The quantum yield of this photoreaction is of the order of one,[203-205] indicating that neither any radiative nor any radiationless deactivation process lies between D and X of Eq. (40). The photochromic reaction of aqueous solutions of the leucosulfite of parafuchsine could be used as a UV dosimeter for the measurement of the UV radiation of sky light.[194] Because of the formal resemblance to phytochrome photochemistry the photoisomerism of the quinoid 1,2-napthoquinone-2-diphenylhydrazone (VII) should be mentioned. By irradiation in polar (ethanol) or nonpolar solvents the isomeric state with an absorption band at 480 nm is transformed into a state with a



(VI)



(VII)

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[199] R. Livingston and V. A. Ryan, *J. Am. Chem. Soc.* **75**, 2176 (1953).

[200] R. Livingston, G. Porter, and M. Windsor, *Nature* **173**, 485 (1954).

[201] E. W. Abrahamson and H. Linschitz, *J. Chem. Phys.* **23**, 2198 (1955).

[202] S. Lifschitz, *Ber. Deut. Chem. Ges.* **61**, 1463 (1928).

[203] E. Weyde and W. Frankenburger, *Trans. Faraday Soc.* **27**, 561 (1931).

[204] E. Weyde, W. Frankenburger, and W. Zimmermann, *Naturwissenschaften* **18**, 206 (1930).

[205] J. G. Calvert and H. J. L. Rechen, *J. Am. Chem. Soc.* **74**, 2101 (1952).

550-nm absorption peak.[206] In the dark the photoequilibrium is shifted back to the normal dark equilibrium with 98% D_{480} in ethanol and 84% D_{480} in the methylcyclohexaneisohexane (nonpolar) solvent. By irradiation at 550 nm the form D_{550} is converted into D_{480}, i.e., there is a resemblance to the important phytochrome conversion mentioned above:

$$\begin{tikzcd} D_{480} \arrow[r, shift left, "480\text{ nm}"] & D_{550}; \arrow[l, shift left, "550\text{ nm}"] \arrow[l, bend left=60, "\text{dark}"] & P_{664} \arrow[r, shift left, "664\text{ nm}"] & P_{724} \arrow[l, shift left, "724\text{ nm}"] \arrow[l, bend left=60, "\text{dark}"] \end{tikzcd}$$

Such color changes which can be reversed by irradiation in the absorption band of the photochromic product species are termed secondary photochromism; see, e.g., Luck[194] and Inoue *et al.*[207] Because of this type of photochromism, reversible color changes need not lead to a small lightfastness of dyes on fabrics.[208] On the contrary, in cases of secondary photochromism an enhancement of lightfastness may be possible by illumination in the absorption band of the photochromic species. As a consequence of the photoreaction

$$D_1 \underset{h\nu_2}{\overset{h\nu_1}{\rightleftarrows}} D_2$$

other irreversible photochemical reactions cannot intervene. These examples show the necessity for experiments on this subject. Such studies are also valuable because of the practical use of phototropic dyestuffs as the basis of a photochemical high speed memory with an erasable image,[209] or as automatic variable-density light filters.[101]

2. *Photoreduction*

a. General Aspects. The photoreduction of excited dye molecules by certain other substances which are present in the system either as the solvent or as a solute is an often-observed process. As a result the substances are oxidized with a simultaneous reduction and consequent photobleaching of the dye. These processes can be simply described by Eq. (41).

$$D + h\nu = D^*; \qquad D^* + R = D_{\text{red}} + R_{\text{ox}} \tag{41}$$

The reaction which leads to a photoreduction involves a hydrogen atom or an electron transfer from the reducing (electron-donating) agents to the dye. That is, we have

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[206] E. Fischer and M. Kagnowich, *Bull. Res. Council Israel* **A10,** 138 (1961).

[207] E. Inoue, H. Kokado, I. Shimizu, and K. Yoshida, *Phot. Sci. Eng.* **11,** 181 (1967).

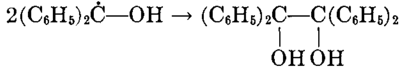
[208] H. Waibel, *Melliand Textilber.* **36,** 737 (1955).

[209] Y. Hirshberg, *J. Am. Chem. Soc.* **78,** 2304 (1956).

$$D^* + RH = D\cdot^- + RH^+ \quad \text{or} \quad D^* + RH = DH\cdot + R\cdot$$

Both the hydrogen atom transfer (which can also be discussed as an electron transfer followed by a proton transfer) and the electron transfer need an electrophilic center in the reduced species. As a classical example of a photoreduction according to the last equation the formation of benzopinacol by irradiation of benzophenone in alcoholic solution should be mentioned. The result of the photoreduction by the hydrogen atom transfer is the formation of ketyl radicals which dimerize to pinacol.[210,211]

$$2(C_6H_5)_2C{=}O^* + CH_3CH_2OH \rightarrow 2(C_6H_5)_2\dot{C}{-}OH + CH_3CH{=}O$$



$$2(C_6H_5)_2\dot{C}{-}OH \rightarrow (C_6H_5)_2\underset{OH}{C}{-}\underset{OH}{C}(C_6H_5)_2$$

For the photobleaching of a dye usually two hydrogen atoms (or two electrons and two protons) must be added to a double bond of the conjugated system of the dye, so that

$$D^* + RH_2 \rightarrow DH_2 + R$$

In considering reductions such as this one it must be noted that reductions in one two-electron step are well known in biochemistry, but this kind of reduction could not clearly be observed in photoreduction experiments. The photoreduction of dyes, e.g., of riboflavin,[80,189] proceeds in two one-electron steps. In such cases the photoreduction gives, in a one-electron step, a semiquinone DH· which by disproportionation is transformed into the leuco form of the dye. For example, with a one-electron reducing agent such as Fe^{2+} we have generally

$$D^* + Fe^{2+} + H^+ \rightarrow DH\cdot + Fe^{3+}; \qquad DH\cdot + DH\cdot \rightarrow D + DH_2$$

In several cases the reduction of the dye may be reversed by hydrogen peroxide or atmospheric oxygen, e.g., according to

$$DH\cdot + O_2 \rightarrow D + HO_2\cdot$$

because

$$e + O_2 \rightarrow O_2\cdot^- \qquad O_2\cdot^- + H^+ \rightarrow HO_2\cdot$$

followed by

$$2HO_2\cdot \rightarrow H_2O_2 + O_2$$

As a result of such effects photobleaching by reduction can be characterized by a very small quantum yield, so that in kinetic studies disturbances by oxygen must strictly be noted.[8,212]

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[210] J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martin, *J. Am. Chem. Soc.* **81**, 1068 (1959).

[211] C. R. Masson, V. Boeckelheide, and W. A. Noyes, Jr., *in* "Technique of Organic Chemistry" (A. Weissberger, ed.), Vol. II, p. 257. Wiley (Interscience), New York, (1956).

[212] A. Polgar, *Z. Wiss. Phot., Photophysik Photochem.* **46,** 188 (1951).

In a series of combinations of dyes and reductants the recovery of the photoreduced dye by oxidation may be so rapid that photoreduction and photobleaching, respectively, are not at all observed. As an example the thionine–ferrous system should be mentioned. In this system the photoreduced thionine is very quickly oxidized by the ferric ion produced.[127,213] Therefore, for the steady state in the photobleaching process the equilibrium between the photoreduction by Fe^{2+} ions and the dark-reoxidation by Fe^{3+} ions is responsible. By diminishing the concentration of ferric ions by the addition of fluoride ions (i.e., formation of $[FeF_6]^{3-}$ complex) the rate of photobleaching can be enhanced; see Havemann and others.[214-216]

b. Thermodynamic Conditions. In this context, it should be taken into account that the course of a redox reaction, either in the dark or in the case of a photoexcited species, depends on the free energy change of the reaction ΔG and the free energy of activation $\Delta G^{\#}$. According to Pietsch[217] the reactions can be classified into two types:

Type I, corresponding to $\Delta G > 0$, is characteristic of reactions which are not thermodynamically spontaneous. In these reactions the free energy difference must be overcome by the energy of the absorbed light. As discussed in Section I,B,1,a the energy associated with visible light is equivalent to 40–60 kcal/mole (about 2 eV), so that this condition can be fulfilled. But it must be remarked that in the case of a small free energy of activation of back reaction $\Delta G^{\#}$ the rate of the reaction may be fast. By this back reaction the photoreduction may be disturbed and also be prevented, as discussed above.

Type II, corresponding to $\Delta G < 0$, is characteristic for reactions which are thermodynamically spontaneous. The slowness of the reaction rate is caused by high values of the free energy of activation $\Delta G^{\#}$. Light energy absorbed by the dye has the function of lowering $\Delta G^{\#}$, as do suitable catalysts.

For the estimation of values of $\Delta G^{\#}$ in redox reactions see references 80 and 218. ΔG can be calculated with the emf of two half-cells of the reacting systems which are related to the standard hydrogen electrode. With E_D as the redox potential of the dye and E_R as the corresponding

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[213] J. Weiss, *Trans. Faraday Soc.* **35,** 48 (1939).

[214] E. Rabinovitch, *J. Chem. Phys.* **8,** 551 (1940).

[215] R. Havemann and H. Pietsch, *Z. Phys. Chem.* **208,** 98 (1957); **209,** 210 (1958); **210,** 232 (1959).

[216] R. Havemann and K. G. Reimer, *Z. Physik. Chem.* (*Leipzig*) **211,** 26, 61 (1959).

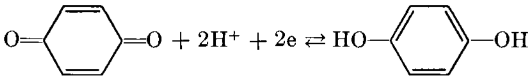
[217] H. Pietsch, *Z. Wiss. Phot., Photophysik Photochem.* **54,** 109 (1960).

[218] L. Michaelis, *J. Biol. Chem.* **96,** 703 (1932).

potential of the reducing agent we have in the general case of Eq. (42) for the free energy change of the reaction

$$\Delta G = 2F(E_{\mathrm{R}} - E_{\mathrm{D}}) = \frac{2 \cdot 96520}{4184}(E_{\mathrm{R}} - E_{\mathrm{D}}) \qquad \text{(kcal per mole)} \qquad (42)$$

where F is Faraday's constant. We see that $\Delta G < 0$ if $E_{\mathrm{D}} > E_{\mathrm{R}}$, and $\Delta G > 0$ if $E_{\mathrm{D}} < E_{\mathrm{R}}$. The emf of the half-cells of the different systems relative to the standard hydrogen electrode, which are tabulated for inorganic and organic systems,[219] depend on the acid concentration and on the concentration ratio of the oxidized and reduced species. For example, we have for the well-known quinone hydroquinone reaction



$$E = E^{\circ} + \frac{RT}{F}\ln[\mathrm{H^+}] + \frac{RT}{2F}\ln\frac{[\text{Quinone}]}{[\text{Hydroquinone}]} \qquad (43)$$

$$E = E^{\circ} + 0.0512 \log[\mathrm{H^+}] + 0.02956 \log\frac{[\text{Quinone}]}{[\text{Hydroquinone}]} \qquad (44)$$

E° is defined as the standard emf with each component at unit activity. With constant ratio between the oxidized and reduced species (e.g., [Quinone] = [Hydroquinone]) the real emf of the half-cell, i.e., the electrode or redox potential, decreases with increasing pH. That means, that for deciding $\Delta G > 0$ or $\Delta G < 0$ we must consider the dye systems and the reducing (or oxidizing) agent at a specified pH. As examples Fig. 9 shows several emf values vs. pH for some dyes and reacting agents. From the figure we see that dyes should be reduced by hydrogen in the presence of a suitable catalyst because of $E_{\mathrm{H_2}/\mathrm{H^+}} < E_{\mathrm{dye}}$. Methylene Blue and thionine are characterized by high redox potentials so that photoreduction can start or be accelerated in the presence of mild reducing agents which have $E_{\mathrm{R}} < E_{\mathrm{D}}$. This case of Pietsch's Type II ($\Delta G < 0$) is found, e.g., for the reduction of methylene blue with ascorbic acid below pH 4.[220] The energy of the absorbed light has to reduce $\Delta G\#$. In neutral solutions Type II is changed to Type I because of a higher redox potential of ascorbic acid ($E_{\mathrm{R}} > E_{\mathrm{D}}$). But, by absorption of visible light the redox potential of the dye is lifted over that of ascorbic acid with the result that a rapid photoreduction of the dye occurs. The condition $\Delta G > 0$ should lead to a slow back reaction. Above all the oxidation of the leucomethylene blue is observed in the presence of

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[219] W. M. Latimer, "Oxidation Potentials," 2nd ed. Prentice-Hall, Englewood Cliffs, New Jersey, 1952.

[220] G. Oster and N. Wotherspoon, *J. Chem. Phys.* **22**, 157 (1954).

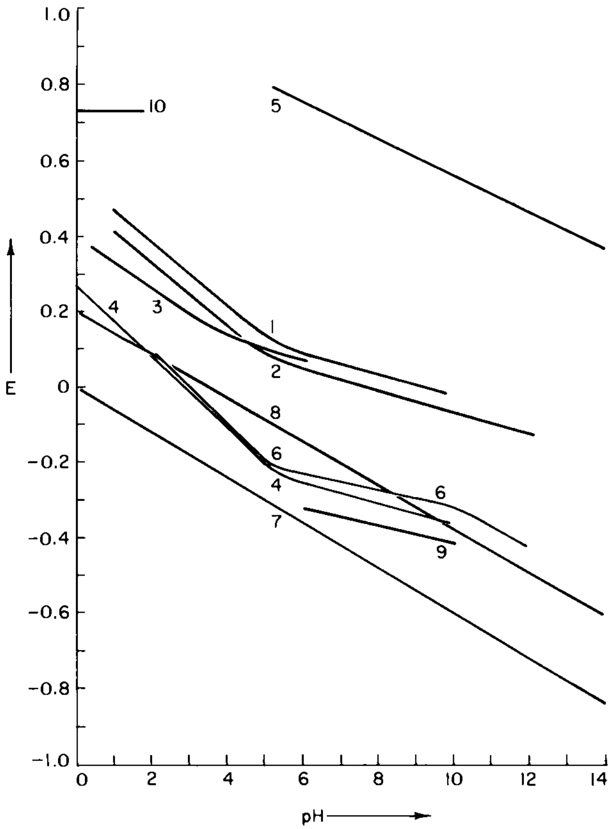

FIG. 9. Emf of half-cells with a hydrogen reference electrode as function of pH: 1, thionine; 2, methylene blue; 3, ascorbic acid; 4, safranine; 5, O_2; 6, riboflavin; 7, H_2–H^+; 8, ethanol; 9, NADH–NAD$^+$; 10, Fe^{2+}–Fe^{3+}.

atmospheric oxygen in a short time and can be accelerated by near UV light absorbed by the leuco dye.

According to Oster,[127] as a *general rule* it can be stated that a photoreduction of Type I systems is possible from an energetic point of view with visible light if the redox potential of the dye does not lie more than 1 eV below that of the reducing agent.

The importance of this rule can be clearly demonstrated with the system thionine–ferrous ions which belongs to Type I. The ferrous ion is characterized by a higher redox potential than thionine; at pH 1 we have $\Delta G = 2\ F(0.75 - 0.5) = 11.4$ kcal (per mole Fe^{2+}) so that ferrous ions cannot bleach thionine in the dark. By absorption of visible light, however, the redox potential of the dye is lifted over that of the $Fe^{2+}/$

Fe^{3+} system. As discussed above, this photoreduction may be disturbed by the back reaction, i.e., by the oxidation of semithionine and leucothionine by Fe^{3+}, as a consequence of $\Delta G > 0$ and a low value of $\Delta G\#$.

In spite of $\Delta G < 0$ over the entire pH range thionine is not reduced with sulfite in acid solutions because of a high value of $\Delta G\#$. However, photoreduction occurs.[217] Riboflavin is reduced with reduced nicotine adenine dinucleotide (NADH or DPNH) in the dark and above all during illumination.[177,221,222] Because of the rapid back reaction ($\Delta G\#$ low, $\Delta G > 0$) ascorbic acid does not reduce riboflavin under anaerobic conditions.[223] But in the presence of atmospheric oxygen, ascorbic acid is oxidized, evidently as a result of an enhanced oxidation of the photoreduced riboflavin by oxygen.[224] In this reaction the dye acts as a sensitizer for ascorbic acid oxidization. See reports of other photoreductions of riboflavin by alcohols, ferrous ions,[80,178,181,225-227] by EDTA,[228,229] and photoreductions of proflavine by allylthiourea.[116,230]

Methylene blue, thionine, and safranine are photoreduced in the presence of acidified stannous chloride ($\Delta G < 0$).[127] The colored form of the dyes is regenerated by the addition of hydrogen peroxide and even in the absence of oxygen by near UV light which is absorbed by the reduced dyes.

There is also a good photoreduction of methylene blue with EDTA[101] which is consumed during the reaction, and of eosin[100] and acridine dyes[115] with allylthiourea.

In this context it should be mentioned that by adsorption to an appropriate high polymer substrate the redox potential of dyes may apparently be raised in several cases. For example, acriflavine and rose bengal, which cannot be photoreduced with ascorbic acid because of their very low redox potential ($\Delta G > 0$), will undergo photoreduction in the presence of ascorbic acid when bound to specific polymers.[124,125,231] Rose bengal can be photoreduced in the unbound state only with a very powerful reducing agent such as chromous chloride.

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[221] C. H. Suelter and D. E. Metzler, *Biochim. Biophys. Acta* **44**, 23 (1960).

[222] W. R. Frisell and C. G. Mackenzie, *Proc. Natl. Acad. Sci. U. S.* **45**, 1568 (1959).

[223] H. M. Habermann and H. Gaffron, *Photochem. Photobiol.* **1**, 159 (1962).

[224] F. G. Hopkins, *Compt. Rend. Trav. Lab. Carlsberg, Ser. Chim.* **22**, 226 (1938).

[225] W. Koschara, *Z. Physiol. Chem.* **229**, 103 (1934).

[226] A. J. Swallow, *Nature* **176**, 793 (1955).

[227] W. J. Rutter, *Acta Chem. Scand.* **12**, 438 (1958).

[228] W. J. Nickerson and J. R. Merkel, *Proc. Natl. Acad. Sci. U. S.* **39**, 901 (1953).

[229] K. Enns and W. H. Burgess, *J. Am. Chem. Soc.* **87**, 5766 (1965).

[230] K. Kikuchi and Y. Usui, *Sci. Rept. Tohoku Univ., First Ser.* **50**, 59 (1967).

[231] A. H. Adelman and G. Oster, *J. Am. Chem. Soc.* **78**, 3977 (1956).

Triphenylmethane dyes (e.g., crystal violet, ethyl violet, and to some extent malachite green), which do not undergo photoreduction at all, can also be reduced with mild reducing agents like ascorbic acid on illumination when bound to high polymer substrates.[232] In contrast with the free dyes the quantum yield of photoreduction increases with increasing dye concentration. These observations seem to be very remarkable because of the fact that chlorophyll exists in plants in the bound state. In transferring results of the photochemical behavior of free chlorophyll to the dye in vivo these differences should be noted. For example, chlorophyll dissolved in pyridine with a trace of water and with a reducing agent is reversibly photoreduced to a pink intermediate which can possibly also be formed in bacteria and algae (Krasnovsky reaction[233]).[122,234] And, by binding the water-soluble derivate chlorophyllin a[235] to a high polymer in agreement with the above-mentioned observations photoreduction is considerably enhanced.[234]

c. Consequences of the Photoreduction Process. From these examples we can see that a knowledge of the redox potentials of dyes and of the reducing agents under different conditions, i.e., of ΔG, and an estimation of $\Delta G^{\#}$ are important for describing the reactivity of photoreducible systems. Furthermore, it is necessary to take account of the fact that the dye in the reduced state can be a very powerful reducing agent. This increased reducing activity can be derived from Eq. (45) because of a decreasing redox potential as a result of a lowering of the [Ox]/[Red] ratio

$$E = E^\circ + 0.0512 \log[\mathrm{H}^+] + 0.02956 \log \frac{[\mathrm{Ox}]}{[\mathrm{Red}]} \tag{45}$$

Therefore the reduced dye has the tendency to donate electrons to other substances and to go back to the oxidized state, which can again be reduced by an appropriate reductant. As an example the decomposition of hydrogen peroxide by leucothionine should be mentioned.

Besides this reactivity the formation of free radicals during the photoreduction of the dye can be of great importance for polymerization.[128] For example, water-soluble vinyl monomers could be polymerized in the presence of rose bengal and a mild reducing agent by visible light.[125,236] In this context it should be mentioned that the creation of short-lived radicals could be detected with flash photolytic studies. For example,

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[232] G. Oster and J. S. Bellin, *J. Am. Chem. Soc.* **79,** 294 (1957).

[233] A. A. Krasnovsky, *Dokl. Akad. Nauk SSSR* **60,** 421 (1948).

[234] G. Oster, J. S. Bellin, and S. B. Broyde, *J. Am. Chem. Soc.* **86,** 1313 (1964).

[235] G. Oster, S. B. Broyde, and J. S. Bellin, *J. Am. Chem. Soc.* **86,** 1309 (1964).

[236] G. Oster, *Nature* **173,** 300 (1954).

Zwicker and Grossweiner[237] observed the semireduced radical monoanion and dianion in the aqueous solutions of eosin. Such transient radical intermediates could also be found during the photoreduction of eosin by ethanol[111,238] or phenol,[239] or as a result of a photoreaction between eosin and amino acids or proteins.[240] Furthermore, in studies of the photoreduction of acridine in ethanol,[241] of uranine in basic alcoholic solutions,[242] of fluorescein[243] by allylthiourea or *p*-phenylenediamine,[108,244] or lumiflavin, riboflavin and its phosphate,[80,119,189,245,246] and of safranine T,[247] radicals could be detected which are created by an electron or hydrogen transfer from the solvent or solute to the dye.

The photoreduction of a dye by external reducing agents may change special photodecomposition reactions of a dye. For instance, instead of an oxidation of the ribityl group in the presence of dissolved reducing agents like methionine, EDTA, or ascorbic acid these agents are oxidized in the anaerobic photobleaching of riboflavin. In other words, EDTA or ascorbic acid have a protecting action on the ribityl group.[80,179]

In most studies on the photoreduction of dyes relatively simple reducing agents have been used. For example, primary and secondary alcohols, ketones and carboxylic acids which contain methyl, methylene, or methine groups adjacent to the carbonyl function, ethers, esters, amines, inorganic ions, etc., act as electron or as hydrogen donors. By the analogy in structure it is to be expected that cellulose (e.g., cotton) and keratin (e.g., wool) can react in the same way. Often the hydrogen-atoms which are abstracted are bound to the reactive methyl, methylene, and methine groups of the reductants, and such groups can also be found in the fibrous materials. The fact that flash photolysis of aqueous eosin solutions containing tyrosine, tryptophan, or ovalbumin seems to produce semireduced eosin on the one hand and tyrosyl and indolyl radicals on the other[240] speaks in favor of a hydrogen-atom transfer of the kind mentioned above.

d. Triplet State as Intermediate. In a series of experiments clear evidence could be obtained that the reactive state of the dyes which are

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[237] E. F. Zwicker and L. I. Grossweiner, *J. Phys. Chem.* **67**, 549 (1963).

[238] S. Kato and M. Koizumi, *Nature* **184**, 1020 (1959).

[239] L. Grossweiner and E. Zwicker, *J. Chem. Phys.* **34**, 1411 (1961).

[240] L. Grossweiner and E. Zwicker, *J. Chem. Phys.* **39**, 2774 (1963).

[241] A. Kira, S. Kato, and M. Koizumi, *Bull. Chem. Soc. Japan* **39**, 1221 (1966).

[242] M. Imamura, *Bull. Chem. Soc. Japan* **31**, 962 (1958).

[243] G. Oster, G. K. Oster, and G. Karg, *J. Phys. Chem.* **66**, 2514 (1962).

[244] V. Kasche and L. Lindqvist, *Photochem. Photobiol.* **4**, 923 (1965).

[245] B. Holmström and L. Tegnér, *Photochem. Photobiol.* **5**, 205 (1966).

[246] H. Beinert, *J. Am. Chem. Soc.* **78**, 5323 (1956).

[247] A. K. Chibisov, B. V. Skvortsov, A. V. Karyakin, and N. N. Shrindt, *Khim. Vys. Energ.* **1**, 529 (1967).

photoreduced by a reducing agent is the triplet state. The first demonstration of the fact that such photoreductions proceed through long-lived excited triplet states of the dye was given by Oster and co-workers.[100,231] The experiments were based on the observation of Perrin and his students[36,248] that in small concentrations which are sufficient for quenching the phosphorescence in glycerol, potassium iodide strongly inhibits the photobleaching of a dye although the fluorescence is only slightly quenched. By studies of the photoreduction of eosin to the leuco form in aqueous solution with allyl thiourea as reducing agent and *p*-phenylenediamine (PPD) or KI as quenchers a lifetime of the triplet of 9.2×10^{-5} seconds could be obtained. Moreover, by plotting the rate of fading in the absence and presence of the quenching molecules Stern-Volmer expressions corresponding to Eq. (32) could be obtained which gave other quenching constants than in the case of fluorescence quenching. It could be shown that KI is about a hundred times as effective as PPD in quenching the triplet state of eosin, and moreover KI in quenching triplets is about a hundred times more effective than in quenching singlets.[100] In these studies, important values of the quantum yield for the triplet formation could firstly be obtained, e.g., $\phi_T = 0.21$ in the case of methylene blue.[101] By the help of quenching experiments it could also clearly be demonstrated that the reductive photobleaching of riboflavin passes through a triplet state.[80,119,182]

The direct proof of the correctness of this interpretation of quenching experiments, i.e., of the formation of a long-lived triplet, has been possible by the flash method. It was shown that by means of a short flash a short-lived transient absorption occurred which, in the presence of a reducing agent, was followed by further transient absorptions corresponding to the formation of semiquinone, etc. In such experiments a clear distinction between triplet and semiquinone is possible because of the different transient absorption and the different sensitivity to oxygen or iodide ions in small concentrations.[188] See, e.g., the studies on the photoreduction of acridine in ethanol,[241,249] eosin in ethanol,[111,240] thionine with allylthiourea,[250] and other flash studies.[80,91,108,216,237–239,244,247,251–253]

e. Kinetic Results

i. Overall quantum yield. The photoreduction depends on a series of conditions as discussed above. Therefore, the overall quantum yields of

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[248] F. Perrin, *Compt. Rend.* **184,** 1121 (1927).

[249] R. Kellmann and J. T. Dubois, *J. Chem. Phys.* **42,** 2518 (1965).

[250] H. Fischer, *Z. Physik. Chem.* (*Frankfurt*) [N.S.] **43,** 177 (1964).

[251] L. I. Grossweiner and E. F. Zwicker, *J. Chem. Phys.* **31,** 1141 (1959).

[252] S. Matsumoto, *Bull. Chem. Soc. Japan* **37,** 491 (1964).

[253] R. M. Danziger, K. H. Bar-Eli, and K. Weiss, *J. Phys. Chem.* **71,** 2633 (1967).

dye photoreduction vary over a large range. For example, the quantum yield of photoreduction of the thionine–stannous chloride system is nearly unity,[127] and for the chlorophyllin–ascorbic acid system $\phi_B = 0.01–0.001$.[248] Other values, some of which are discussed in a review by Bourdon and Schnuriger,[254] are as follows: acridine dyes–allylthiourea, $\phi_B \leqslant 0.01$[101]; fluorescein–allylthiourea, $\phi_B = 0.01 - 0.1$[231]; thionine–anethole, $\phi_B = 0.1 - 0.27$[8]; methylene blue–allylthiourea, $\phi_B = 0.01$[9]; methylene blue–EDTA, $\phi_B \leqslant 0.01$[9]; eosin–allylthiourea, $\phi_B \leqslant 0.092$[100,255]; triphenylmethanes (adsorbed on polymers), $\phi_B = 0.001–0.1$[232]; eosin–EDTA, $\phi_B = 0.01$[255]; proflavine–allylthiourea, $\phi_B \leqslant 0.01$.[116,230]

In a series of experiments it could be shown that usually the photoreduction of dye solutions in the presence of reducing agents is of the pseudo first order. That is, the relation between $\ln\{\exp(\alpha[D]d) - 1\}$ or $\log(\text{O.D.} - 1)$ and time is linear as derived in Eqs. (15)–(20). This relation holds in cases in which the dye concentration is not too high and the concentration of the reductant is not too low, e.g., in the photoreduction of methylene blue with EDTA with an EDTA concentration $>1.0 \times 10^{-4}\,M$ and a dye concentration $<10^{-5}\,M$.[9] Under such conditions the quantum efficiency can easily be calculated from the slope of the $\log(\text{O.D.} - 1)$ time plots by help of Eq. (20) (Section I,B,1,c). Corresponding to the pseudo-first-order character of such photoprocesses ϕ_B [Eq. (20)] and $k_{L,I}$ [Eq. (28)], respectively, depend on the concentration of the reductant (Fig. 10).

ii. Switchover from first-order to second-order photobleaching. When the concentration of the reducing agent is decreased there may be a switchover from first-order photobleaching to a second-order reaction

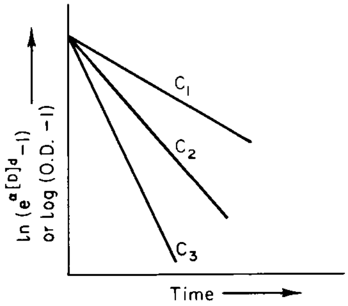

FIG. 10. Scheme of log(O.D. — 1)–time plots of photoreductions in the presence of a reducing agent (with concentrations $C_1 < C_2 < C_3$).

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[254] J. Bourdon and B. Schnuriger, *Phys. Chem. Org. Solid State* **3**, 59–131 (1967).
[255] T. Ohno, Y. Usui, and M. Koizumi, *Bull. Chem. Soc. Japan* **38**, 1022 (1965).

with regard to the dye. This can be observed by the annulling of the linearity of the log(O.D. — 1)–time plot and the possibility of describing the photobleaching process by Eq. (29), i.e., by a linear plot between 1/O.D. and time.

A switchover from one mechanism to another was for the first time observed by Koizumi and co-workers[255] in connection with the photoreduction of eosin by allylthiourea, and during the photoreduction of methylene blue by allylthiourea and EDTA.[8] The second-order process can be taken as analogous to the photobleaching of thiazine dyes which undergo a photoreaction in the absence of any reductant. In such a photoreaction the primary process results from an electron transfer between the dye in the triplet state and in the ground state (D–D mechanism[191,193,256,257]). This means that in the case of a relatively high concentration of the reducing agent there is the usually observed D–R mechanism with an electron transfer or hydrogen transfer from the reductant to the dye which follows as a result of lowering the reductants by a D–D mechanism.

iii. Quantum efficiency of intersystem crossing from $S_1 \rightarrow T_1$. Besides the statements on the overall quantum yield ϕ and on the bleaching mechanism, kinetic experiments give valuable data of the quantum efficiencies and rate constants of various primary processes [see Eq. (1)]. Above all the fundamentally important transition probability of the first singlet excited state to the triplet state, i.e., the triplet quantum efficiency $\varphi_{\mathrm{S-T}}$, can be measured:

(1) A simple method for determination $\varphi_{\mathrm{S-T}}$ values is based on photoreactions which are characterized by a definite reaction of the triplets of the dye. For example, such conditions obtain in photoreductions which lead to leuco dyes. Corresponding to Section I,B,3 and the scheme of Fig. 11A we have

$$\mathrm{D} + h\nu = \mathrm{D_T} \qquad d[\mathrm{D_T}]/dt = \varphi_{\mathrm{S-T}} I_{\mathrm{A}} \tag{46a}$$

$$\mathrm{D_T} = \mathrm{D} + \text{heat} \qquad -d[\mathrm{D_T}]/dt = k_{\mathrm{d}}[\mathrm{D_T}] \tag{46b}$$

$$\mathrm{D_T} + \mathrm{R} = \mathrm{P} \qquad -d[\mathrm{D_T}]/dt = k_{\mathrm{r}}[\mathrm{R}][\mathrm{D_T}] \equiv d[\mathrm{P}]/dt \tag{46c}$$

With the steady-state condition $d[\mathrm{D_T}]/dt = 0$ one obtains

$$\varphi_{\mathrm{S-T}} I_{\mathrm{A}} = k_{\mathrm{d}}[\mathrm{D_T}] + k_{\mathrm{r}}[\mathrm{R}][\mathrm{D_T}] \qquad \text{and} \qquad [\mathrm{D_T}] = \frac{\varphi_{\mathrm{S-T}} I_{\mathrm{A}}}{k_{\mathrm{d}} + k_{\mathrm{r}}[\mathrm{R}]} \tag{46d}$$

Equations (46d) and (46c) give

$$d[\mathrm{P}]/dt = \frac{\varphi_{\mathrm{S-T}} k_{\mathrm{r}}[\mathrm{R}] I_{\mathrm{A}}}{k_{\mathrm{d}} + k_{\mathrm{r}}[\mathrm{R}]} \tag{46e}$$

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[256] M. Koizumi, H. Obata, and S. Hayashi, *Bull. Chem. Soc. Japan* **37**, 108 (1964).

[257] S. Kato, M. Morita, and M. Koizumi, *Bull. Chem. Soc. Japan* **37**, 117 (1964).

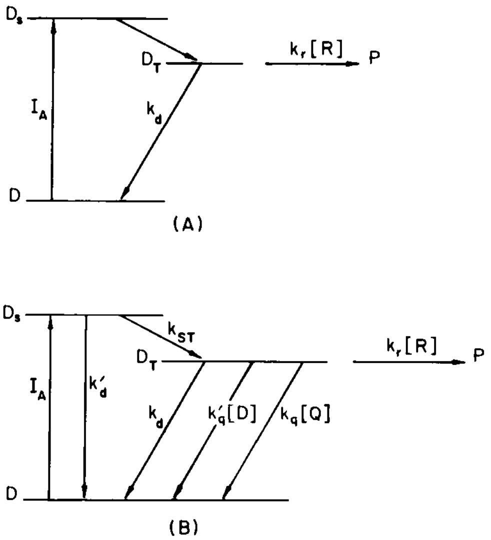

FIG. 11. Scheme for determination φ_{S-T} in photoreductions. (A) Case 1. (B) Case 2.

Because of

$$\phi = \frac{d[P]/dt}{I_A}$$

it follows that

$$\phi = \frac{\varphi_{S-T} k_r[R]}{k_d + k_r[R]} \tag{46f}$$

For calculating φ_{S-T} we get

$$\frac{1}{\phi} = \frac{1}{\varphi_{S-T}} + \frac{1}{\varphi_{S-T}} \frac{k_d}{k_r[R]} \tag{46g}$$

By plotting $1/\phi$ against $1/[R]$ we get a straight line with $1/\varphi_{S-T}$ as an intercept on the $1/\phi$ ordinate.

(2) By taking into consideration the different possibilities of deactivation of the excited singlet and triplet state (e.g., radiationless and radiative transitions, quenching by the unexcited dye or any other quencher Q) Oster, Koizumi, and their co-workers[9,100,231,255] obtained more exact values of φ_{S-T}. Moreover, the influence of an enhancement of the concentration of the dye, reductant, and other foreign molecules could be measured and important rate constants of the different primary processes could be obtained. Corresponding to Fig. 11B the following kinetic scheme holds:

$$\begin{array}{rclll}
 & & & \text{Rate} & \\
\mathrm{D} + h\nu & = & \mathrm{D_S} & I_\mathrm{A} & (47\mathrm{a}) \\
\mathrm{D_S} & = & \mathrm{D} & k'_\mathrm{d}[\mathrm{D_S}] & (47\mathrm{b}) \\
\mathrm{D_S} & = & \mathrm{D_T} & k_\mathrm{ST}[\mathrm{D_S}] & (47\mathrm{c}) \\
\mathrm{D_T} + \mathrm{R} & = & \mathrm{P} & k_\mathrm{r}[\mathrm{R}][\mathrm{D_T}] & (47\mathrm{d}) \\
\mathrm{D_T} & = & \mathrm{D} & k_\mathrm{d}[\mathrm{D_T}] & (47\mathrm{e}) \\
\mathrm{D_T} + \mathrm{D} & = & 2\mathrm{D} & k'_\mathrm{q}[\mathrm{D}][\mathrm{D_T}] & (47\mathrm{f}) \\
\mathrm{D_T} + \mathrm{Q} & = & \mathrm{D} + \mathrm{Q} & k_\mathrm{q}[\mathrm{Q}][\mathrm{D_T}] & (47\mathrm{g})
\end{array}$$

During the photobleaching the product P is formed with the reaction rate $d[\mathrm{P}]/dt = k_\mathrm{r}[\mathrm{D_T}][\mathrm{R}]$ which corresponds the photofading rate $—d[\mathrm{D}]/dt$.

Because of the short lifetimes of the excited species relative to P the steady-state assumption is possible, so that

$$I_\mathrm{A} = k'_\mathrm{d}[\mathrm{D_S}] + k_\mathrm{ST}[\mathrm{D_S}]; \qquad \text{or} \qquad [\mathrm{D_S}] = \frac{I_\mathrm{A}}{k'_\mathrm{d} + k_\mathrm{ST}} \tag{48a}$$

For the triplet formation we can write

$$k_\mathrm{ST}[\mathrm{D_S}] = k_\mathrm{r}[\mathrm{R}][\mathrm{D_T}] + k_\mathrm{d}[\mathrm{D_T}] + k'_\mathrm{q}[\mathrm{D}][\mathrm{D_T}] + k_\mathrm{q}[\mathrm{Q}][\mathrm{D_T}] \tag{48b}$$

$$[\mathrm{D_T}] = \frac{k_\mathrm{ST}[\mathrm{D_S}]}{k_\mathrm{r}[\mathrm{R}] + k_\mathrm{d} + k'_\mathrm{q}[\mathrm{D}] + k_\mathrm{q}[\mathrm{Q}]} \tag{48c}$$

By introducing Eq. (48a) into Eq. (48c) it follows for the bleaching rate that

$$-\frac{d[\mathrm{D}]}{dt} = +\frac{d[\mathrm{P}]}{dt} = \frac{k_\mathrm{ST}k_\mathrm{r}[\mathrm{R}]I_\mathrm{A}}{(k'_\mathrm{d} + k_\mathrm{ST})(k_\mathrm{r}[\mathrm{R}] + k_\mathrm{d} + k'_\mathrm{q}[\mathrm{D}] + k_\mathrm{q}[\mathrm{Q}])} \tag{48d}$$

In Eq. (48d) the expression $k_\mathrm{ST}/(k'_\mathrm{d} + k_\mathrm{ST})$ corresponds to the quantum efficiency of S → T intersystem crossing

$$\varphi_\mathrm{S-T} = \frac{d[\mathrm{D_T}]/dt}{I_\mathrm{A}} = \frac{k_\mathrm{ST}[\mathrm{D_S}]}{I_\mathrm{A}} = \frac{k_\mathrm{ST}}{k'_\mathrm{d} + k_\mathrm{ST}} \tag{49}$$

because of Eq. (48a). The quantum yield of the overall photoprocess is given by

$$\phi = \frac{-d[\mathrm{D}]/dt}{I_\mathrm{A}} = \frac{\varphi_\mathrm{S-T}k_\mathrm{r}[\mathrm{R}]}{k_\mathrm{r}[\mathrm{R}] + k_\mathrm{d} + k'_\mathrm{q}[\mathrm{D}] + k_\mathrm{q}[\mathrm{Q}]} \tag{50}$$

By taking the inverse plot one gets

$$\frac{1}{\phi} = \frac{1}{\varphi_\mathrm{S-T}} + \frac{k_\mathrm{d} + k'_\mathrm{q}[\mathrm{D}]}{\varphi_\mathrm{S-T}k_\mathrm{r}}\,\frac{1}{[\mathrm{R}]} + \frac{k_\mathrm{q}[\mathrm{Q}]}{\varphi_\mathrm{S-T}k_\mathrm{r}[\mathrm{R}]} \tag{51}$$

Without quenching additives ($[\mathrm{Q}] = 0$) a plot of $1/\phi$ versus $1/[\mathrm{R}]$ should be linear, so that from the intercept (corresponding to the quantum yield at infinite reductant concentration) values of $1/\varphi_\mathrm{S-T}$ can be calculated. Moreover with constant $[\mathrm{R}]$ a plot of $1/\phi$ versus $[\mathrm{D}]$ should be linear. Likewise with constant [D] and [R] the $1/\phi$ vs. [Q] plots should be linear. From the slopes of these plots one gets with known $\varphi_{S\text{-}T}$, values of k_d, k_r, k_q, and k'_q; see references 9, 100, 231, and 255. With allylthiourea as reducing agent $\varphi_{S\text{-}T} = 0.092\text{–}0.15$ for eosin, and $\varphi_{S\text{-}T} = 0.020$ for erythrosin have been measured.[100,255] Values of k'_q and k_r are in the order of 10^8 and 10^5, respectively. In the photoreduction process of benzophenone by benzylhydrol $\varphi_{S\text{-}T} = 1$ for benzophenone could be determined.[120,258] In order to get an insight into the quenching action of different compounds Eq. (50) must be transformed into a Stern-Volmer expression corresponding to Eq. (32). Instead of the quantum yields ϕ_0, ϕ_Q (i.e., with and without quencher) the rates of bleaching R_0 and R_Q can be inserted. Because of the proportionality between the rate of fading for a given initial dye concentration and the *initial* slope of fading curves [O.D. plot against time; see Eq. (22)] R_0 and R_Q may be determined from these curves.

$$\frac{R_0}{R_Q} = 1 + \frac{k_q}{k_r[R] + k_d + k'_q[D]}[Q] \tag{52}$$

By a comparison of the quenching constants $K_q = k_q/(k_r[R] + k_d + k'_q[D])$ the effectiveness of different compounds in quenching triplet states can be determined. For example, K_q (KI) $> K_q$ (*p*-phenylenediamine). Oxygen also is characterized by a great quenching effectiveness against triplets.[259]

(3) Besides the photoreduction principle of $\varphi_{S\text{-}T}$ determination the following methods have been used: Chemical spectroscopy, which is a triplet counting method based on the triplet-sensitized cis–trans isomerization of piperylene (1,3-pentadiene)[260,261]; methods which depend on light emission processes[55,262,263]; measurements of yields and lifetimes of radiative processes [see Eq. (49)][264-268]; measurements of small changes

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[258] G. S. Hammond, W. P. Baker, and W. M. Moore, *J. Am. Chem. Soc.* **83**, 2795 (1961).

[259] R. Livingston, *Record Chem. Progr.* (*Kresge-Hooker Sci. Lib.*) **16**, 13 (1955).

[260] A. A. Lamola, Ph.D. Thesis, California Institute of Technology, Pasadena, California, 1965 (cited in Turro,[2] pp. 130–131).

[261] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.* **43**, 2129 (1965).

[262] R. E. Kellog and R. G. Bennett, *J. Chem. Phys.* **41**, 3042 (1964).

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[264] C. A. Parker and C. G. Hatchard, *Analyst* **87**, 664 (1962).

[265] G. Weber and F. W. Teale, *Trans. Faraday Soc.* **53**, 646 (1957).

[266] A. S. Cherkasov, V. A. Mochanov, T. M. Vember, and K. G. Voldaikina, *Soviet Phys. "Doklady"* (*English Transl.*) **1**, 427 (1957).

[267] E. C. Lim, *J. Chem. Phys.* **36**, 3497 (1962).

[268] V. L. Ermolaev, *Opt. Spectry.* (*USSR*) (*English Transl.*) **11**, 266 (1961); **13**, 49 (1962).

in optical density under chopped cross illumination[269]; and flash methods.[41,55,270-273]

In Table I some φ_{S-T} values are given. These data show that triplets are formed in solutions for many dyes with a great quantum efficiency. Moreover, the influence of the intramolecular heavy atom effect, which has been described in Eq. (36) (see Section I,C,2,b,*ii*) in combination with Eq. (49) is demonstrated: φ_{S-T} depends on the atomic number of

TABLE I

TRIPLET QUANTUM EFFICIENCIES φ_{S-T}

Compound	*Solvent*	φ_{S-T}	φ_F	*References*
Chlorophyll a	Ether	0.64	0.32	41
	3-Me pentane	<0.10	<0.01	41
Chlorophyll b	Ether	0.88	0.12	41
	3-Me pentane	0.17	<0.01	41
Fluorescein (F)	Aqueous	0.05	0.92	270
	Aqueous	0.02	—	100
Dibromfluorescein (FBr_2)	Aqueous	0.49	—	270
Eosin (FBr_4)	Aqueous	0.71	0.19	270
	Aqueous	0.15	—	255
	Glycerol	0.06	—	274
	Ethanol	0.02	—	274
Erythrosine (FI_4)	Aqueous	1.07	0.02	270
	PVA films	0.94	—	272
Methylene blue	Aqueous	0.21	—	101
	Aqueous	0.24	—	9
Anthraquinone	—	0.90	—	261
Acridine	—	0.76	—	275
1,1′-Diethyl-2,2′-cyanine iodide[1]	PVA films	0.02	0.12	272
1,1′-Diethyl-6-bromo-2,2′-cyanine iodide	PVA films	0.08	0.10	272
1,1′-Diethyl-6-iodo-2,2′-cyanine iodide	PVA films	0.25	0.11	272
1-Nitronaphthalene	—	0.63	—	276

[1] Structure of 2,2′-cyanine dyes, in (VIII) X = H, Br, or I.

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[269] H. Labhardt, *Helv. Chim. Acta* **47,** 2279 (1964).

[270] P. G. Bowers and G. Porter, *Proc. Roy. Soc.* **A299,** 348 (1967).

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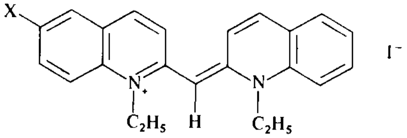
[274] C. A. Parker and C. G. Hatchard, *Trans. Faraday Soc.* **57,** 1894 (1961).

[275] A. R. Horrocks and F. Wilkinson, unpublished data (cited in Wilkinson and Dubois[392]).

[276] R. Hurley and A. C. Testa, *J. Am. Chem. Soc.* **90,** 1949 (1968).



(VIII)

substituting elements, e.g., in cyanines (VIII), and in addition on the number of heavy substituents, e.g., in xanthene dyes. In this context it should be mentioned that by application of the intramolecular heavy atom effect a determination of φ_{S-T} is possible because of the connection between the quantum efficiency of fluorescence and intersystem crossing from the lowest excited singlet to the triplet state. With molecules containing different heavy atoms the fluorescence is quenched by an enhanced formation of triplets.[271] The correlation which has been determined

$$\varphi_F + \varphi_{S-T} \approx 1 \tag{53}$$

by Porter and Bowers[41] for the chlorophylls in polar solvents (e.g., ether) and for xanthene dyes shows that the radiationless transition from the excited singlet to the ground state may often be quite small, similar to polyacenes and other compounds.[55,68,261,277,278] However, the values of φ_F and φ_{S-T} are low for chlorophylls—similar to other compounds[273,279]—in nonpolar solvents (pure hydrocarbons) in which chlorophyll molecules are dimerized.[280] This observation may be important in explaining the influence of the environment and the state of aggregation on the photochemical behavior of the chlorophylls in the chloroplast.[199,281-285] It should be pointed out that the formation of aggregates can influence triplet formation in different ways. As in chlorophylls the formation of aggregates reduces the triplet state formation in aromatic amino acids, purines, and nucleosides.[286] In contrast with chlorophylls the quantum efficiency

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[277] V. L. Ermolaev and E. B. Sveshnikova, *Opt. Spectry. (USSR) (English Transl.)* **16,** 320 (1964).

[278] J. D. Laposa, E. C. Lim, and R. E. Kellogg, *J. Chem. Phys.* **42,** 3025 (1965).

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[281] A. Müller, B. Rumberg, and H. T. Witt, *Proc. Roy. Soc.* **B157,** 313 (1963).

[282] J. C. Goedheer, *Biochim. Biophys. Acta* **51,** 494 (1961).

[283] G. W. Robinson, *Proc. Natl. Acad. Sci. U. S.* **49,** 521 (1963).

[284] J. Franck, J. L. Rosenberg, and C. Weiss, Jr., *in* "Luminescence of Organic and Inorganic Materials" (H. P. Kallman and G. M. Spruch, eds.), pp. 11-29. Wiley, New York, 1962.

[285] G. Porter and G. Strauss, *Proc. Roy. Soc.* **A295,** 1 (1966).

[286] C. Helene, R. Santus, and M. Ptak, *Compt. Rend.* **262,** 1349 (1966).

of triplet formation may be increased by the formation of dimers or aggregates, e.g., in cyanine dyes, under certain conditions. This effect, which can be expected from mechanisms postulated by Förster and Scheibe,[14,287,288] has been demonstrated by West *et al.*[289] using phosphorescence experiments in concentrated solutions, and has been considered in connection with possible changes in the quantum yield of photochemical reactions with increasing dye concentration.[254] Some values of quantum efficiences $\varphi_{S\text{-}T}$ of cyanines are given in Table I. The $\varphi_{S\text{-}T}$ and φ_F values are not very high, so that in discussing mechanisms of spectral sensitization in photography which are based on the production of triplets (e.g., triplet–triplet annihilation[290]) the relatively high quantum efficiencies of the S_1–S_0 radiationless decay must not be disregarded.

3. *Photooxidation*

a. Mechanism

i. Earlier mechanisms. The photobleaching of dyes by an oxidation of the dye was clearly demonstrated in the 1930s by Weigert, Hibbert, and others.[291-294] The finding of the oxidation products of dyes on faded cotton,[292,293,295,296] e.g., isatin as the oxidation product of indigo,[289] has proved that the dye can be photooxidized. The necessity for oxygen for a photooxidation[297] and the possibility of both photooxidation and photoreduction of the same dye in solution was shown.[298] However, oxygen was not postulated as a direct oxidizing agent of the excited dyes.[298-300] For example, in aqueous solutions, a splitting of water into hydrogen atoms and hydroxyl radicals has been discussed by Hillson and Rideal.[298] The excited dye should react with water according to

$$D + h\nu = D^*, \qquad D^* + HOH = DOH\cdot + H\cdot$$

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[287] T. Förster, *Naturwissenschaften* **33**, 166 (1946).

[288] G. Scheibe, *Z. Elektrochem.* **52**, 283 (1948).

[289] W. West, A. V. Buettner, and W. Cooper, *Congr. Intern. Phot. Sci., Paris, 1965* p. 315. Focal Press, London, 1967.

[290] J. E. Lu Valle, *Symp. Spectral Sensitization, Bressanone, 1967* p. 207. Focal Press, London, 1970.

[291] E. Hibbert, *J. Soc. Dyers Colourists* **43**, 292 (1927).

[292] R. Halbert and G. Ziersch, *Melliand Textilber.* **10**, 951 (1929).

[293] R. Halbert and G. Ziersch, *Angew. Chem.* **43**, 209 (1930).

[294] F. Weigert, *Z. Physik.* **5**, 410 (1921); *Naturwissenschaften* **9**, 583 (1921).

[295] M. Couper, *Textile Res. J.* **21**, 720 (1951).

[296] H. C. A. van Beek and P. M. Heertjes, *J. Chem. Soc.* **80**, 83 (1962).

[297] P. Lasareff, *Trans. Faraday Soc.* **21**, 475 (1925).

[298] P. J. Hillson and E. K. Rideal, *Proc. Roy. Soc.* **A216**, 458 (1953).

[299] H. F. Blum and C. R. Spealman, *J. Phys. Chem.* **37**, 1123 (1933).

[300] M. Koizumi, Z. Kuroda, and W. Watanabe, *J. Inst. Polytech. Osaka City Uni.* **C2**, 1 (1951).

and the free hydrogen atoms (which try to reduce the oxidation of the dye) may produce $HO_2\cdot$radicals by a reaction with oxygen. From the reactions of these radicals the production of H_2O_2, which can oxidize the dye both in the dark and during illumination, seems possible. For example, azo dyes should be photodecomposed to colorless azooxy compounds by such mechanisms.

Blum and Spealman,[299] who studied the photooxidative bleaching of xanthene dyes by oxygen, postulated the decomposition of the dye by $\cdot OH$ and $HO_2\cdot$ radicals formed by the following reactions:

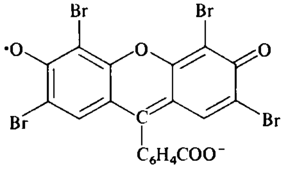
$$D^* + O_2 \rightarrow D + O_2^* \qquad O_2^* + H_2O \rightarrow \cdot OH + HO_2\cdot$$

According to this assumption the production of hydrogen peroxide should not directly be connected with the decomposition of the dye.

ii. Important intermediate species. Flash photolytic work has given strong evidence that the photooxidation of dyes is connected with the formation of a semioxidized species of the dye as the result of an electron transfer between the excited dye and an oxidizing agent.[244] This means that photooxidation can be considered as the reverse of the reaction which occurs during photoreduction. Therefore, the process can simply be described by

$$D + h\nu = D^*, \qquad D^* + O = D_{ox} + O_{red} \tag{54}$$

In the process of photooxidation the dye in the lowest triplet state can be considered as an important intermediate. In this state dyes are oxidized by suitable oxidants,[108-110] e.g., eosin[108] and erythrosine,[108] by potassium ferricyanide, and transformed into semioxidized eosin (IX) and semioxidized erythrosine, respectively.



(IX)

The observation of the attack on triplet states of dyes by oxidants can be taken as strong evidence for the possibility of a direct reaction also between *oxygen* and the triplet state. Therefore, according to Weiss, Imamura, and others,[301-304] photooxidative bleaching seems to be in many

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[301] M. Imamura and M. Koizumi, *Bull. Chem. Soc. Japan* **28,** 117 (1955).

[302] M. Imamura, *J. Inst. Polytech. Osaka City Univ.* **5,** 85 (1956).

[303] J. Weiss, *J. Soc. Dyers Colourists* **65,** 719 (1949).

[304] N. Uri, *Chem. Rev.* **50,** 375 (1952).

cases the result of the primary production of a semioxidized dye radical and a semireduced oxygen molecule.

$$^3D + O_2 \rightarrow D\cdot^+ + O_2\cdot^-$$

iii. Switchover from D–O to D–D mechanism. In discussing the last-mentioned reaction it should be taken into account that, e.g., in the case of fluorescein, permanent products are formed from the semioxidized dye.[108] However, according to the investigations of Imamura *et al.*[301,302,305] the attack of the oxygen on the triplet dye probably occurs only in the case of low concentrations of the dye relative to the oxygen content, i.e., with dye concentrations of the order of $\leqslant 10^{-5}\,M$ because $[O_2] \approx 2.5 \times 10^{-4}\,M$ in air-saturated solutions. Up to a limit of 0.2 of the $[D]/[O_2]$ ratio the photobleaching rate of xanthene dyes shows proportionality to the absorption of light, as can be seen from the linearity of the $\ln\{\exp(\alpha[D]d) - 1\}$ vs. time plot [first-order bleaching corresponding to Eq. (19)]. However, with higher $[D]/[O_2]$ ratios this simple relationship is no longer valid and the bleaching rate is enhanced. With increasing dye concentration the rate of oxygen consumption increases up to a dye concentration of about $10^{-4}\,M$ and then becomes constant. When the dye concentration was high the ratio of the consumed oxygen to the bleached dye was larger than at low concentrations, and furthermore, the production of hydrogen peroxide of about the same quantity as that of the bleached dye could be observed. At low $[D]/[O_2]$ ratios the production of hydrogen peroxide could not be detected. From these results Koizumi *et al.*[266] concluded that there is a switchover from a D–O mechanism at low concentrations of the dye to another mechanism at higher dye concentrations. Koizumi postulated that the mechanism at a higher dye concentration can be considered as a D–D mechanism in which electron transfer between the triplet state and the ground-state dye becomes the decisive process. The possibility of such an electron transfer with a subsequent production of the semireduced and the semioxidized dye has been shown by Lindqvist[108,244] with flash photolytic experiments. For example, the appearance of semireduced eosin with a peak at 405 nm, and of semioxidized eosin with a peak at 462 nm as a result of the electron dismutation reactions

$$^3D + {}^3D \rightarrow D^+ + D^- \qquad {}^3D + D \rightarrow D^+ + D^-$$

and the recombination of these radical species (which are characterized by a lifetime an order of magnitude larger than that of the triplet state) could be demonstrated.

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[305] Y. Usui, K. Itoh, and M. Koizumi, *Bull. Chem. Soc. Japan* **38**, 1015 (1965).

On the basis of these results. Koizumi suggested the following steps for the photooxidative bleaching:

$$^3D + D \rightarrow D^+ \cdot\cdot\cdot\cdot D^-$$
$$D^+ \cdot\cdot\cdot\cdot D^- + O_2 + H^+ \rightarrow HO_2\cdot + D^+ + D$$

and alternatively

$$^3D + D \rightarrow D^+ + D^-$$
$$D^- + H^+ + O_2 \rightarrow HO_2\cdot + D$$

iv. The production of hydrogen peroxide. Because of the influence of experimental conditions and of the nature of the dye on the lifetime of the redox intermediate $D^+ \cdot\cdot\cdot\cdot D^-$, and on the formation of free radicals D^+ and D^-, the quantum yields of photobleaching can sometimes be very different. However, the mechanism explains that the formation of hydrogen peroxide must not be the reason for the photobleaching of the dye: Firstly, the conversion of D^+ into the colorless form is possible, e.g., by reaction with oxygen or by dimerization of D^+. Secondly, by the formation of $HO_2\cdot$, which can eventually reduce D^+ to the original dye, hydrogen peroxide is independently produced by the reaction.[306]

$$2HO_2\cdot \rightarrow H_2O_2 + O_2$$

In discussing the D–O and D–D mechanisms of the photooxidative bleaching one must take into account the possibility of H_2O_2 production from the semireduced oxygen molecule[300] by

$$O_2\cdot^- + H^+ \rightarrow HO_2\cdot \quad \text{and} \quad 2HO_2\cdot \rightarrow H_2O_2 + O_2$$

whereby the $O_2\cdot^-$ radical should be produced in the primary D–O step. In fact, there exists information on the possibility of such a process from photolytic work [108,110] which has proved that oxygen can act both as physical [Eq. (55a)] and chemical quencher [Eq. (55b)].

$$^3D + O_2 \rightarrow D + O_2 \tag{55a}$$
$$^3D + O_2 \rightarrow D^+ + O_2\cdot^- \tag{55b}$$

The rate constant of the $^3D + O_2$ reaction which leads to the $D^+ \ldots O_2^-$ species is of the order of $2.5\text{–}3.1 \times 10^8\ M^{-1}\ \text{sec}^{-1}$.[307] The production of H_2O_2 by the participation of $O_2\cdot^-$ was observed in the case of an excitation of dyes (e.g., acriflavine, eosin, vat dyes) and white pigments (e.g., zinc oxide, zinc sulfide), respectively, in the presence of oxygen and water.[308]

v. Formation of $[D \cdot\cdot\cdot\cdot O_2]$ *complexes.* Besides the production of

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[306] J. G. Calvert, K. Theurer, G. T. Rankin, and W. McNevin, *J. Am. Chem. Soc.* **76,** 2575 (1954).

[307] Y. Usui and M. Koizumi, *Bull. Chem. Soc. Japan* **40,** 440 (1967).

[308] G. S. Egerton, *Nature* **204,** 1153 (1964).

semioxidized dye radical and the semireduced oxygen molecule, which leads to hydrogen peroxide, the formation of a metastable intermediate photoperoxide with a lifetime of $\tau < 10^{-5}$ seconds must be discussed as intermediate in photooxidation process of dyes. The production of this metastable photoperoxide between the dye triplet and oxygen $[D \cdot \cdot \cdot \cdot O_2]$ has been postulated by Schenck[309-312] and discussed with the help of kinetic and other experiments as a collision,[313] charge-transfer,[314] or radical complex.[315,316] In this context, it should be mentioned that Havemann and co-workers[317] found that the photooxidative bleaching of thionine involves the formation of a complex between dye and oxygen [Thionine H^+O_2].

In summary, we see that in the photooxidation of dyes several intermediates can be produced such as semioxidized dye radicals, metastable photoperoxides, $O_2 \cdot^-$, and other species. Because of this variety differences in dye structure and in experimental conditions can result in remarkable differences in oxidative photobleaching. However, there seems to be no doubt that the triplet state is the reactive state of the dye in photooxidation. Moreover, it is important to take into consideration that the dye which is oxidized in the presence of an oxidizing agent may act in several cases as a powerful oxidizing agent. The oxidized dye can oxidize other substances by a transfer of activated oxygen from the peroxide intermediate or by removing electrons, whereby the dye returns to its ground state.

b. Quantum Yields and Dye Classification. The quantum yield for the photobleaching of dyes by an oxidation of the dye is generally very low. For example, the quantum yield ϕ_B for the destruction of the yellow color of acriflavine is of the order of 4×10^{-4}.[127] For cyanines ϕ_B between 10^{-2} and 10^{-3},[318,319] has been measured, and the values are, for thionine 8×10^{-4},[317] and for eosin about 3×10^{-4}.[305]

In discussing photobleaching processes we could see that dyes in the

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[309] G. O. Schenck. *Naturwissenschaften* **35,** 28 (1948); **40,** 205 (1953).

[310] G. O. Schenck, K. G. Knikel, and E. Koch, *Naturwissenschaften* **41,** 425 (1954).

[311] K. Gollnick and G. O. Schenck, "I.U.P.A.C. Symposium on Organic Photochemistry, Strassbourg," pp. 507–526. Butterworth, London and Washington, D. C., 1965.

[312] G. O. Schenck and E. Koch, *Z. Elektrochem.* **64,** 170 (1960).

[313] G. Porter and M. R. Wright, *Discussions Faraday Soc.* **27,** 18 (1959).

[314] H. Linschitz and L. Pekkarinen, *J. Am. Chem. Soc.* **82,** 2411 (1960).

[315] L. Santamaria, *Bull. Soc. Chim. Belges* **71,** 889 (1962).

[316] P. Mauchner and J. Duchesne, *Compt. Rend.* **262,** 705 (1966).

[317] R. Havemann, H. Pietsch, and J. Barnikov, *Z. Wiss. Phot., Photophysik Photochem.* **58,** 125 (1964).

[318] C. Winther, *Z. Wiss. Phot., Photophysik Photochem.* **11,** 92 (1911).

[319] P. Lasareff, *Z. Physik. Chem.* **78,** 557 (1912).

triplet state are generally photoreduced in the presence of a reducing agent, and photooxidized in the presence of an oxidant. However, there exist differences in the reactivity of dyes against photoreduction and photooxidation, which can be seen from differences of quantum yields between dye photoreduction and dye-photosensitized oxidation. According to Bourdon and Schnuriger[254] dyes can be classified into three types corresponding to their photochemical reactivity against oxidizing and reducing agents.

Dyes of Class I are characterized by a higher reactivity for oxygen than for reducing agents. Among those dyes which are fluorescent, photoreducible, and active as photosensitizers, acridines, xanthene-type dyes, thiazines, some porphyrins and riboflavin are included.[320,321] The common feature of these dyes seems to be a triplet (π, π^*) as the lowest excited state.[121,254,322] Taking the quantum yield of the photosensitized oxidation as a criterion for primary dye photooxidation it can be seen that these dyes have a higher probability for reacting with oxygen than with reductants. For example, the quantum yield of photosensitized oxidation (of *p*-toluenediamine) by chlorophyllin is of the order of 0.2–0.7, but that of photoreduction with ascorbic acid is of the order of 0.01–0.001;[234] see further examples in reference 254.

Dyes of Class II are characterized by a high reactivity against reducing agents, i.e., hydrogen donors. These dyes belong above all to vat dyes (i.e., derivatives of anthraquinone, indanthrone, etc.) and have a triplet (n, π^*) state as lowest excited state. They have high phototendering activity.

Dyes of Class III belong, like dyes of Class II, to vat dyes. However, their lowest excited state is triplet (π, π^*), so that they are characterized by photochemical behavior similar to that of dyes of Class I, i.e., these dyes have only a low activity for phototendering, but a noticeable reactivity towards oxygen.

The possibility of dye classification indicates that the structure of the dye is of primary importance for the photoreactivity of dyes in spite of the influence of a series of external factors on photobleaching reactions. According to van Beek and Heertjes,[131] dyes which contain the structures shown in Fig. 12A can act as oxidizing agents, i.e., can be photoreduced in the presence of reducing agents. Dyes which contain the structures of Fig. 12B behave as reducing agents, so that in the

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[320] G. Oster, J. Bellin, R. Kimball, and M. Schrader, *J. Am. Chem. Soc.* **81**, 5095 (1959).

[321] G. O. Schenck, *Z. Elektrochem.* **56**, 855 (1952).

[322] J. W. Sidman, *Chem. Rev.* **58**, 689 (1958).

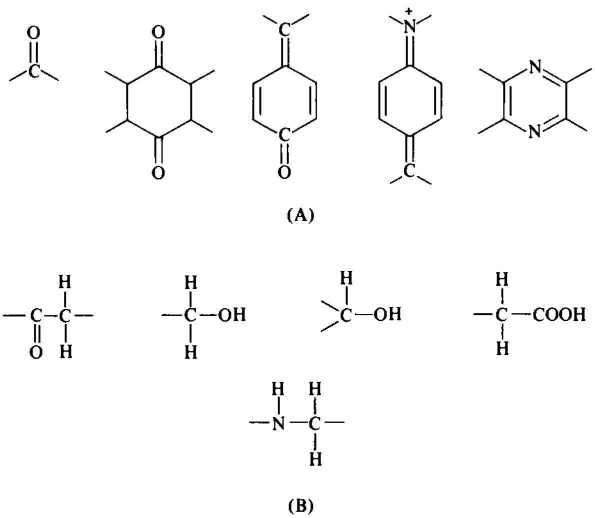
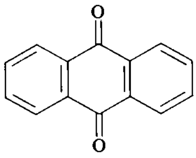


Fig. 12. (A) Structures that give dyes a photooxidizing reactivity against other compounds (corresponding to Class II). (B) Structures which give dyes a photoreducing reactivity, and which can lead to a photooxidation of the dye in the presence of oxygen with subsequent sensitized photooxidation of other compounds (corresponding to Class I).

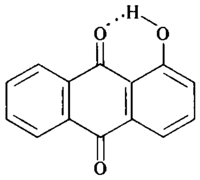
presence of oxygen the dye can be photooxidized as discussed in this section.

In this context it must be stressed that the photochemical activity can be dramatically changed by the addition of groups or substituents to these structures. This can be the result of changing the nature of the lowest excited state (e.g., change of Class I to Class II), or of producing short-lived intramolecular intermediates which can rapidly deactivate the absorbed energy by a radiationless process. The last-mentioned decreasing of activity can be seen from the fact that the strong oxidizing agent anthraquinone (X) becomes inactive by substitution which leads to 1-hydroxyanthraquinone (XI).

In discussing the photobleaching of dyes by photooxidation it should be noted that the photodecomposition can be decreased not only by an



(X)



(XI)

elimination of oxygen. A protection against fading is also observed upon addition of mild reducing agents (e.g., in the case of acriflavine by ascorbic acid[123,124,127]), or binding of the dye to a water-soluble high polymeric acid (e.g., phosphoric acid or nucleic acid[124]). For example, the photooxidation of rose bengal could be stopped by small amounts of polyvinylpyrrolidone.[125]

4. *Photodecomposition of Dyes by Excitation of Other Substances*

a. Principle of the Reaction. Photodecomposition of a dye is possible by the excitation of compounds which, together with dye molecules, are in the same system. In such photochemical processes the foreign molecules F react in their excited state with dye molecules according to the scheme:

$$F + h\nu \rightarrow F^*, \qquad F^* + D \rightarrow F' + \text{Products} \tag{56}$$

Compounds reacting in this manner with dyes are above all the same as those which tend to reduce excited dyes, i.e., hydrogen-donors such as primary and secondary alcohols, ketones, carboxylic acids, amines, and others. The reducing activity of these compounds is strongly enhanced by excitation, so that the hydrogen-atoms of methyl, methylene, or methine groups which are activated by adjacent carboxyl, hydroxyl, amino aryl groups, etc. can be transferred to dyes. In such reactions the action spectrum of dye photodecomposition is determined by the absorption spectrum of the reducing compound and not by that of the dye.

As an example the conversion of azo dyes into the corresponding amines, by mandelic acid, studied by van Beek and Heertjes,[323,324] is given (XII).

b. Wavelength Dependence of Photochemical Reactions. Because of structural analogy with simple compounds fibrous materials can react by excitation with UV light in the same way. This may be the reason for a different reactivity against different wavelengths in many cases. For example, simple direct azo dyes which showed only small photo-

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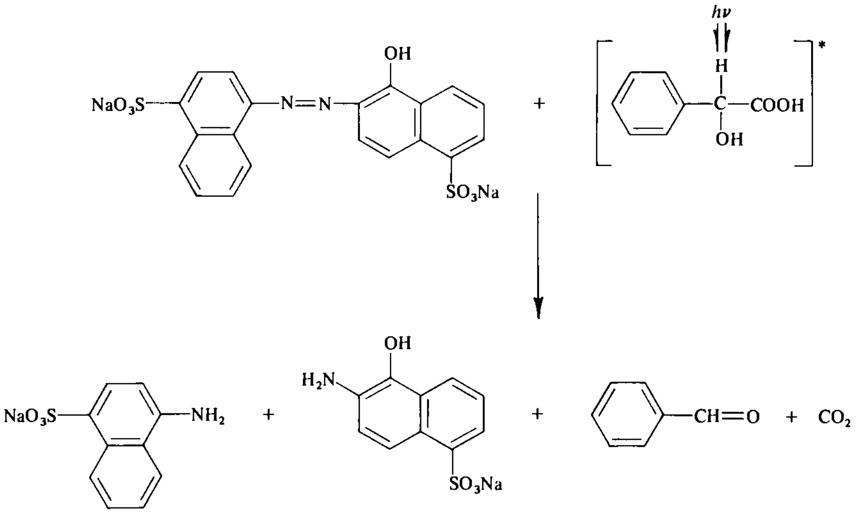
[323] H. C. A. van Beek and P. M. Heertjes, *J. Soc. Dyers Colourists* **79,** 661 (1963).

[324] H. C. A. van Beek and P. M. Heertjes, *J. Phys. Chem.* **70,** 1704 (1966).



(XII)

fading effect on cotton upon irradiation with visible light, were very sensitive when illuminated with UV ($\lambda \sim 360$ nm[325]). 2,2-Diphenyl-1-picrylhydrazyl dissolved in cumene could be photoreduced by UV light ($\lambda = 313$ nm) but not when illuminated in its visible absorption band ($\lambda = 520$ nm) because the isopropyl group of the excited hydrocarbon can be active as reducing agent.[326] It seems to be very probable that fast dyes which are only sensitive to UV below 400 nm are photodecomposed by the absorption of light by a fibrous material.[131]

However, in discussing such reactions the possibility of other mechanisms should be considered. For example, methylene blue, which is normally reduced in the presence of reducing agents with visible light, can be photoreduced without any agent in aqueous solutions with far UV ($\lambda < 250$ nm), but not by excluding this UV region. Probably, the dye in a higher excited singlet state formed by far UV can react with water as the reducing agent.[327] Lumiflavine can also be photoreduced by water to the semiquinone with wavelengths below 340 nm but not when irradiated with visible light.[80] Again, there may be differences in photochemical behavior also as a result of a different reactivity of in-

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[325] R. E. Bedford, *J. Soc. Dyers Colourists* **75**, 37 (1959).

[326] J. N. Pitts, Jr., E. A. Schuck, and J. K. S. Wan, *J. Am. Chem. Soc.* **86**, 296 (1964).

[327] C. A. Parker, *J. Phys. Chem.* **63**, 26 (1959).

dependent electronic systems. Oster[328] observed that in triphenylmethane dyes (e.g., in malachite green) which are capable of being photoreduced and of showing fluorescence only when bound to polymers, excitation of the long-wavelength band caused an effect that was different from the excitation of the short-wavelength band. In methylene blue, chlorophyll, and other dyes the two absorption peaks correspond to two excited successive singlet levels (S_1, S_2), but in triphenylmethane dyes in which not all three phenyl groups are equally substituted the two absorption bands (called x and y bands[329]) are independent electronic systems with a characteristic behavior: On excitation of the longer wavelength dichroic axis with red light the long-wavelength peak disappears with a parallel production of a long-lived intermediate absorbing at 380 nm. The excitation of the short-wavelength dichroic axis with blue light caused a reversible decrease of the two absorption peaks with the production of a long-lived species; similar effects have been found in purines and pyrimidines.[330] It is interesting to see that the production of metastable species (triplet states with a lifetime of 10^{-4} seconds) is not influenced (contrary to xanthene or thiazine dyes) by increasing dye concentration, probably because of the reaction between the singlet excited dye and the unexcited dye ($^1D + D_0 \rightarrow {}^3D + D_0$).[232] Moreover, there is only a small quenching effect by oxygen on bound triphenylmethane dyes.

These examples show that there are several possibilities for differences in reactivity of dyed systems on excitation with different wavelengths. In addition, there also exists the possibility that dyes which are not photoactive under certain conditions, can be photochemically active in binary dye systems. For example, by the excitation of acriflavine, triphenylmethane dyes can be photoreduced in solutions in the presence of reducing agents. Acriflavine serves as photosensitizer for the photoreduction of triphenylmethane dyes.[127]

5. *Photocatalytic Processes*

In photocatalytic processes an excited photocatalyst reacts with the dye or with any other substance in the system with resultant decomposition of the dye and a continuous regeneration of the catalyst. The action spectrum of this photodecomposition of a dye coincides with the absorption spectrum of the photocatalyst. Usually, in these processes the excited catalyst is photoreduced in the first photochemical step by a

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[328] G. Oster and G. K. Oster, *in* "Luminescence of Organic and Inorganic Materials" (H. P. Kallmann and G. M. Spruch, eds.), pp. 186–195. Wiley, New York, 1962.

[329] G. N. Lewis and J. Bigeleisen, *J. Am. Chem. Soc.* **65**, 2102 (1943).

[330] R. F. Stewart and N. Davidson, *J. Chem. Phys.* **39**, 255 (1963).

suitable reducing agent and then reoxidized by an oxidizing compound. With dyes as oxidizing agents the photocatalytic process can lead to an irreversible reduction of dyes. Because of a reoxidization the catalyst is continuously regenerated.

As an example a scheme of the photocatalytic reduction of thionine[331] by ethanol and the catalyst $(FeCl_4)^-$ is given in Fig. 13. Thionine is converted into leucothionine, and ethanol into acetaldehyde without any change of $(FeCl_4)^-$. The reduction of azo dyes by mandelic acid can also take a catalytic course with sodium 9,10-anthraquinone 2-sulfonate as a catalyst.[332]

C. RELATION BETWEEN THE PHOTOREATIVITY OF DYES AND THE NATURE OF THE EXCITED STATES

1. *General Aspects*

The photochemical reactions of dyes which lead to photobleaching or phototendering of fibrous materials depend on several structural factors: on the nature of the excited state from which the reaction can proceed, on the position of this state in relation to other states, on the lifetime, and on the probability of its formation and deactivation by intramolecular and intermolecular effects.

Flash photolytic work and other experiments have shown that many—but not all—photochemical reactions of dyes proceed via the lowest excited triplet state which can be produced under certain conditions with

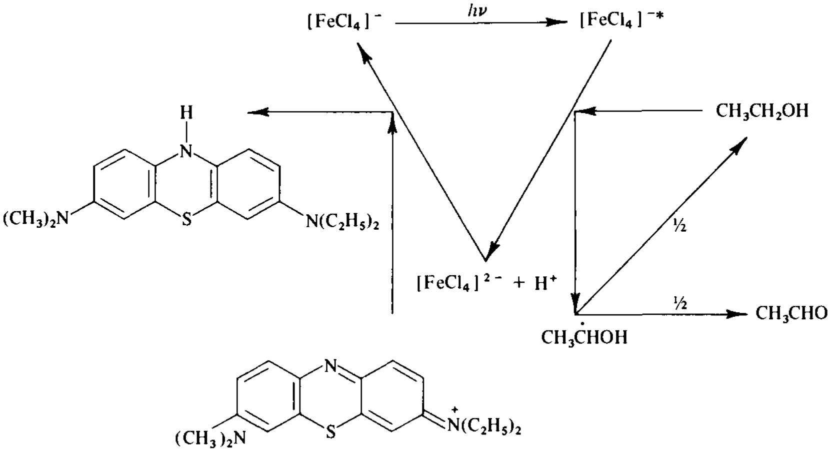

FIG. 13. Photocatalytic reduction of thionine by ethanol with the catalyst $(FeCl_4)^-$.

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[331] G. J. Brealey and N. Uri, *J. Chem. Phys.* **20,** 257 (1952).

[332] H. C. A. van Beek, P. M. Heertjes, and F. M. Visscher, *J. Soc. Dyers Colourists* **81,** 400 (1965).

high efficiency from the lowest excited singlet state by intersystem crossing. However, the course of photochemical reactions depends not only on the singlet or triplet nature of the lowest excited state, but also on its n, π^*; π, π^*; or CT character. The mutual position of these states is not constant in dye classes; it can be changed by substituents and solvents so that the photochemical behavior of dyes of a special class may be remarkably different. At first sight the color of the dye resulting from transitions into the singlet state seems not to be related to photoreactions proceeding via the triplet state. But because of the connection between the probability of triplet state formation and singlet–triplet split, relations between color and photochemistry are possible. Apart from this connection, n, π^* and CT states can influence absorption bands.

It should be stressed that in studying these problems most progress was made by the studies on model systems. The most important results are the following ones.

2. *Results on Model Systems*

a. Vat (Anthraquinoid) Dyes. The model system technique first used by Bolland and Cooper[93] has given significant insight into the mechanism of the fading and phototendering caused by vat dyes. Before the use of this technique a series of regularities had been observed without any possibility of a satisfactory explanation, e.g., the necessity for the presence of oxygen,[333,334] the reduction of the activity by negative (basic electron donor) substituents,[88,335] the greater tendering of anthraquinonoid dyes by substitution in the 2-position than in the 1-position, the definite activity of unsubstituted quinones (anthraquinones, naphthoquinones, dibenzpyrenequinones, or pyranthrone),[85,336] and above all the fact of the marked phototendering activity of yellow and orange vat dyes (which otherwise can show good qualities) with absorption below 550 nm and the inactivity (in most cases) of the green and blue dyes with an absorption in the long-wavelength region ($\lambda > 550$ nm).[337-340]

In the model systems of vat dyes the commercial dyes are replaced

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[333] H. Lanigan, *J. Textile Inst.* **39,** T285 (1948).

[334] R. A. Stillings and J. J. van Nostrand, *J. Am. Chem. Soc.* **66,** 753 (1944).

[335] K. Venkataraman, "The Chemistry of Synthetic Dyes," Vol. II, p. 1247. Academic Press, New York, 1952.

[336] M. R. Fox, *J. Soc. Dyers Colourists* **65,** 523 (1949).

[337] A. Landolt, *Melliand Textilber.* **10,** 533 (1929); **11,** 937 (1930); **14,** 32 (1933).

[338] F. Scholefield and E. H. Goodyear, *Melliand Textilber.* **10,** 867 (1929).

[339] E. Bauer, *Helv. Chim. Acta* **20,** 880 (1937).

[340] D. Ashton, D. Clibbens, and M. E. Probert, *in* "Proceedings of a Symposium on Photochemistry in Relation to Textiles," pp. 66–74. Soc. Dyers Colourists, Bradford, Yorkshire, 1950.

by ketones (e.g., benzophenone) and quinones (e.g., simple anthraquinones), and the textile materials by appropriate organic solvents (ethanol, isopropyl alcohol, etc.). By the study of these systems (flash photolysis,[91,341,342] quantum yield measurements, etc.[120,343-346]) many former observations on the photoreduction of ketones[346] could be explained and a "phototendering mechanism" was postulated. According to this mechanism, in aqueous, nonalkaline solutions there exists an efficient cyclic process in which hydrogen is abstracted from the carbon atom α to the hydroxyl group[93,345] of ethanol by the excited ketone or quinone. The semiquinone radical formed by this photoreaction is relatively stable in deoxygenated irradiated solutions,[91] but it becomes rapidly reconverted to the original quinone in the presence of oxygen so that a renewed excitation and hydrogen abstraction from the "substrate" is possible. In other words, the reaction can be considered as the photosensitized oxidation of alcohols by oxygen in the presence of the quinone. As the hydrogen abstraction with the formation of a semiquinone is possible only with bond energies lower than 100 kcal/mole between R and H of the substrate there can be an intense reaction, e.g., between benzophenone and alcohols or toluene ($E = 75$ kcal/mole) but not with benzene.[343,347] The general scheme is

$$\mathrm{D} + h\nu \rightarrow \mathrm{D}^* \qquad \mathrm{D}^* + \mathrm{RH} \rightarrow \mathrm{DH}\cdot + \mathrm{R}\cdot$$
$$\mathrm{DH}\cdot + \mathrm{O}_2 \rightarrow \mathrm{D} + \mathrm{HO}_2\cdot \qquad \mathrm{R}\cdot + \mathrm{O}_2 \rightarrow \text{Phototendering products}$$

In discussing this scheme the problem which arises on comparing the photosensitized oxidation of ethanol with the photosensitized oxidation of textile fibers (see Egerton *et al.*[96-99,348,349]) should not be overlooked. For example, the desensitization of the cellulose degradation by anthraquinone dyes in the far UV region[350,351] is in contradiction to the intense hydrogen transfer between ethanol and aminoanthraquinone in the far UV, near UV, and visible region. Moreover, it is doubtful whether the reactive part of the dye and an abstractable hydrogen atom of the

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[341] N. K. Bridge and G. Porter, *Proc. Roy. Soc.* **A244**, 259 (1958).

[342] N. K. Bridge and G. Porter, *Proc. Roy. Soc.* **A244**, 276 (1958).

[343] A. Beckett and G. Porter, *Trans. Faraday Soc.* **59**, 2038 (1963).

[344] G. S. Egerton and A. G. Roach, *J. Soc. Dyers Colourists* **74**, 408, 415 (1958).

[345] C. F. Wells, *Trans. Faraday Soc.* **57**, 1703 (1961).

[346] H. L. Bäckström, *Z. Physik. Chem.* **B25**, 99 (1934).

[347] D. Brück and G. Scheibe, *Z. Elektrochem.* **61**, 901 (1957).

[348] G. S. Egerton, J. M. Gleadle, and A. G. Roach, *Nature* **202**, 345 (1964).

[349] G. S. Egerton, N. E. N. Assaad, and N. D. Uffindel, *J. Soc. Dyers Colourists* **83**, 409 (1967).

[350] G. S. Egerton, *J. Soc. Dyers Colourists* **65**, 764 (1949).

[351] G. S. Egerton, E. Attle, F. Guirguis, and M. A. Rathor, *J. Soc. Dyers Colourists* **79**, 49 (1963).

polymer or textile fiber can be in the necessary contact in a series of cases. But, as discussed in this section, the photofading of a dye can proceed with different mechanisms. For instance, in dyed materials without any possibility for direct hydrogen-abstraction the photosensitized degradation of textile fibers, in dry oxygen-containing atmospheres, may be the result of the attack of the fibers by $O_2\cdot^-$ radicals,[308,352] by electronically excited oxygen,[353-355] or by vibrationally excited oxygen,[356,357] i.e., phototendering may occur in a similar manner to the photoreaction of acriflavine or eosine discussed above. In the presence of water vapor, photodegradation of the fiber by hydrogen peroxide is possible.[304,306]

However, in cases of both a good dye–fiber interaction and the presence of abstractable hydrogen atoms, the phototendering may occur above all by a mechanism analogous to that derived from work on model systems. As a decisive consequence of an application of the ketone–alcohol model to the phototendering action of vat dyes on fibers the photochemical reactivity of the dye can be related to the nature of the lowest electronically excited state.[358]

In a series of studies, including flash photolysis, absorption spectroscopic and fluorescence measurements, the photochemically reactive state in quinone-sensitized reactions and the influence of substituents and solvents on the reactivity of this state could be explained; see the papers and reviews of Bridge, Dörr, and others.[5,6,92,121,254,359-366] Nowadays, it is well established that the active state of the ketones and quinones (anthraquinone dyes, etc.) in the hydrogen abstraction process is the n,π^*

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[352] J. Weiss, *Naturwissenschaften* **35,** 610 (1935).

[353] H. Kautsky, H. de Brujn, H. Neuwirth, and W. Baumeister, *Chem. Ber.* **66,** 1588 (1933).

[354] H. Kautsky, *Trans. Faraday Soc.* **35,** 216 (1939).

[355] C. S. Foote, *Accounts Chem. Res.* **1,** 104 (1968).

[356] J. L. Rosenberg and D. J. Shombert, *J. Am. Chem. Soc.* **82,** 3257 (1960).

[357] J. L. Rosenberg and F. S. Humphries, *Photochem. Photobiol.* **3,** 343 (1964); **4,** 1185 (1965).

[358] J. Moran and J. Stonehill, *J. Chem. Soc.* p. 788 (1957).

[359] N. K. Bridge, *J. Soc. Dyers Colourists* **76,** 484 (1960).

[360] E. W. Abrahamson, I. Panik, and K. V. Sakranen, *Proc. 2nd Cellulose Conf., Syracuse, 1959* pp. 127–141. State Univ. Coll. Forestry, Syracuse University, Syracuse, New York; *J. Soc. Dyers Colourists* **76,** 309 (1960).

[361] F. Dörr, *in* "Optische Anregung organischer Systeme. 2nd Internationales Farbensymposium" pp. 732–743 (W. Foerst, ed.), Verlag Chemie, Weinheim, 1966.

[362] G. Eigenmann, *Chimia (Aarau)* **19,** 333 (1965).

[363] K. Nitzl and F. Dörr, *Melliand Textilber.* **45,** 893 (1964).

[364] G. O. Philips and J. C. Arthur, Jr., *Textile Res. J.* **34,** 572 (1964).

[365] Z. Yoshida and F. Takabayashi, *Tetrahedron* **24,** 933 (1968).

[366] J. W. Cumming, C. H. Giles, and A. E. McEachran, *J. Soc. Dyers Colourists* **72,** 373 (1956).

triplet state. Observations of singlet state reactivity of duroquinone (tetramethyl-*p*-benzoquinone) may be the result of an intramolecular reaction.[46,341] The reactivity of the n, π^* triplet state of the carbonyl compounds, which results from a promotion of a nonbonding n electron to the antibonding π (i.e., π^*) orbital followed by rapid intersystem crossing can be demonstrated by a comparison of ground state and n, π^* excited state; see Fig. 14.

The n, π^* state may be considered as a resonance hybrid of two structures with the promoted electron in the oxygen p_x orbital or in the carbon p_x orbital. Besides the enhancement of the total electron density of the π-system in the excited state resulting from the addition of one p_y electron there is also a reduction or reversal of the ground-state polarization $C^{\delta+}{=}O^{\delta-}$ because of the positive and of the negative charges on oxygen and carbon, respectively, in one of the resonance structures. The electron deficiency of the oxygen atom after the removal of the n elec-

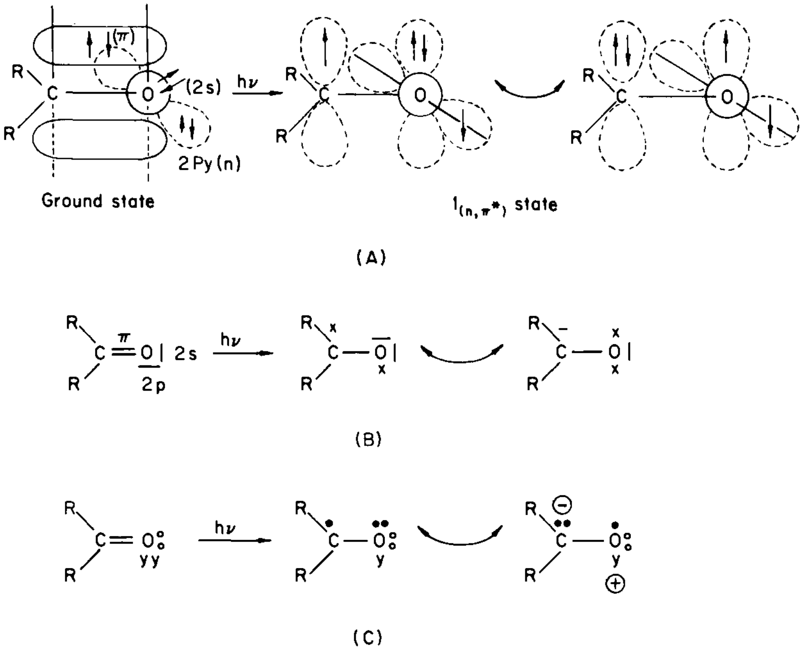

FIG. 14. n–π^* Excitation process: (A) simple atomic orbital representation; (B) usual valence bond notation; (C) notation according to Zimmerman[383] (π-electrons are indicated as solid dots, *s* electrons as circular dots, and the p_y electrons as small *y*'s).

tron leads to an electrophilic center at the carbonyl oxygen[367–369] which, moreover, is characterized by a free radical character[347,370] by way of the small overlapping of the n orbital with other molecular orbitals. Therefore, the n, π^* state of carbonyl compounds has a high reactivity for abstracting a hydrogen atom or an electron from other substances.

In principle, the tendency for hydrogen abstraction may be similar for $^1(n,\pi^*)$ and $^3(n,\pi^*)$. But a better opportunity of reacting comes from the longer lifetime for the triplet than for the singlet state. And as a result of the small singlet–triplet energy difference [see Eqs. (36) and (37)] there is a rapid intersystem crossing from $^1(n,\pi^*)$ to $^3(n,\pi^*)$, so that the $^3(n,\pi^*)$ may usually be the reactive state in carbonyl compounds.

In a series of anthraquinone dyes similar to benzophenone the n, π^* state is the lowest state and hence the reactive one. In such compounds the weak n–π^* transition ($\epsilon_{\max} \sim 20$–100) to the $^1(n,\pi^*)$ state corresponds to the longest wavelength absorption which is followed by an intense π–π^* absorption. In many cases n, π^* transitions can only be detected from spectra of polarized luminescence.[64]

The n–π^* excitation energy of carbonyl compounds is equal to the energy of the CO π-bond of formaldehyde[347] [$E(\text{C}{=}\text{O}) - E(\text{C}{-}\text{O}) \approx$ 80 kcal/mole] including resonance energies of the ground state (E_g) and the excited state (E_e) which are conditioned by the resonance between the carbonyl group and substituting groups, i.e., $h\nu(n \rightarrow \pi^*) = 80 + E_g - E_e$ (kcal/mole) with $E_e > E_g$.[121] Therefore, the wavelength of the n, π^* absorption bands of different carbonyl compounds (ketones, quinones, etc.) usually are in the UV and at the short-wavelength side of the visible region.[371–373] In this context it should be stressed that there is no need for a direct n–π^* excitation. By irradiation in the intense π–π^* absorption band the initially formed $^1(\pi,\pi^*)$ state is transformed rapidly to the n, π^* state by internal conversion, as discussed in Section I,C.

For the distinct reactivity of anthraquinone vat dyes (and other carbonyl compounds) the following points are decisive:

[367] P. L. Goodfriend, F. W. Birss, and A. B. Duncan, *Rev. Mod. Phys.* **32**, 307 (1960).

[368] H. E. Zimmerman, *Advan. Photochem.* **1**, 184–208 (1963).

[369] T. Godfrey, G. Porter, and P. Suppan, *Discussions Faraday Soc.* **39**, 194 (1965).

[370] C. Walling and M. J. Gibian, *J. Am. Chem. Soc.* **86**, 3902 (1964).

[371] J. W. Sidman and D. S. McClure, *J. Am. Chem. Soc.* **77**, 6461 (1955).

[372] T. Anno, I. Matubara, and A. Sado, *Bull. Chem. Soc. Japan* **30**, 168 (1957); **31**, 728 (1958).

[373] A. Kuboyama, *Bull. Chem. Soc. Japan* **31**, 752 (1958).

(1) Substitution by electron-donating groups has only a small effect on the position of n, π^* states, however, π, π^* states may be very strongly lowered because of conjugation with the aromatic nucleus. The weak n–π^* bands usually lying on the long-wavelength side of the spectrum are hidden by intense longest wavelength π–π^* bands.

(2) According to Porter and Suppan[46,48] it is possible that, in compounds with strongly electron-donating groups (such as hydroxy or amino groups), intense intramolecular CT states may be the lowest states.

(3) In compounds with similar positions of n, π^*, π, π^*, and CT states different mutual positions in different solvents are possible. For example, in polar solvents (e.g., alcohol) the $^3(\pi, \pi^*)$ state and the CT state may be the lowest states as a result of the hypsochromic shift of n, π^* states and of the bathochromic shift of π, π^* and CT states, respectively, compared to nonpolar solvents (hydrocarbon).

(4) In the case of π, π^* triplet, and especially, when the CT state is the lowest excited state, there is an electronic shift toward the oxygen of the carbonyl group opposite to the shift which occurs in the n, π^* state. While in the n, π^* state the oxygen of the carbonyl is characterized by a positive charge of one of the resonance structures there is an increasing negative charging of oxygen from the (π, π^*) state towards the (CT) state. Thus, the reactivity of excited molecules for hydrogen and electron abstraction depends on the nature of the lowest excited state: An intense abstraction effect occurs in the n, π^* state, a very small or undetectable effect in the π, π^* state, and no abstraction is possible in the CT state.

These rules are confirmed by a series of experiments on the reactivity of carbonyl compounds toward photoreduction in relation to substituents and environment; see Turro, Porter, and others.[2,46,121,254,362,374] For example, *p*-aminobenzophenone can abstract hydrogen from cyclohexane but not from isopropanol because the lowest state is $^3(\mathrm{n}, \pi^*)$ in cyclohexane, and ^{3}(CT) in the alcoholic solution.

Above all, with the given concept the distinct phototendering activity of vat dyes can be explained. The scheme of the energy states of anthraquinone and substituted anthraquinoid dyes, given in Fig. 15, shows that the yellow and orange dyes are characterized by a lowest $^3(\mathrm{n}, \pi^*)$ state. That is, these dyes should have a remarkable photoreactivity against hydrogen donors, an effect which is in agreement with the well-known phototendering activity of these types of anthraquinoid vat dyes. On the other hand, the blue and green anthraquinoid dyes with the absorption in the long-wavelength absorption region have a lowest $^3(\pi,\pi^*)$ state, so that no remarkable reactivity for hydrogen abstraction

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[374] P. J. Wagner and G. S. Hammond, *Advan. Photochem.* **5**, 99–104 (1968).

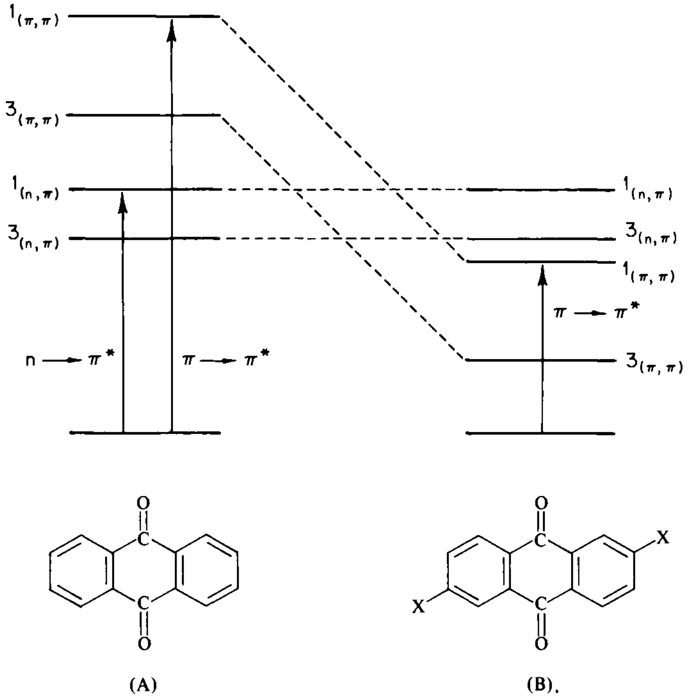

FIG. 15. Dependence of the position of $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ in anthraquinone on electron-donating substituents X: (A) high photoreactivity towards H abstraction; (B) no photoreactivity towards H abstraction.

should exist in these dyes. Therefore, the absence of photosensitized oxidation of alcohols and the low phototendering reactivity in the case of blue and green anthraquinoid dyes can be explained with the given hypothesis.

In addition, when discussing photoreactivity, factors which influence the n–π^* and π–π^* transition must be taken into account. For example, a hydrogen bond involving the n electrons on the carbonyl oxygen or the binding of a proton to it can render the n–π^* transition more difficult, so that the photochemical activity of a dye can be diminished.[375] In this context the discussion of Venkataraman[85] on hydrogen bonding of vat dyes in solid (cellulose) polymers must be noted because in this bonding the n–π^* transition will be influenced. Moreover, it should not be overlooked that dyes which are poor sensitizers have the possibility of reacting in the $^3(\pi,\pi^*)$ state with the substrate by a primary photooxidation of the dye in the presence of oxygen (see Class III dyes).

[375] H. Rau, *Ber. Bunsenges. Phys. Chem.* **72**, 408 (1968).

In discussing the fading and phototendering induced by anthraquinoid dyes it is to be noted that there exists a crude parallelism between the redox potential and the photoactivity of any one dye: The higher the redox potential, the higher the reactivity. But there are deviations resulting from the fact that electrons in the electrochemical reduction are taken up from the free π-orbital (i.e., π^*-orbital), so that semiquinone radicals are formed. On the other hand, in the optical n–π^* transition the excited electron is taken up in the primary step from the nonbonding oxygen orbital. That is, the free energies of both reactions need not be equal in all dyes; see Scheibe and others.[347,361,376,377]

b. Azo Dyes. There are only a few investigations on the fading of azo dyes in solution. Of these, the experiments of van Beek and Heertjes[323,324] on the photochemical behavior of aqueous solutions of azo dyes in the presence of different soluble substrates gave valuable results. It could be shown that azo dyes fade by reduction as a result of an interaction between the excited substrate molecules and the unexcited or excited dye molecules. The fading reactions are of first order with respect to the concentration of the excited substrate molecules. Oxygen can inhibit the fading of the dye by the reoxidation of reduced dye radicals. In oxygen-free solutions amines are the end products of the reduction.

Besides these results the investigations of Hillson and Rideal[298] on measurements of the Becquerel effect should be mentioned because in these experiments both oxidation and reduction of azo dyes have been observed. There exists no full understanding of the fading mechanism of azo dyes, as can be seen from studies on color transformations of azo compounds produced by ultraviolet radiation.[378] There is a great interest in elucidating not only the mechanism of fading but also the structural effects with which lightfastness can be enhanced, e.g., in dye photography.[379]

In the discussion on the lightfastness of the azo dyes investigations on the emission properties of simple models of azo dyes [i.e., aromatic molecules which contain two neighboring nitrogen atoms such as 9,10-diazaphenanthrene (XIII)] are of great interest.[375] From these studies and comparisons with *cis*- and *trans*-azobenzene it can be concluded that there is a very rapid radiationless deactivation via the $^3(\mathrm{n},\pi^*)$ state when the mixing $^1(\mathrm{n},\pi^*)$ and $^3(\mathrm{n},\pi^*)$ states (e.g., as a result of the nonplanarity of the molecules) are the lowest states. There could not

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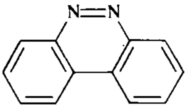
[376] G. M. Nabar and V. A. Shenai, *Textile Res. J.* **33**, 471 (1963).

[377] G. M. Nabar, V. A. Shenai, and R. B. P. Sinha, *Indian J. Technol.* **4**, 182 (1966).

[378] E. R. Champlin and R. L. Fyans, *Am. Dyestuff Reptr.* **54**, 1000 (1965).

[379] R. Gröger and H. Pietrzok, *Veroeffentl. Wiss. Photolab. AGFA* **10**, 309–315 (1965).



(XIII)

be observed any phosphorescence from the $^3(n,\pi^*)$ state, so that a real lifetime $<10^{-9}$ sec has been discussed for these triplet states. As an important consequence, azo compounds with the lowest $^3(n,\pi^*)$ state should be characterized by high lightfastness (in contrast with anthraquinoid dyes).[380] On the other hand, azo compounds with lowest $^1(\pi,\pi^*)$ states show fluorescence. This fact indicates a longer lifetime of the excited state and photoreactivity of azo dyes with lowest π,π^* states. The limiting cases of the position of n,π^* and π,π^* states for photoactivity and inactivity are given in Fig. 16. In discussing this scheme it must be noticed that n,π^* states can be realized by adsorption on fibers or by binding of a proton to the n electrons. This may result in fluorescence of adsorbed dyes[381] and in photoreactivity of the azo compounds when $(n,\pi^*) > (\pi,\pi^*)$; e.g., *cis*-azobenzene under acid conditions gives with $\lambda = 405$ nm 9,10-diazaphenanthrene and hydrazobenzene[375] (XIV). Further work seems to be necessary on these relationships.

c. Acridine Dyes. The studies on the photoreactivity of a number of acridine dyes (which are resistant to reduction in the dark[382]) in the presence of allylthiourea showed that acridine with amino substituents

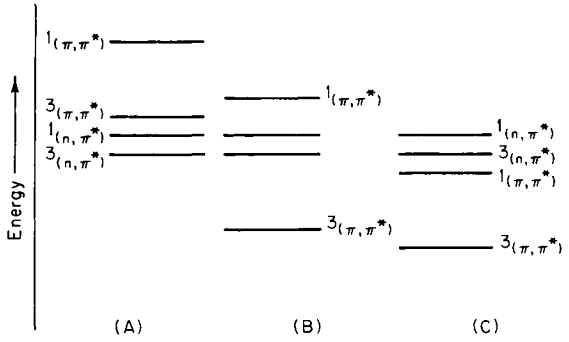
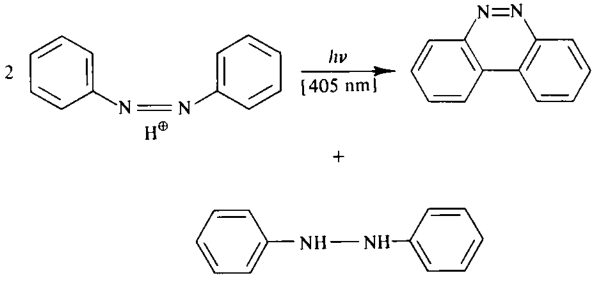


FIG. 16. Lightfastness of azo dyes: (A), (B), high lightfastness; (C), small lightfastness. [Note: B corresponds to *cis*-azobenzol.]

[380] B. E. Blaisdell, *J. Soc. Dyers Colourists* **65**, 618 (1949).

[381] P. Pringsheim, "Fluorescence and Phosphorescence," p. 122. Wiley (Interscience), New York, 1949.

[382] R. M. Acheson and L. E. Orgel, "Acridines." Wiley (Interscience), New York, 1956.



(XIV)

in both the 3- and 6-position are rapidly photoreduced to their leuco forms.[115,124] Acridines with 9-alkylamino substituents or quaternized at the 10-position are slowly photoreduced while others, e.g., 2-aminoacridine, 2,6-diaminoacridine bis(trypaflavin) have not been photoreduced. According to Oster and others[124,249,383-386] the photoreaction proceeds via a long-lived triplet state. From the observation that upon irradiation in alcoholic solution acridine yields diacridane, the concentration of acridine being above $10^{-3}\,M$[384,387-389] and from an influence of oxygen which depends on its concentration two pathways of photoreduction of acridine have been discussed.[390] Because of observations on the influence of the photoreactivity of acridine by triplet sensitizing molecules[241,391] and quenchers such as KI, Wilkinson and Dubois[392] concluded that the reactive state af acridine probably is $^1(\pi,\pi^*)$. As a further limit on the reactivity of the singlet state the increased pK_a value of the excited state compared to the ground state ($pK^*_a = 10.6$; $pK_a = 5.4$)[393] has been discussed. Because of an increase in the electron distribution on nitrogen in the excited state nitrogen should not be active in hydrogen abstraction. However, the study of the question of the

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[383] A. Kellmann and G. Oster, *J. Chim. Phys.* **58**, 355 (1961).

[384] V. Zanker, E. Erhardt, F. Mader, and J. Thies, *Z. Naturforsch.* **21b**, 102 (1966).

[385] M. Koizumi, Y. Ikeda, and H. Yamashita, *Bull. Chem. Soc. Japan* **41**, 1056 (1968).

[386] A. Kira, Y. Ikeda, and M. Koizumi, *Bull. Chem. Soc. Japan* **39**, 1073 (1966).

[387] A. Kellmann, *J. Chim. Phys.* **57**, 1 (1960).

[388] V. Zanker and P. Schmidt, *Z. Physik. Chem.* (*Frankfurt*) [N.S.] **17**, 11 (1958).

[389] M. Guirgea, G. Mikai, V. Topa, and M. Masa, *J. Chim. Phys.* **61**, 619 (1964).

[390] S. Kato, S. Minagawa, and M. Koizumi, *Bull. Chem. Soc. Japan* **37**, 1026 (1962).

[391] E. Vander-Donekt and G. Porter, *J. Chem. Phys.* **46**, 1173 (1967).

[392] F. Wilkinson and J. T. Dubois, *J. Chem. Phys.* **48**, 2651 (1968).

[393] A. Weller, *Z. Elektrochem.* **51**, 956 (1957).

reactive state of acridine cannot be considered as finished; see, e.g., references 384, 389, and 394–396.

III. Photochemistry of Dyes on Substrates

A. TESTING METHODS

1. *Measurements of Lightfastness*

It has been known for many years that the rate of fading depends on the substrate (see Bancroft, 1814[84]), on the humidity of the atmosphere,[397-399] on the temperature,[400,401] and on the spectral distribution of the radiation.[402,403] In spite of the complexity of the different fading factors there seems to be no doubt that the primary photochemical process of dyed materials will be analogous to one of the mechanisms studied in detail in model systems, in which not only the importance of the dye structure but also the influence of reducing or oxidizing agents, of oxygen, and of water could clearly be demonstrated.

Because of the influence of the different factors on the fading rate the lightfastness of a dye can only be defined exactly in a certain medium and under definite conditions. In principle the rate of fading may be determined by measurements of the optical density of dyes in solution or adsorbed in solid films,[3,404] or of the reflectance[403,405] as a function of the time of illumination, using a spectrophotometer and a spectroreflectometer, respectively. For practical purposes, however, a method with which a rapid distinction between dyes of different lightfastness on substrates is possible, is necessary.

In the U.S.A. a method is used in which the time necessary for a certain amount of fading by irradiation with a standard light source is

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[394] J. B. Birks and D. J. Dyson, *Proc. Roy. Soc.* **A275,** 135 (1963).

[395] M. Kleinerman, L. Azarraga, and S. P. McGlynn, *in* "Luminescence of Organic and Inorganic Materials" (H. P. Kallmann and G. M. Spruch, eds.), p. 196. Wiley, New York, 1962.

[396] G. Coppens, J. Nasielski, C. Gillet, and E. Vander-Donekt, *Spectrochim. Acta* **18,** 1441 (1962).

[397] J. J. Hedges, *J. Soc. Dyers Colourists* **43,** 261 (1927); **44,** 52 (1928).

[398] W. L. Lead, *J. Soc. Dyers Colourists* **65,** 723 (1949).

[399] P. W. Cunliffe, *J. Soc. Dyers Colourists* **72,** 330 (1956).

[400] M. J. Babey, *Am. Dyestuff Reptr.* **42,** 748 (1953).

[401] K. McLaren, *J. Soc. Dyers Colourists* **72,** 86, 527 (1956).

[402] W. Appel and W. C. Smith, *Am. Dyestuff Reptr.* **17,** 410 (1928).

[403] R. E. Bedford, *J. Soc. Dyers Colourists* **75,** 37 (1959).

[404] C. H. Giles, S. M. K. Rahman, and D. Smith, *J. Chem. Soc.* p. 1209 (1961).

[405] E. Coates and B. Rigg, *J. Soc. Dyers Colourists* **81,** 469 (1965).

determined. As standard light sources daylight and artificial light have been used. Yet, because of fluctuations of the ratio of actinic to total radiation (e.g., fluctuations of the UV content) of the daylight and other disadvantages, the enclosed carbon arc (known as Fade-Ometer) has become a standard light source. Therefore, the usually applied parameter of lightfastness in the U.S.A. is the Standard Fade-Ometer Hour.[87] However, there are differences in the composition of the carbon arc light and daylight,[406] so that the use of the xenon arc as standard source has been discussed.

The difficulties which are connected with standard-source methods are avoided in the British Standard (BS) method,[407] in which the rate of fading is determined by comparison with the fading of a set of standard dyeings which are exposed at the same time.[408] This method is in principle the same which in 1729 Dufay used in his systematic studies on lightfastness. However, much work has been necessary for developing qualified dyes for lightfastness standards (termed actinometer). While in a former method (BA method)[409] *one* standard had been employed which was replaced by a fresh standard after a noticeable fading of the specimen [corresponding to one standard fading period (SFP)], nowadays in the SDC Blue scale (ISO Recommendation No. 117, part 11) *eight* standards are used.[410-413] These (BS) standards, used in Europe, are pieces of wool which are dyed with different blue dyes. The lightfastness Standard 1 fades noticeably after 1 hour exposure to bright summer sunshine corresponding to 37 langleys [cal/cm^2] ($\approx 37 \times 1200$ lux hours).[408,414] The other standards are chosen in such a manner that Standard 1 fades about twice as fast as Standard 2 (i.e., this standard needs 82 langleys) and so on up to Standard 6. Standard 7 is about 4 times as fast as Standard 6, and Standard 8 twice as fast as Standard 7 (i.e., 5400 langleys must be irradiated in the case of Standard 8).[415] The lightfastness Standard 1 (XVI)[401] contains reactive methylene groups so that fading can be the result of an intramolecular or intermolecular

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[406] K. McLaren, *J. Soc. Dyers Colourists* **70,** 553 (1954).

[407] British Standard 1006 (1953).

[408] T. Padfield and S. Landi, *Studies Conserv.* **11,** 181 (1966).

[409] T. E. Thorpe, J. J. Hummel, W. H. Perkin, W. J. Russell, W. de W. Abney, W. Strond, and R. Meldola, *Rept. Brit. Assoc. Advan. Sci.* **63,** 373 (1893); **64,** 238 (1894); **65,** 263 (1895); **69,** 363 (1899).

[410] The Society of Dyers and Colourists, "Standard Methods for the Determination of the Colour Fastness of Textiles," p. 46. Yorkshire, England, 1962.

[411] J. C. Schofield, *J. Soc. Dyers Colourists* **80,** 642 (1964).

[412] H. Zukriegel, *Melliand Textilber.* **46,** 1213 (1965).

[413] W. Bubser, *Ber. Original Hanau Quarzlampen GmbH* **1,** Part 2, 63 (1968).

[414] O. Rawland, *J. Soc. Dyers Colourists* **79,** 697 (1963).

[415] K. McLaren, *J. Soc. Dyers Colourists* **80,** 250 (1964).

(D–D) oxidation–reduction process or of a photoreaction with oxygen[131] as discussed in Section II.

In the U.S.A. another blue scale (recommended by AATCC) is used, in which a rapid fading dye (Mordant Blue 1, CI 43830) mixed in different ratios with a very fast dye (Solubilized Vat Blue 8, CI 73801) is dyed on cotton pieces; the grades are about one grade over that of the European ISO scale.

In the practical testing of lightfastness the colored specimen is exposed with the standards until a perceptible fading can be observed. The dyes are classed by the number of the standard which shows the same fading. For an exact determination of lightfastness instead of referring to the "first break" the change of the color is referred to the standard gray scale (GS)[416–418] which defines the contrast between two colored areas (DIN 54001). It is possible to determine the lightfastness of a dyed specimen with a standard deviation of only about 0.5 grade.[419,420]

In this context it should be noted that the official method of determining lightfastness (BS 1006: 1953) was confined to daylight exposures because of remarkable differences between fading-lamp and daylight fastness numbers. McLaren[406,421] could show that discrepancies are caused not only by the differences in spectral composition of fading lamps and sunlight but above all by the surface moisture content during exposure depending on surface temperature and on the relative humidity of the surrounding air.[86,422] Today there is a general tendency to irradiate materials by light from the xenon arc lamp, which in combination with appropriate filters gives the best possibility of reproducing natural exposure conditions.[423,424] Moreover, in the Xenotest apparatus (Quarzlampen GmbH, Hanau, Germany) there is the possibility of a good adaptation of exposure conditions to natural exposure conditions, e.g., humidity, black-panel temperature.[413,423,425]

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[416] British Standard 2662 (1961).

[417] R. S. Asquith, E. Coates, A. T. Peters, and R. E. Todd, *J. Soc. Dyers Colourists* **81**, 360 (1965).

[418] P. Rabe, *Reyon Zellwolle* **12**, 855 (1957).

[419] K. McLaren, *J. Soc. Dyers Colourists* **75**, 597 (1959).

[420] S. M. Jaeckel, C. D. Ward, and D. M. Hutchings, *J. Soc. Dyers Colourists* **79**, 702 (1963).

[421] K. McLaren, *J. Soc. Dyers Colourists* **73**, 121 (1957).

[422] K. McLaren, *J. Soc. Dyers Colourists* **79**, 618 (1963).

[423] L. F. C. Friele, *J. Soc. Dyers Colourists* **79**, 623 (1963).

[424] W. Ingamells, *in* "Optische Anregung organischer Systeme. pp. 744–768. 2nd Internationales Farbensymposium" (W. Foerst, ed.), Verlag Chemie, Weinheim, 1966.

[425] H. Toepffer, *Melliand Textilber.* **39**, 1 (1958).

The necessity for definite fading conditions[86] can be seen, e.g., from the fact that dyed textiles, which in their fading properties are not affected by moisture, fade more rapidly at higher temperatures. On the other hand, dyed textiles which are moisture-sensitive may fade more slowly at higher temperatures because of a reduction of the moisture content. Therefore, a curtain in a north-facing room may eventually fade faster than in a south-facing room.[421] However, in discussing this observation the quality of the light should be also taken into account.[426] On further problems of lightfastness measurements see the reviews given by Brunnschweiler, Giles, McLaren, and others.[87,89,408,427–430]

2. *Measurement of Phototendering*

As discussed in Section II there exists the possibility of a catalytic tendering of dyed fibers in which the fabric disintegrates without a noticeable fading of the dye.[431,432] This occurs in practice above all with certain fast and fugitive vat dyes. In experiments it could be shown[433] that, e.g., after exposure to daylight for 4 weeks, there occurred a loss in tensile strength of cotton of the order of 40% with CI Vat Yellow 2, CI Vat Orange 9, and other vat dyes.

As the fading of the dye cannot be taken as an exact parameter for phototendering activity the loss in tensile strength of the fiber must be determined. The most accurate indications of photochemical degradation can be reached with the measurement of cuprammonium fluidities, or (the reciprocal of fluidity) viscosities. Moreover, an increase in copper number or in acidity (uronic acid measured as percent of carbon dioxide) can be taken; see for these possibilities references 434–436. In this context it should be mentioned that precise results are often difficult to obtain because of the nonuniformity of damage.[437] In many cases the

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[426] A. H. Little and J. W. Clayton, *J. Soc. Dyers Colourists* **79**, 671 (1963).

[427] E. Brunnschweiler, *Textil-Rundschau* **14**, 508 (1959); **18**, 8 (1963); **19**, 463 (1964).

[428] E. Brunnschweiler, *Textilveredlung* **1**, 399 (1966).

[429] E. Brunnschweiler, *SVF Fachorgan Textilveredlung* **19**, 521 (1964).

[430] C. H. Giles, *J. Appl. Chem.* **15**, 541 (1965).

[431] G. S. Egerton, *J. Soc. Dyers Colourists* **63**, 161 (1947); **64**, 336 (1948); **65**, 764 (1949).

[432] A. Schaeffer, *Melliand Textilber.* **37**, 94 (1956).

[433] D. Ashton, D. Clibbens, and M. E. Probert, *J. Soc. Dyers Colourists* **65**, 650 (1949).

[434] D. K. Appleby, *Am. Dyestuff Reptr.* **38**, 149 (1949).

[435] C. H. Bamford and M. J. S. Dewar, *J. Soc. Dyers Colourists* **65**, 674 (1949).

[436] T. N. Kleinert, *Textil-Rundschau* **20**, 336 (1965).

[437] A. Little, *J. Soc. Dyers Colourists* **80**, 527 (1964).

interior portions may still be unaffected, in spite of a serious attack of the crowns of the exposed threads.

3. *Testing of the Fading Products*

In order to get an insight into the nature of degradation products analytical studies of these products can be used. For example, a comparison with chemically formed redox products is possible by applying spectrophotometric methods or a chromatographic testing.[295,366] Possibly the Weisz ring-oven technique, which has been used for the semiquantitative determination of microamounts of dyes,[438] can be applied.

4. *Measurements of the Rate of Fading*

From measurements of the rate of fading of dyed materials valuable conclusions on the physical state of dyes in the fiber are possible, and above all improvements of the lightfastness of dyed fabrics which can be obtained by special processes can be studied; see Giles *et al.*[6,7,430,439,440] The following types of plots have been used for examining fastness data.

a. Fading-rate Curves. Fading-rate curves which are obtained by plotting the residual dye concentration (or its logarithm) against time can be divided into several groups:

(1) In the case of fading the rate decreases exponentially with time according to a first-order or pseudo-first-order law (Fig. 17,A), i.e., the percentage of unchanged dye present with time follows a normal exponential curve [see Eq. (27) of Section I]. This order can be observed

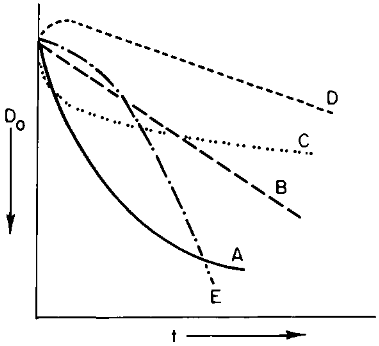

FIG. 17. Types of fading-rate curves (A–E: see text).

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[438] M. B. Celap, T. J. Janjić, and V. D. Jevtić, *Microchim. Ichnoanal. Acta* No. 4, 647 (1965).

[439] C. H. Giles, S. M. K. Rahman, and D. Smith, *Textile Res. J.* **31**, 679 (1961).

[440] P. W. Cunliffe and P. N. Lambert, *J. Soc. Dyers Colourists* **45**, 313 (1929).

with molecular dispersed dyes; e.g., merocyanine dyes in collodion, and water-soluble surface-active azo dyes in methylethylcellulose have shown true first-order fading curves.[7]

(2) Fading according to the zero order can be detected from a constant fading rate [see Eq. (26) of Section I], i.e., from a straight-line relationship between the amount of dye present and time (Fig. 17,B). This fading rate occurs in dyed materials with large particles of dyestuffs. Particularly, pigments and fast dyes show this kinetic of fading.

(3) The course of fading of a mixture of monomeric and aggregated forms of dyes is given at the beginning by a first-order expression corresponding to the fading of the monomers, followed by a slow zero-order fading of the undecomposed large particles (Fig. 17,C). This type of fading occurs most frequently in practice.[7]

(4) Negative initial fading, i.e., an increase of the fading rate with time, can occur under special conditions when large dye particles disintegrate in the heat of illumination (see Fig. 17,D). Because of an increase of the optical density of a given weight of dye resulting from a decreased particle size, the fading-rate curve at the beginning outweighs the decrease which results from the quicker fading of the smaller colored particles.[7,441] The newly formed particles tend to reaggregate in the dark, so that the dye seems to fade in the dark with restoration during illumination;[442] Fig. 18 gives a scheme of the fading routes which occur during the illumination of such dyes.

(5) In some dyed materials, e.g., in the case of some insoluble azo dyes in cellulose, the fading can be accelerated with time because of a continuous breakdown of dye particles (Fig. 17,E).

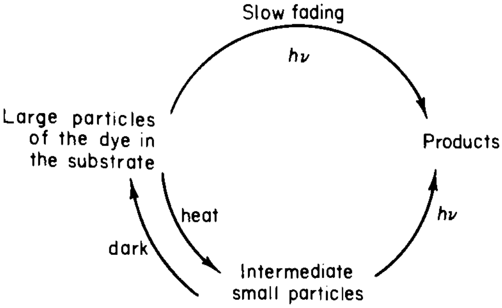

FIG. 18. For explaining of the abnormal fading behavior of a dyed material (Type D of Fig. 16); O.D. of intermediate particles > O.D. of large particles.

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[441] H. R. Chipalkatti, N. F. Desai, C. H. Giles, and N. Macaulay, *J. Soc. Dyers Colourists* **70**, 487 (1954).

[442] C. H. Giles, G. Baxter, and S. M. K. Rahman, *Textile Res. J.* **31**, 831 (1961).

The short discussion given for explaining fading-rate curves shows that fading curves can be correlated with different fading behavior of various dyed materials.[7,430,440] For the problems of measurements of the optical density of dyed materials and the determination of fading types see references 443–446.

b. Characteristic Fastness-grade (CFG) Curves. The long-known fact that the lightfastness of a dye on textile fibers in many cases increases with an increase in depth can be used for constructing characteristic fastness-grade (CFG) curves, which give valuable information about the physical state of the dyes in the fibers. According to Giles[447] CFG curves are obtained as straight lines by plotting average lightfastness grades of dye classes against their relative depth, i.e., against the logarithm of the original dye concentration in the fiber.

The possibility of constructing CFG curves had been shown spectrophotometrically by Baxter and Giles *et al.*[444,448] by confirming the linearity of the relationship between $\log[D_0]$ and $\log t$ for a given amount of fading as could be expected from empirical rules given by Cunliff and Lambert.[440]

In an extensive study Giles[447] found out that in many cases the slopes of CFG curves differed between dye classes or between fibers. By considering the slope of the CFG curve as being related to the rate at which the distribution of sizes of dye particles changes with an increase in the dye concentration in the fiber two limits for slopes have been given:

Low slopes are typical for systems in which the dye particle sizes at various concentrations are very similar. There is no appreciable change of lightfastness with an increased dye concentration, a case which is possible when the dye forms only very small particles (low lightfastness) or only very large particles (high lightfastness).

High slopes are observed in systems with nonuniform dye particles which grow larger by an increasing concentration of the dye. In this context it should be mentioned that this explanation of CFG slopes (see Fig. 19), confirmed by observation, is based on the general rule that the

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[443] C. H. Giles, *Proc. 2nd Intern. Congr. Surface Activity, London,* 1957 Vol. 1, pp. 92, 140. Academic Press, New York, 1958.

[444] D. S. E. Campbell, D. Cathcart, C. H. Giles, and S. M. K. Rahman, *Trans. Faraday Soc.* **55**, 1631 (1959).

[445] L. Weissbein and G. E. Coven, *Textile Res. J.* **30**, 58 (1960).

[446] T. H. Morton, *J. Soc. Dyers Colourists* **65**, 597 (1949).

[447] C. H. Giles, *J. Soc. Dyers Colourists* **73**, 127 (1957).

[448] G. Baxter, C. H. Giles, M. N. McKee, and N. Macaulay, *J. Soc. Dyers Colourists* **71**, 218 (1955).

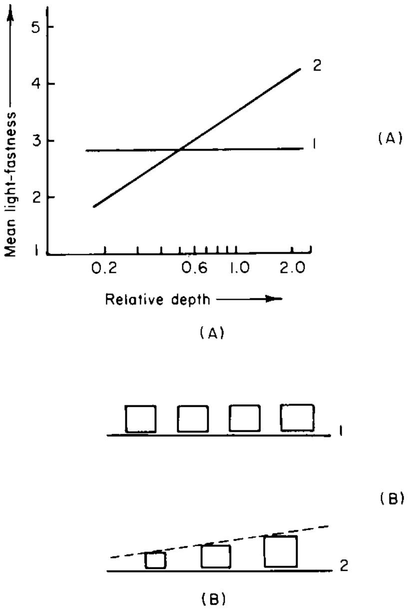

FIG. 19. (A) Example of CFG curves. (B) Scheme of particle-growth possibility with increasing dye concentration (according to Giles[447]): 1, number of particles increased (see curve 1 of A); 2, range of sizes of particles increased (see curve 2 of A).

rate of fading depends on the surface of the dye particles: Large particles will fade more slowly than small particles because the smaller particles with their large surface can be better reached by light, air, moisture, and can better interact with the fiber material.

On the basis of the given hypothesis of CFG curves Giles[447] discussed a series of important relationships. For example, it could be shown that the slope of the CFG curve is highest on fibers of large pore size, or that the slopes are higher for insoluble (azoic and sulfur) dyes than for soluble dye classes because of a hindering of dye association (i.e., growth) by solvating water molecules. Moreover, from CFG data it can be concluded that besides taking into consideration the impossibility of defining the lightfastness of a dye alone (i.e., the necessity for defining lightfastness of particular systems such as dye + fiber + components) the fact must be regarded that in many cases the fastness applies exactly only to one concentration (i.e., depth) of the dye on a special fiber.

c. *Characteristic Fading (CF) Curves.* CF or characteristic fading curves (formerly CFO curves) are obtained by plotting the logarithm of the time of fading t_F for a given proportion of the original dye concentration $[D_0]$ (e.g., a percentage loss of 10%) against the logarithm of $[D_0]$.[447–449] The CF curves differ from the characteristic fastness grade (CFG) curves in using the log t_F value in place of the fastness grade. However, fastness grades and log t_F values are equivalent. The plotting of CF curves is possible from the data of simple fading-rate curves in which the fall in optical density or reflectance during irradiation with various initial dye concentrations is registered (see Fig. 20).

Like CFG curves the CF curves of Fig. 20 are normally linear and can give information on the physical state of the dye in the fiber. The slope of the CF curve is very low in systems with the same state of particle size distribution at all concentrations of the dye, i.e., with constant surface area/weight ratio. Systems which contain, e.g., a completely monodisperse dye or a uniformly mixed pigment fade according to a first-order reaction. While true monodisperse systems characterized by very low lightfastness are seldom encountered, vat dyes, some fast-to-light direct cotton dyes, and neutral-dyeing metal complex dyes may usually form relatively large particles of uniform size with low CF slopes.[450] On the other hand, when dyes form a wide range of sizes of particles which grow with increasing dye concentration, the slope of the CF curves is high.[4,448] The fastness of such dyes, as, for example, azoic

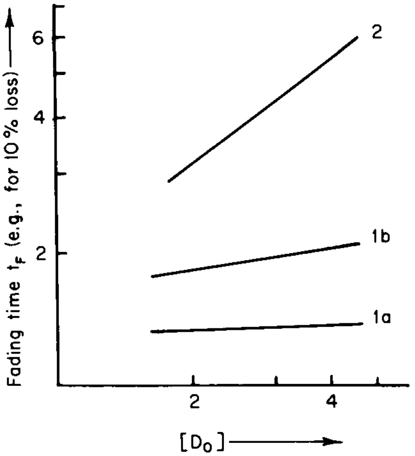

FIG. 20. Scheme of CF curves (see text): 1, low slope (fastness of 1b higher than that of 1a); 2, high slope (fastness higher than dye–substrate system 1).

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[449] D. S. E. Campbell and C. H. Giles, *J. Soc. Dyers Colourists* **74,** 164 (1958).

[450] C. H. Giles, *Ind. Chim. Belge* **2,** 490 (1959).

and sulfur dyes, is lower at a low concentration (i.e., at a low depth of shade) than at a high concentration.[447]

According to Giles[450] both fading rate and CF (or CFG) curves should be plotted for obtaining "a true picture of the lightfastness characteristics of any dye." For instance, by observing the shifting of the CF curve of a dye–fiber system by any treatment valuable hints on methods for the production of high lightfastness can be derived. Moreover, by comparing CF curves of various dye classes, and of dyes on fibers with different regain, i.e., with different sizes of the internal pores, important rules have been obtained. For example, it could be shown that the fastness of a dye increases with depth in hydrophilic fibers with high porosity (i.e., regain) at a greater rate than in fibers with low porosity. Furthermore, the general rule of fastness increasing in hydrophilic fibers with rise in regain was derived from the measurements of CF curves.

d. Comparison Method. In order to get an insight into the different photochemical behavior of various fibers, Giles[447] proposed a comparison method in which the fastness of individual dyes of the same dyeing class on one fiber is plotted against the fastness on another fiber. As only in the case of the same fastness of each dye on two fibers the "equivalence line" of Fig. 21 would be obtained, any different influence of fibers on fastness can be seen from deviations of the measured line from the equivalence line. For example, the measured line lies above the equivalence line if dyes on the one fiber (fastness grade as ordinate) have a higher fastness than on the other.

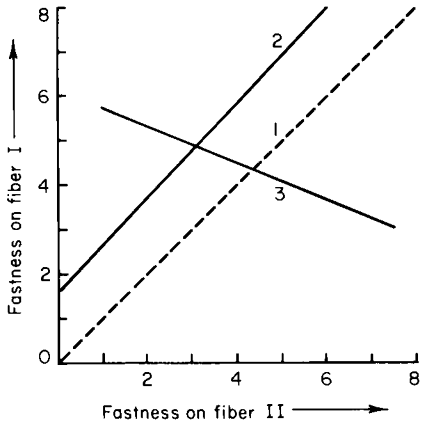
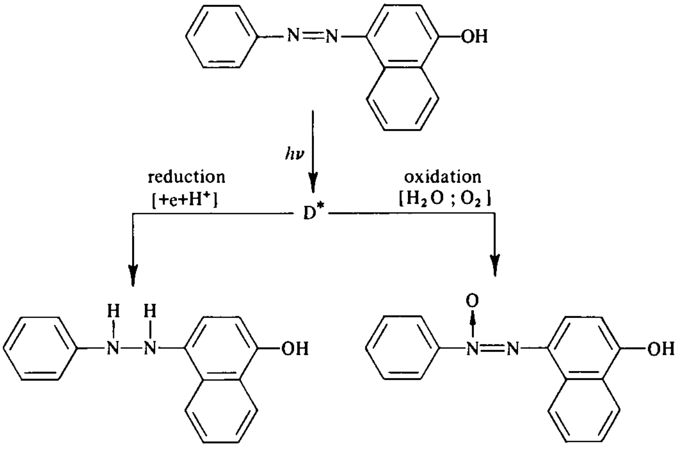


FIG. 21. Comparison method: 1, equivalence line; no difference in effect of fastness; 2, dyes of fiber I have higher fastness than on II; 3, difference in chemical nature of fading; e.g., in the case of I, protein, and II as nonprotein substrate.

It is interesting to note that a photochemically different behavior of protein and nonprotein substrates can be seen from an intersection of the equivalence line by the measured protein/nonprotein fastness-grade line of different series of dyes.[336,447]

5. *Photoelectric Measurements*

a. Becquerel Effect. In Becquerel photoelectric cells the potential change of a platinum electrode coated with a dye is measured. With this method Hillson and Rideal[298] found out that both oxidation and reduction of the same dye is possible under irradiation. A reduction had been observed when the dyes (e.g., azo dyes and triphenylmethanes) were in contact with the electrode, whereas oxidation of the dyes occurred distant from the electrode in the solution (see Section II,B,3,a,i). Therefore, azo dyes may be photodecomposed by reduction to colorless hydrazo compounds, or by oxidation to colorless azoxy compounds, e.g., as in (XV). From these reactions the possibility of photoreductive and photooxidative fading of dyes on fibers could be deduced: for instance, photoreduction in the presence of fibers with reducing groups such as in proteins, or photooxidation in other substrates in the presence of water and oxygen (see Section III,D,1).



(XV)

b. Photoconductivity of Dyes

i. Effect of temperature. Although many investigations on the photoconductivity of organic dyes have been published since the first independent studies in the early 1950s by Vartanyan,[451] Nelson,[452] Noddack and co-workers,[453–455] only a few hints could be obtained on the application of the photoconduction of dyes for the study of the photobleaching process. The study of a large number of dyes of various classes indicated that the photoconduction of dyes is caused by the formation and migration of electronic charge carriers, and is not due to impurities of photochemical decomposition. The agreement between photoconduction phenomena of organic and inorganic photoconductors leads to the conclusion that the phenomena of dark- and light-induced conduction in dyes can be interpreted in the same way as in inorganic semiconductors. It would be beyond the scope of this chapter to discuss all these phenomena; see the reviews in references 6, and 456–461. It should only be mentioned that the dark conductivity σ_D increased with temperature according to[462]

$$\sigma_D = \sigma_{0,D} \exp(-E_D/2kT) \tag{57}$$

where E_D is the activation energy for semiconduction, and that the photoconductivity shows a similar relationship[463]

$$\sigma_{Phot} = \sigma_{0,Ph} \exp(-E_{Ph}/kT) \tag{58}$$

From the slope of the linear plots of log σ_D or of log σ_{Phot} and $1/T$ (°K) the activation energies for dark conductivity and photoconductivity can be derived. While E_D seems to be related to the number of π-electrons in the molecule,[464] i.e., to the structure of the organic solid, E_{Ph} (in the order of 0.2–0.6 eV) can probably be ascribed to the depth of trapping centers.[6,463,465]

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[451] A. T. Vartanyan, *Zh. Fiz. Khim.* **20,** 1065 (1946); **24,** 1361 (1950); **27,** 272 (1953).

[452] R. C. Nelson, *J. Chem. Phys.* **19,** 798 (1951); **20,** 1327 (1952).

[453] W. Noddack, G. Eckert, and H. Meier, *Z. Elektrochem.* **56,** 735 (1952).

[454] W. Noddack and H. Meier, *Z. Elektrochem.* **57,** 691 (1953).

[455] H. Meier, *Z. Elektrochem.* **58,** 859 (1954).

[456] H. Meier, *Angew. Chem.* **77,** 633 (1965); *Angew. Chem. Intern. Ed. Engl.* **4,** 619 (1965).

[457] H. Meier, "Spectral Sensitization." Focal Press, London, 1968.

[458] F. Gutman and L. E. Lyons, "Organic Semiconductors." Wiley, New York, 1967.

[459] D. D. Eley, *in* "Optische Anregung organischer Systeme. 2nd Internationales Farbensymposium" (W. Foerst, ed.), pp. 600–633. Verlag Chemie, Weinheim, 1966.

[460] O. H. LeBlanc, Jr., *Phys. Chem. Org. Solid State* Vol. 3, 133–198 (1967).

[461] M. Smith and J. W. Weigl, *in* "Xerography and Related Processes" (J. H. Dessauer and H. E. Clark, eds.), pp. 169–199. Focal Press, London, 1965.

[462] H. Meier, *Z. Physik. Chem.* (*Leipzig*) **208,** 325 (1958).

[463] H. Meier, *Z. Physik. Chem.* (*Leipzig*) **208,** 340 (1958).

[464] D. D. Eley and G. D. Parfitt, *Trans. Faraday Soc.* **51,** 1529 (1955).

[465] R. C. Nelson, *J. Chem. Phys.* **22,** 892 (1954).

ii. n- *and* p-*Type conduction.* Dyes can be divided into *n*- and *p*-type conductors with electrons or holes as majority carriers, as first recognized by the effect of oxygen[466] on the conductivity of dye layers: In some dyes (e.g., triphenylmethane dyes, rhodamines) the conductivity decreases in oxygen (*n*-type), and in other dyes (merocyanines, phthalocyanines, etc.) the conductivity is enlarged in the presence of oxygen. Hydrogen behaves in the reverse manner.[467] Nowadays this classification is confirmed by Hall effect measurements,[468-470] thermoelectric power measurements,[471,472] and photoflash studies.[473] When *n*-type and *p*-type dyes are combined, e.g., rhodamine B (*n*), merocyanine (*p*), photocurrents of the order of 10^{-8} to 10^{-9} A without any external voltage are found, indicating an electron transfer from the *p* conductor to the *n* conductor independent of the direction of illumination[6,473-476] corresponding to the theory of *pn* barrier layers. Analogous photovoltaic effects are obtained by coupling dyes with aromatic amines[477] or inorganic semiconductors,[478] i.e., in cases in which dyes are combined with materials which have another chemical potential of electrons (Fermi potential) than that in the dyes.[457] The photovoltaic effects could be enhanced by increasing the conductivity of the combined organic substances,[457,479] e.g., by doping with small amounts of electron acceptors.[480,480a] In this context it should be mentioned that the lightfastness of dispersed dyes decreases with an increase in the electrical conductivity of insulating substrates, e.g., in the sequence polyacrilonitrile, polyesters, polyamide,

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[466] H. Meier, *Z. Wiss. Phot., Photophysik Photochem.* **53,** 1 (1958).

[467] H. Meier, *Z. Physik. Chem.* (*Leipzig*) **212,** 73 (1959).

[468] G. H. Heilmeier and G. Warfield, *J. Chem. Phys.* **38,** 163 (1963).

[469] A. Epstein and B. Wildi, *in* "Symposium on Electrical Conductivity in Organic Solids" (H. Kallmann and M. Silver, eds.) pp. 337–357. Wiley (Interscience), New York, 1961.

[470] G. Delacote and M. Schott, *Phys. Status Solidi* **2,** 14, 60 (1962).

[471] C. Hamann and I. Storbeck, *Naturwissenschaften* **50,** 327 (1963).

[472] N. Petruzella and R. C. Nelson, *J. Chem. Phys.* **37,** 3010 (1961).

[473] H. Meier and W. Albrecht, *Z. Naturforsch.* *24a,* 257 (1969).

[474] W. Noddack, H. Meier, and A. Haus, *Z. Wiss. Phot., Photophysik Photochem.* **55,** 7 (1961).

[475] H. Meier, *J. Phys. Chem.* **69,** 719 (1965).

[476] H. Meier and A. Haus, *Angew. Chem.* **72,** 631 (1960).

[477] D. R. Kearns and M. Calvin, *J. Chem. Phys.* **29,** 950 (1959).

[478] H. Meier and W. Albrecht, *Z. Elektrochem.* **68,** 64 (1964).

[479] H. Meier and W. Albrecht, *Z. Elektrochem.* **69,** 160 (1965).

[480] H. Meier and W. Albrecht, *Z. Physik. Chem.* (*Frankfurt*) [N.S.] **39,** 249 (1963).

[480a] H. Meier, W. Albrecht, and U. Tschirwitz, *Ber. Bunsenges. Phys. Chem.* **73,** 795 (1970).

and secondary acetate.[481] In this sequence increased photovoltaic effects should be expected between dye particles and substrates, if the relation between fiber resistance and lightfastness results from a slowing up of the charge transfer not only between dye particles but also between dye molecules and the substrate.

iii. Effects of oxygen and water vapor. In discussing any relation between the photoconduction of dyes and fading it must be noted that, normally, the conductivity of dyes is measured under conditions of low pressure ($< 10^{-5}$ mm Hg) and without any contact with reducing or oxidizing substances, i.e., under conditions which favor high stability under irradiation. These studies show that in the aggregated state dyes can transfer electronic charge carriers throughout the crystal. The *n*-conducting dyes should above all be capable of reducing, and the *p*-conducting dyes of oxidizing any other contacting materials.[361] The observations on the influence of gases[6,466] which lead to the classification of dyes in *n*- and *p*-type dyes, and which demonstrated a reaction of excited dyes with adsorbed oxygen seem to be of particular interest for the effect of fading. This effect is analogous to the observations with inorganic semiconductors[482-484] and seems to be in conformity with the production of $O_2\cdot^-$ as an intermediate in photooxidation;[308] see Section II,B,3,a,*iv* and the study on ZnO-sensitized photochemical reduction and oxidation.[485] From these observations a relation between "oxygen-conducting" dyes and photodynamically active dyes has been postulated.[6] In accordance with the importance of the physical state of the dye for the fading process (see Section III,C,1) high effectiveness of thin layers (monolayers),[486] and reactivity of traces of water vapor on the electrical (and fading) properties of dyes have been detected.[487] It is interesting to note that usually dry oxygen brought about reversible changes of conductivity without indicating any photodecomposition. However, in the presence of humidity the reversibility was disturbed as a result of a photochemical reaction of the dye, and, moreover, in several dyes a negative photoelectric current has been observed.[487] Such negative effects have recently been reported also from measurements of viscose staple fiber yarn dyed with Direct Violet and Direct Bright Light Blue.[488] Yet, other dyed

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[481] D. Patterson and B. Pilling, *Trans. Faraday Soc.* **62**, 1976 (1966).

[482] K. Hauffe, "Reaktionen in und an festen Stoffen." Springer, Berlin, 1955.

[483] G.-M. Schwab and J. Block, *Z. Physik. Chem.* (*Frankfurt*) [N.S.] **1**, 42 (1954).

[484] R. Suhrmann, *Z. Elektrochem.* **60**, 804 (1956).

[485] G. Oster and M. Yamamoto, *J. Phys. Chem.* **70**, 3033 (1966).

[486] W. Noddack, H. Meier, and A. Haus, *Z. Physik. Chem.* (*Leipzig*) **212**, 55 (1959).

[487] H. Meier, *Z. Wiss. Phot., Photophysik Photochem.* **53**, 117 (1959).

[488] R. W. Moncrieff, *Textile Mfr.* **92**, 462 (1966).

fibers and fabrics showed normal photoeffects,[489] so that a comparison with lightfastness data would be necessary for discussing any relation between negative effects and photodegradation.

iv. Kinetic relationships. It can be expected that any photochemical reaction which leads to products of degradation will change the conductivity of dye layers. As it is only in a few cases that photobleaching is the result of an intramolecular process (see Section II,B,1) and, moreover, is characterized by a low quantum efficiency, it is difficult to find a relation between the change in the conductivity and the amount of products. Yet, it must be stressed that there cannot at all be expected a direct relation between the kinetics of photodecomposition and photoconductivity in dyes of high lightfastness. This relation would only arise in the case of the formation of products, e.g., radicals, which can be responsible for the buildup or change of photoconduction in the whole layer.[490,491] Usually, photobleaching—both as a result of intramolecular and intermolecular reaction—should bring about *secondary* changes of conductivity under intense illumination. As examples of such conductivity measurements on intramolecular fading dyes the studies on the triphenylmethane dyes used in the first three standards of the ISO fastness test (Recommendation 105, part 11) should be mentioned.[481] There was no connection between the time of the half-buildup of photoconductivity (in the order of seconds) and the induction period for photobleaching (in the order of minutes), however, the conductivity decreased after the beginning of the bleaching of the dye films to the leuco dye.

v. Relation between lightfastness and E_{Ph}. It is very important that a *relation* between fastness and thermal activation energy E_{Ph} [see Eq. (58)] of photoconductivity was found. E_{Ph} increases with lightfastness, i.e., CT Acid Blue 104 (XVI) ($E_{\text{Ph}} = 0.39$ eV; $\tau_{\text{Bleaching}} = 9$ min); CI Acid Blue 109 (XVII) (0.48; 25); CI Acid Blue 83 (XVIII) (0.58; 60).[481] This relationship only holds for dyes of similar chemical structure, so that, e.g., there is no connection between E_{Ph} of CI Acid Blue 104 and E_{Ph} of copper phthalocyanine (fastness grade 7; $E_{\text{Ph}} = 0.25$ eV). However, it is shown that small changes in structure, i.e., an increase of the electrophilic nature of the substituents in the side chain which results in a stronger localization of the positive charge on the central carbon atom of triphenylmethane or on the nitrogen atom, influence

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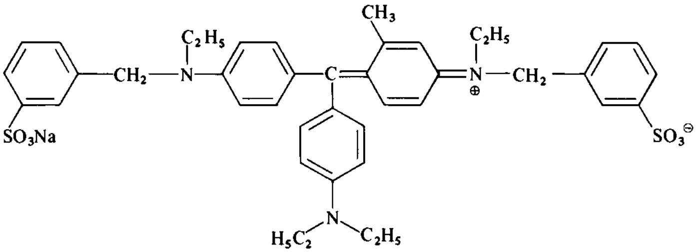
[489] I. P. Fedotov and B. M. Yavorskii, *Izv. Vysshikh Uchebn. Zavedenii, Tekhnol. Tekstil'n. Prom.* No. 2, 115 (1966).

[490] D. D. Eley and M. R. Willis, *in* "Pigments" (D. Patterson, ed.), pp. 66–83. Elsevier, Amsterdam, 1967.

[491] T. Hayashi, K. Maeda, S. Shida, and K. Nakada, *J. Chem. Phys.* **32**, 1568 (1960).

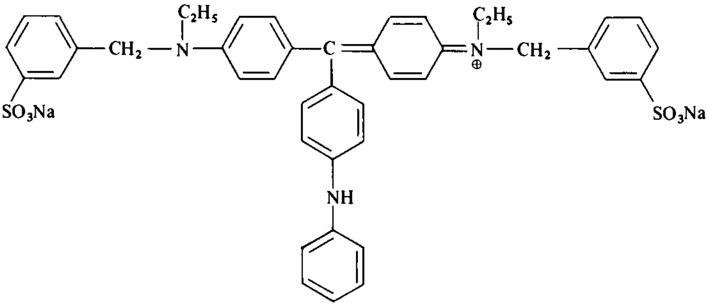
photoconductivity and lightfastness; see also the study on the relation between the quantum yield of photoconductivity and structure in references 6 and 492.

From this relationship a mechanism similar to that given by Patterson and Pilling[481] for the fading of triphenylmethane dyes and the influence



(XVI)

of structure on quantum efficiency and E_{Ph} can be discussed. According to this mechanism electrons and holes formed by the absorption of light are trapped with different efficiency. Because of a very efficient trapping of holes and a low mobility of these positive charge carriers, the quantum efficiency of photoconduction and the value of E_{Ph} depends on the mobility and concentration of electrons (n-type conduction), i.e., on the trapping of electrons by single dye molecules and, therefore, on the localization of the positive charge in the molecule. With an increasing localization the trapping influence increases, as seen from the high acti-



(XVII)

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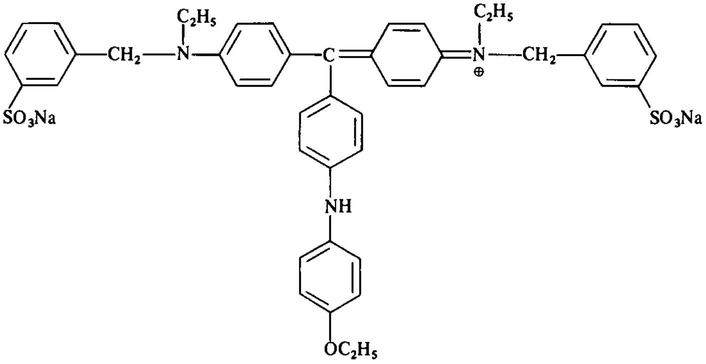
[492] W. Noddack, H. Meier, and A. Haus, *Z. Physik. Chem.* (*Frankfurt*) [N.S.] **20,** 233 (1959).



(XVIII)

vation energies E_{Ph} and from low values of quantum efficiency. On the other hand, by this trapping of electrons, uniradicals are formed which, by a disproportionation between two short-lived uniradicals, produce a biradical and a molecule of the leuco dye. The probability for this reaction in the solid state depends on the probability of the formation of such species close to one another, which increases with an increase in the diffusion (mobility) of the electrons through the layer.

The discussion given above allows much scope for the use of photoconduction as a means of studying the photofading of dyes. Valuable hints can be obtained on the mechanism of bleaching, and on the influence of gases and substrates. Perhaps, further work will lead to a relationship such as that between E_{Ph} and fading grades, from which methods for gradation fastness ratings and for the increase of the lightfastness of dyes can be derived; in dyes with the same chromophoric system, for example, an increase of lightfastness may be possible by the localization of charges at some point in the molecule.[481]

B. External Influences on Light Fading

There are various external factors which greatly influence the fading rate of dyed materials.

1. *Oxygen*

In many cases, oxygen of the atmosphere accelerates the fading of dyes, a fact which has been known since Lasareff's studies[319,493] on the fading properties of cyanine dyes in 1907. There seems to be no doubt

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[493] P. Lasareff, *Ann. Phys.* [4] **24,** 661 (1907).

that oxygen is necessary in the photodegradation of dyed textile fibers (cotton, rayon, linen).[89,494,495] For example, as discussed in Section II,C,2,a, phototendering in the case of vat dyes can be considered as a dye-sensitized process in which the reduced dye is reconverted to the original dye by oxygen. Moreover, the possibility of an attack of the fiber by hydrogen peroxide in the presence of water arises, and oxygen can become reactive by an interaction with $^3(\pi, \pi^*)$ excited dyes of Class I or III (see Section II,B,3,b). In this context Egerton's experiments[350] should be mentioned, in which a tendering occurred in fibers separated from the dye (xanthene and acridine dyes) by distances of the order of millimeters. Because of the necessity for the presence of water the production of H_2O_2 as oxidizing agent is probable. However, Egerton proposed that at low oxygen pressure and at short distances excited singlet oxygen or $O_2{\cdot}^-$ (see Section II,B,3,a) should also be able to oxidize in accordance with the hypothesis of Kautsky[354]; see the review of Bourdon and Schnuriger.[254]

On the other hand, oxygen, in some cases, has an inhibitory effect on fading. For example, diazacyanine blue on cellulose or protein fibers showed a higher fastness in oxygen than in nitrogen,[496] similar to the fading effects of azo dyes in solution under UV irradiation[380,403] and of other materials.[497–499] Because of the complex character of fading reactions a simple explanation of these effects cannot be given. Perhaps the quenching effect of oxygen on excited photochemical active states must be taken into consideration. According to van Beek and Heertjes[131] the amount of inhibition depends upon the relative rates of the possible processes in which the excited substrate either donates hydrogen to the dye or is oxidized by the formation of peroxides in the presence of oxygen.

2. *Humidity*

In a series of experiments McLaren *et al.*[86,396,398,399,406,426,440,500] could clearly demonstrate that, by the addition of water vapor, the fading rate is accelerated. For example, many vat and azoic dyes decrease in fastness with a rise in humidity.[426] In this connection it is interesting to note that the knowledge of the effect of oxygen and moisture led, in 1893, to

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[494] W. Scharwin and A. Pakschwer, *Z. Angew. Chem.* **40,** 1008 (1927).

[495] W. Aston, Report and Memoirs Advisory Committee for Aeronautics, No. 396 (1917).

[496] G. Schwen and G. Schmidt, *J. Soc. Dyers Colourists* **75,** 101 (1959).

[497] A. Richardson, *Rept. Brit. Assoc. Advan. Sci.* **58,** 641 (1888).

[498] V. Watson and H. F. Clay, *J. Oil Colour Chemists' Assoc.* **38,** 167 (1955).

[499] A. Seyewetz and D. Mounier, *Bull. Soc. Chim. Belges* **43,** 648 (1928).

[500] F. Gasser and H. Zukriegel, *Melliand Textilber.* **33,** 44 (1952).

a method of protecting paintings by sealing them in glass cases *in vacuo*[87,408] or by surrounding dyed materials by an inert gas such as nitrogen or argon.[408] Dyeings on wool are not so sensitive to any change of humidity as those on cotton. Therefore, for fastness standards, pieces of wool are preferred.[86,89,399,430] An explanation of the humidity effect is not simple.[89] There seems to be no doubt that the production of H_2O_2 in the presence of oxygen can play a part in the humidity effects. However, the photochemical reactions leading to a fading and tendering are often complicated so that various reaction steps may be affected by humidity in a different way. This opinion is supported by observations on the influence of copper on the effect of relative humidity on tendering caused by vat dyes.[426,437] Moreover, kinetic effects can be discussed, as in the case of diffusion-controlled bimolecular fading the diffusion of reaction partners towards one another is rendered more difficult at lower humidity, so that the probability of energy dissipation increases.[131] Humidity can also be responsible for the effects of photodimerization in fiber materials.[501]

3. *Temperature*

Because of the small activation energy (about 2 kcal/mole) of dark reactions in the course of photofading there is only a small effect of temperature under controlled humidity.[396,430] This effect can be more pronounced at high fiber regains, and some special cases are reported in which high temperature under dry conditions has caused a rapid fading.[89,400]

Usually, the diminishing of the moisture content of the fibers, brought about by high temperature, retards photofading (see Section III,A,1).

4. *Spectral Conditions*

From the survey on photochemical reactions of dyes given in Section II, differences in the photochemical behavior of different wavelengths can be expected. For example, not only an excitation of the dye in the visible region but also an excitation of substances of the fibers by UV light may be effective in fading. In an extensive study on dyes of most chemical classes McLaren[401] found a relation between the effectiveness of different spectral regions and lightfastness of the dye on the substrate: Firstly, the proportion of fading with UV radiation increases with the fastness of the dye–fiber system. Secondly, whereas fugitive dyes can fade by UV and visible light, fast dyes can only fade by light below a critical wavelength, i.e., by UV light which is, e.g., absorbed by sub-

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[501] Shih Yi Wang, *Nature* **200**, 879 (1963).

stances in the fibers. In this context a recent study on photofading spectra of azo dyes (e.g., Congo Red, Direct Fast F) on cellophane films should be mentioned; it has shown that the dyes faded strongly at 350 nm, i.e., in an absorption band which results from the transition of the naphthalene nucleus along the short axis.[502]

C. Internal Physical Factors

1. *Physical State of the Dye*

The physical state of the dye and of the environment is very important for the fading of dyed materials. In a series of theoretical and practical experiments Giles and co-workers[430,439,447,450] clearly showed the importance of the relationship between fading and the position of the dye molecules in the fiber: Because of the influence of water and oxygen on a fading dye, molecules in accessible positions fade more rapidly than other molecules which cannot be reached by oxygen and moisture. In this context it should be noted that important rules on the influence of physical factors are derived from fading rate curves (see Section III,A,4), and from effects brought about by additives.

For example, kinetic data have demonstrated that the lightfastness increases with an increase in the average size of the aggregated dye particles. This rule results from the fact that only dye molecules at the surface of the particles can react. There seems to be no doubt that the physical state of the dye and of the fiber influences the dye stability to a high degree. Above all, any treatment which changes the size of dye aggregates can reduce or increase the fading properties of a dyed material. Many procedures for the alteration of the lightfastness of dyes and many well-known effects are based on these physical state effects. Some should be mentioned:

The increasing of fastness grades, linearly with the logarithm of dye concentration (i.e., of the depth of the dye), results from an increase in particle sizes of the dye, so that deep shades fade more slowly than pale shades.[442,447,448] Dyes of a high solubility which are more finely dispersed in substrates than dyes of a small solubility are characterized by a more rapid fading.[503] Because of changes in the state of aggregation by alterations in the surface activity changes in lightfastness are possible[450,503]: For example, by the addition of long paraffin chains the dye becomes surface-active, so that the dye will spread as a monolayer of small light stability, whereas dyes with short alkyl chains form micelles with a

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[502] H. Tsuneaki, K. Takashi, M. Osamu, and H. Hachiro, *Kogyo Kagaku Zasshi* **70,** 1538 (1967).

[503] C. H. Giles, G. Baxter, W. A. Black, N. Macaulay, and S. M. R. Rahman, *Textile Res. J.* **30,** 934 (1960).

higher lightfastness than that of the monolayer state. Surface activity is also high in planar dyes with sulfonate groups at one end only, or along one side because the rest of the molecule can be considered as a large hydrophobic group.[504] These dyes have a lower fastness than dyes of low surface activity with sulfonate groups which are all situated round the molecule[450,505]; see the measurement of Giles and co-workers[502] on several series of dyes of the sulfonated anthraquinone, sulfonated and unsulfonated azo, azomethine, and merocyanine classes.

Cationic surface-active agents (e.g., cetylpyridinium bromide) may disaggregate dye particles and reduce light stability in hydrophilic fibers. But these agents in high concentration may also promote aggregation and increase lightfastness. Because of the effect of the production of micelles the fading of dispersed dyes may also be reduced by surface-active agents. Other agents such as phenols or urea which are used as dyebath assistants can also reduce the average particle size and therefore decrease lightfastness.[7,89,430,443,447,449] The disaggregating effect of urea could be observed from absorption changes of methylene blue in gelatine and methylethylcellulose.[443]

2. *Physical State of the Fiber*

The growth of dye particles and the diffusion of water to the aggregates depend on the porosity of fibers. Hence, there are relationships between lightfastness and the physical state of the fiber.[7,441,450] For example, the light stability increases on hydrophilic fibers with an increase in porosity because large aggregates can be produced in this environment. On the other hand, lightfastness can be reduced by incorporation of any solid material (e.g., titanium dioxide used as delusterant or resins used for crease resistance[506]) in the fiber because of a reduction of the porosity.

However, hydrophobic fibers with small porosity restrict the diffusion of moisture to incorporated dye particles, so that fading is reduced.

In discussing the effects of added agents the possibility of secondary chemical reactions of such substances should not be overlooked. For example, the effect of the methylol amide agents which are used in the finishing of dyed cotton fabric for wrinkle resistance and wash-and-wear properties seems to be the result of a direct participation of the agent in the photochemical reaction leading to accelerated light-fading.[506,507] Probably, the acceleration of the fading of vat dyes and Cu phthalo-

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[504] A. Cameron and C. H. Giles, *J. Chem. Soc.* p. 3140 (1957).

[505] B. M. Boguslovsky and F. I. Sadov, *Tekstil'. Prom.* **12,** 31 (1952); *J. Soc. Dyers Colourists* **68,** 269 (1952).

[506] W. Ingamells, *J. Soc. Dyers Colourists* **79,** 651 (1963).

[507] J. G. Frick, Jr., R. M. H. Kullman, R. M. Reinhardt, and J. D. Reid, *Textile Res. J.* **37,** 894 (1967).

cyanines by such resins[508,509] may be attributed to the photooxidative formation of an oxygen-rich intermediate, or a photochemical reaction corresponding to the reaction discussed in Section II,B,4.[131]

The examples given above clearly demonstrate the important relationship between lightfastness and the aggregation of dyes. The high lightfastness of vat and naphthol dyeings, in which the dyes are insolubilized and developed upon application to form large aggregates in the fiber, can clearly be explained with this rule.[510-514] On the other hand, the fact that the lightfastness of materials dyed with water-soluble dyes should in the same way depend on the physical state of the dyes in the fibers was not evident because the monomolecular sorption of direct dyes on the cellulose chains of the fibers could not be excluded.[445,513,515,516] However, besides the kinetic studies of fading by Giles *et al.*[7,430,448,450] which point to the incorporation of water-soluble dyes in part as aggregates or crystals of submicroscopic size in the fibers, direct evidence for this aggregation could be obtained by Weissbein and Coven.[445] An examination of the physical state of direct dyes in viscose by an electron microscope method showed that direct dyes with the highest lightfastness on cellulose are the most highly aggregated.

3. *Relation between Dye Symmetry and Lightfastness*

In this context the attempt of Giles and co-workers[517] to find a relation between the molecular symmetry or molecular weight of dyes and their lightfastness in fibers should be mentioned. A relation could only be detected for vat dyes and for monosulfonated acid dyes, demonstrating that molecules with high symmetry seem to favor the formation of more stable dye micelles. However, it is interesting to see that there is a significant relation between symmetry (given by the molecular axial ratio of maximum length to breadth) and McLaren's fading ratio,[401,412] which gives the ratio of the fading caused by visible light to UV light (whereby a

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[508] A. B. Boldstein and D. N. Koenig, *Textile Res. J.* **29**, 66 (1959).

[509] G. Eigenmann, *Helv. Chim. Acta* **46**, 298 (1963).

[510] G. S. Egerton and A. G. Roach, *Nature* **180**, 1349 (1957); *J. Soc. Dyers Colourists* **74**, 401 (1958).

[511] E. Kornreich, *J. Soc. Dyers Colourists* **62**, 318 (1946).

[512] E. I. Valko, *J. Am. Chem. Soc.* **63**, 1433 (1941).

[513] T. Vickerstuff, "The Physical Chemistry of Dyeing," pp. 167–284. Oliver & Boyd, London, 1954.

[514] J. Weinstein and G. M. Wyman, *J. Am. Chem. Soc.* **78**, 2387 (1956).

[515] R. A. Brooks, *Dyer* **120**, 161 (1958).

[516] E. I. Valko, *Textile Res. J.* **27**, 883 (1957).

[517] C. H. Giles, K. V. Datye, B. J. Hojiwala, N. B. Shah, and D. Smith, *Textile Res. J.* **36**, 587 (1966).

high fading ratio corresponds to low lightfastness). As a low fading ratio (i.e., high lightfastness) is connected with a low axial ratio (i.e., high symmetry) the favored formation of stable micelles in the case of dyes with high symmetry is indicated. Moreover it can be concluded that with a shortening of the axial ratio higher energy, i.e., UV radiation, is necessary for breaking these structures. A further examination of these aspects seems to be very promising. In discussing the relation between lightfastness and aggregation the fact should also be taken into account that according to Scheibe[288] the lifetime of the excited photoreactive state of a dye can be diminished by the formation of large aggregates.

D. INTERNAL CHEMICAL FACTORS

The physical state of the dyes in substrates can be the reason for not finding any relation between the lightfastness and chemical structure of dyes in many cases. Differences in the physical state may often mask differences in the chemical reactivity so that conclusions on any correlations with structure are impossible. However, in spite of this difficulty, some chemical factors could be detected and should help further work on this problem.

1. *Relation between the Fading Mechanism and Substrate*

From the results of Chipalkatti, Cumming, Giles, and others[89,366,441,450] the general and important rule can be postulated that normally dyes are oxidized when fading on any nonprotein substrates, e.g., cellulose (cotton, viscose rayon, linen), cellulose acetate, polyester, nylon, and reduced on protein substrates, e.g., wool, silk, gelatin.

a. Fastness Differences. By the comparison method (see Section III,A,4,d) a difference of lightfastness gradings on protein and nonprotein substrates could be detected by Giles[447] with a large number of dyes. The fastness comparison curves showed negative slopes according to the differences in the chemical nature of fading on the different fibers. This fact can be expected from the opposite nature of reduction and oxidation, which leads to an opposite sequence of dyes arranged in the order of increasing fastness on protein and nonprotein fibers. That is, if dyes increase in lightfastness on proteins in the order A → B → C, they increase in fastness on nonproteins in the order C → B → A (see Fig. 22 and examples in references 447 and 450). Because of an influence of physical factors this opposite sequence may often be disturbed. But according to Giles,[447] usually dyes of high fastness on nonproteins are about one or two grades less fast on proteins, and dyes of low fastness on nonproteins often show one or two higher fastness grades on proteins. In this

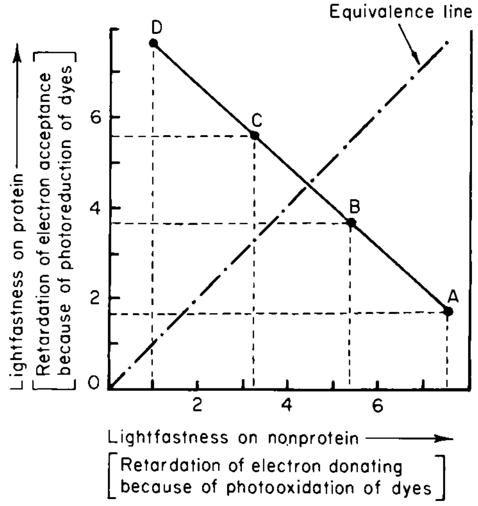

FIG. 22. Comparison of lightfastness of dyes on protein and nonprotein fibers. Sequence of fastness: On protein A → B → C → D; on nonprotein D → C → B → A.

connection it should be mentioned that the histidine and the tryptophan side chains of proteins are probably responsible for the reduction of the dye.[450,518]

b. Relation with Hammett σ-values. Studies on the relative fading rates of several series of dyes with different substituent groups on protein and nonprotein substrates have given a relation between the Hammett σ-values of the substitutents and lightfastness.[89,366,441] This relation was expected from the different fading character of fibers which suggests that electron-donating groups (e.g., NH_2, OCH_3) should accelerate oxidation in the dark and during irradiation (i.e., fading) on cellulose or any nonprotein substrate, and retard the reductive fading on proteins. On the other hand, electron-attracting groups (e.g., NO_2 and Cl), which increase the resistance to oxidation, should decrease the fading on nonproteins and accelerate fading on proteins. It is interesting to note that Chipalkatti *et al.*[366,441] observed a linear relationship between the relative fading rate and the Hammett σ-values of meta and para substituents in the benzene nucleus of a series of dyes of the same basic chemical structure, e.g., in phenylazonaphthalene dyes. According to the different photochemical behavior of substrates in the case of proteins, lines of positive slope, and on nonproteins, lines of negative slopes have been found (see Fig. 23).

There is no doubt that this experimental evidence on the relation between substituent-group influence and lightfastness can be disturbed

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[518] A. Kirkpatrick and J. A. Maclaren, *Textile Res. J.* **34**, 1082 (1964).

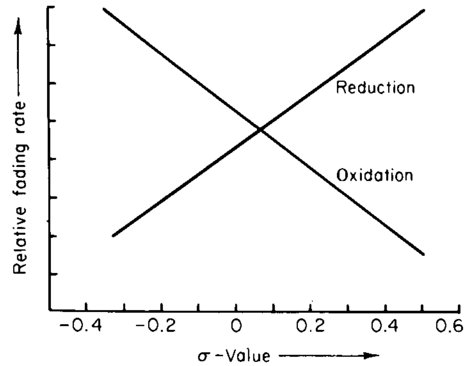

FIG. 23. Scheme of relation between relative fading rate and σ-value. Examples of σ-values: *p*-NH_2, −0.66; *m*-NH_2, −0.16; *p*-OH, −0.357; *p*-OCH_3, −0.27; *p*-Cl, +0.23; *m*-Cl, +0.37; *p*-NO_2, +0.778; *m*-NO_2, +0.71.

in many cases by competitive processes which result from differences in the physical state of dyes within the fibers or from photochemical reactions caused by other substances incorporated in the substrate. However, the relation seems to be correct in a series of dye–fiber systems. In this context it is interesting to note that the application of Hammett σ-values which are derived from the dark-dissociation equilibrium of substituted benzoic acids (and which specifies the relative electron density for various substituents at the sites of reaction in the meta or para position to the substituent) is not in contradiction to the electron density distribution in the excited state of dyes. Measurements of the acid–base equilibrium constant of a number of molecules showed large changes between the first excited singlet state and ground state,[519,520] but only small differences between the triplet state and ground state.[46,521] From this result it can be concluded that the electron density distribution of the triplet state, which may often be the reactive one in photofading, is similar to that of the ground state. For a discussion on this relationship in the case of triphenylmethane dyes and nitrodiphenylamine dyes see the work of Zollinger and others.[6,522–524]

[519] T. Förster, *Naturwissenschaften* **36**, 186 (1949).

[520] A. Weller, "Progress in Reaction Kinetics," Vol. I, p. 187. Pergamon Press, Oxford, 1961.

[521] G. Jackson and G. Porter, *Proc. Roy. Soc.* **A260**, 13 (1961).

[522] R. F. Johnson, O. A. Stamm, and H. Zollinger, *in* "Optische Anregung organischer Systeme. 2nd Internationales Farbensymposium" (W. Foerst, ed.), pp. 375–390. Verlag Chemie, Weinheim, 1966.

[523] F. Feichtmayr and J. Schlag, *in* "Optische Anregung organischer Systeme. 2nd Internationales Farbensymposium" (W. Foerst, ed.), pp. 356–374. Verlag Chemie, Weinheim, 1966.

[524] R. S. Asquith and B. Campbell, *J. Soc. Dyers Colourists* **79**, 678 (1963).

2. *Relation between the Fading Mechanism and Dye Structure*

In spite of the influence of substrates on the fading mechanism the importance of the structure of the dye in fading properties should not be overlooked. Therefore, dyes which are readily reduced but oxidized with difficulty may be reduced during the fading on nonproteins. The same structural influence can lead to photooxidation of a dye on proteins, e.g., in the case of hematin. In this context the classification of dyes and the important structures given in Section II,B,3,b should be considered. They clearly demonstrate the relation between photochemical reactivity against oxidizing or reducing agents and the structure of the dyes. For example, vat dyes characterized by very strong oxidizing carbonyl (i.e., hydrogen-abstracting) groups when the lowest excited state is $^3(n,\pi^*)$, may be photoreduced on (normally photooxidizing) nonprotein substrates. From this example it can be seen that mechanisms of fading of the dye–fiber systems can be derived in many cases from studies on the simple model systems. The general mechanisms derived from model systems are responsible for fading in complicated systems; however, in a series of cases, they are masked and impaired by other physical and chemical processes.

E. PRODUCTION OF HIGH LIGHTFASTNESS

From the facts discussed above it can be concluded that there is a series of methods for preventing the photodestruction of the dye and for retarding phototendering.

Above all it can be seen that by changing the physical state of dyestuffs or fibers, an increase of lightfastness is possible: For example, according to Giles[525] the reduction of the proportion of small particles to a minimum is very important because these particles fade first, and because fading is judged by the rate of destroying the dye in the earlier stages. Furthermore, methods for developing dye aggregates can reduce fading by using, e.g., dyes with low solubility in water, fibers with high or very low regain which contain no solid, by avoiding hydrogen-bonding agents or cationic-active agents, or by subsequent treatments such as steaming, etc.[526] Moreover, because of the relations discussed the incorporation of traces of oxidizing agents in protein fibers or of reducing agents (e.g., formaldehyde) in nonproteins can increase fastness. Pigments are of high fastness especially in pale colors. The influence of the photochromic effect can also be used (see Section II,B,1) for increasing lightfastness; but see also reference 527. Moreover, by embedding dyes in

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[525] Z. Hajós and J. Fodor, *Acta Chim. Acad. Sci. Hung.* **16,** 291 (1958).

[526] C. T. Speiser, *Am. Dyestuff Reptr.* **41,** 349 (1952).

[527] G. von Hornuff, *Textil-Praxis* **20,** No. 3, 225 (1965).

a polar medium, e.g., in KBr, or by using acid dyes in the coloring of anodized aluminium the lightfastness could be remarkably enhanced.[481] Similar results are obtained by precipitating certain basic dyes with complex phosphotungstomolybdic acids.[528]

It would be beyond the scope of this section to discuss all the different possibilities for improving lightfastness by special treatments or additives; see, e.g., the review given by Pestemer[90] and other studies.[428,525,526,529-533] In one series of methods the photoexcited states are deactivated without any disturbing reaction, whereas in other processes the substances which react photochemically with the dyes are chemically modified.[131] As an example of improving the lightfastness of dye layers by deactivation by help of a radiationless energy-transfer process a recent patent of H. Kuhn *et al.*[534] should be mentioned. In this method the lightfastness of a dye is improved when a layer of another suitable dye or of metal (e.g., Au), which can be separated from one another by a thin layer of barium stearate, is applied.

In this context it is interesting to note that analogous effects of increasing stability against light are very important in nature because of the necessity of protection of cells from photosensitized destruction catalyzed, e.g., by chlorophyll. Observations on the blue-green mutant strain of the nonsulfur bacterium *Rhodopseudomonas spheroides* pointed to the possibility that carotenoids are universally responsible for inhibition effects[535,536] because of an interaction between them and the potentially lethal photosensitizing chlorophyll and bacteriochlorophyll; see the review of Krinsky.[537] A series of experiments have demonstrated that chlorophyll-catalyzed photooxidations,[538,539] photoreductions, etc.,[540-542]

[528] *BIOS* **1661**, p. 19 (cited in Patterson and Pilling[481]).

[529] G. Eigenmann, Schweiz. P. 405229.

[530] H. Kling, and F. Galil, *Textil-Praxis* **5**, 336 (1967).

[531] Northern Piedmont Section, *Am. Dyestuff Reptr.* **54**, 37 (1965).

[532] H. Herzog and J. Koszticza, *Am. Dyestuff Reptr.* **54**, 29 (1965).

[533] Nippon Rayon Co. Ltd., *JP* 8377/64; *BP* 984,485.

[534] H. Kuhn, K. H. Drexhage, and F. P. Schäfer, *DBP* 1260432.

[535] M. Griffiths, W. R. Sistrom, G. Cohen-Bazire, and R. Y. Stanier, *Nature* **176**, 1211 (1955).

[536] W. R. Sistrom, M. Griffiths, and R. Y. Stanier, *J. Cellular Comp. Physiol.* **48**, 473 (1956).

[537] N. I. Krinsky, *in* "Photophysiology" (A. C. Giese, ed.), Vol. 3, pp. 122–195. Academic Press, New York, 1968.

[538] S. Aronoff and G. Mackinney, *J. Am. Chem. Soc.* **65**, 956 (1943).

[539] E. Fujimori and R. Livingston, *Nature* **180**, 1036 (1957).

[540] A. A. Krasnovskii, N. N. Drozdova, and E. V. Pakshina, *Biokimiya* **25**, 288 (1960).

[541] E. Fujimori and M. Tavla, *Photochem. Photobiol.* **5**, 877 (1966).

[542] W. A. Maxwell, J. D. Macmillan, and C. O. Chichester, *Photochem. Photobiol.* **5**, 567 (1966).

and the self-destruction (i.e., oxidative photobleaching) of chlorophyll by high light intensities in the presence of air could be prevented by the addition of carotenes with more than seven conjugated double bonds.[543,544] A great many mechanisms for explaining the inhibition effect deal with the possibility of quenching the triplet state of chlorophyll.[539,545,546] Direct evidence has recently been given that this quenching results from a triplet–triplet energy-transfer process from chlorophyll to carotenoids which degrades light energy without any damage.[547]

IV. Photosensitizing Action of Dyes

A. General Aspects

The photosensitizing action of dyes results from the ability of the dyes to act either as strong oxidizing or as strong reducing agents in the presence of reducing or oxidizing substances, with subsequent regeneration and returning to the normal state. Moreover, in many reactions dyes are predestined sensitizers because the chemically most reactive triplet state is produced in dyes with high efficiency by intersystem crossing from the first excited singlet state. Dye molecules excited in the triplet state are not only reactive in the course of redox reactions, but they can also transfer the energy of the triplet state to other molecules and thereby start specific reactions. Furthermore, dye molecules as light-sensitive chromophores associated with large molecules of protein can, by absorption of light, initiate key processes of life, without any irreversible destruction. In addition, aggregated dye molecules are able to react in the excited state with contacting systems and, thereby, induce important physical and chemical processes which could not start without dyes under the influence of visible light.

In Fig. 24 a survey of the various processes which are possible in photosensitization with dyes is given. The principles of these reactions (sensitized photooxidation, sensitized photoreduction, etc.) have been discussed in Sections II and III, so that in the following sections only a summary of the different reactions seems to be necessary; for reviews see references 6 and 254.

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[543] H. Claes and T. O. M. Nakayama, *Z. Naturforsch.* **14b**, 746 (1959).

[544] H. Claes, *Biochem. Biophys. Res. Commun.* 3, 585 (1960).

[545] H. Gaffron, *Proc. 5th Intern. Congr. Biochem., Moscow, 1961* Vol. 6, p. 223. Pergamon Press, Oxford, 1963.

[546] R. K. Clayton, "Molecular Physics in Photosynthesis," p. 103. Ginn (Blaisdell), Boston, Massachusetts, 1965.

[547] M. Chesin, R. Livingston, and T. G. Truscott, *Trans. Faraday Soc.* **62**, 1519 (1966).

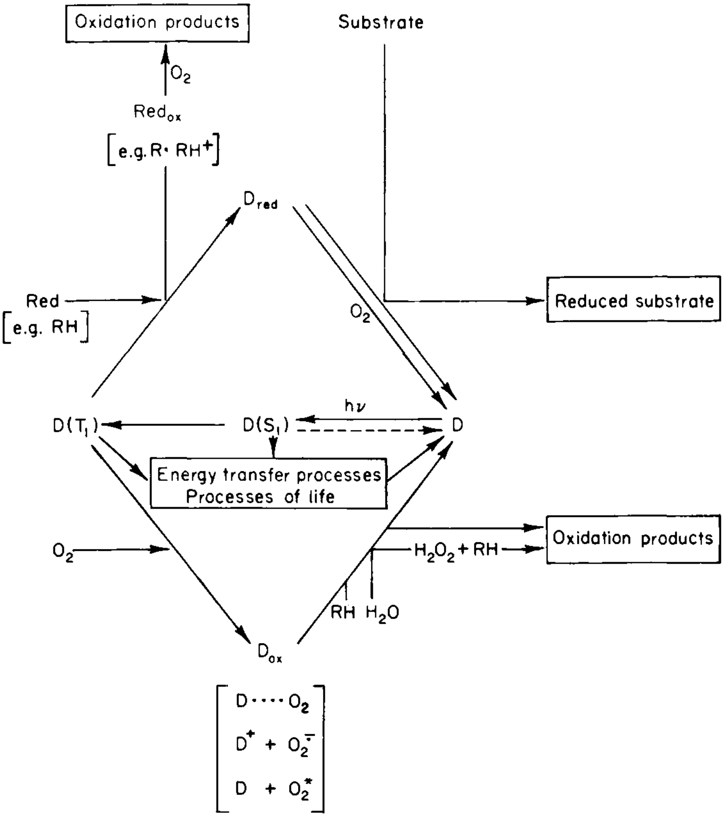

FIG. 24. Scheme of sensitization processes with dyes.

B. SENSITIZED PHOTOREDUCTIONS

1. *Principles*

By the absorption of visible light many dyes are reduced in the presence of reducing substances (electron donors such as cysteine, allylthiourea, ascorbic acid, or chelating agents with secondary or tertiary nitrogens, e.g., EDTA) and thereby are able to donate electrons to other compounds. The reduction potential of the reduced dye can reach a value of —1.3 V (e.g., proflavine[101]), so that a variety of substances including metal ions,[548] e.g., Hg^{2+}, Ag^+, Ti^{4+}, CrO_4^{2-}, or MoO_4^{2-}, can be reduced. The production of triplet states with high efficiency can be of great importance for the course of such reactions.

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[548] G. K. Oster and G. Oster, *J. Am. Chem. Soc.* **81**, 5543 (1959).

Because of returning to the normal state after reducing other substances the dye can act as photosensitizer for chemical reductions several times.

2. *Dye-Sensitized Photopolymerization*

The polymerization of vinyl compounds can be initiated by free radicals which may be produced by the direct photolysis of the monomers (UV light of about 3000 Å). Oster found that the quantum yield of acrylonitrile photopolymerization which can be extended to the visible range by dyes[549] is considerably enhanced in the presence of mild reducing agents and oxygen.[236] Since the first photosensitized polymerizations of water-soluble vinyl monomers by dye–reducing agent systems a variety of such processes have been reported.[102,126,127,130,550-560] As reducing agents ascorbic acid, phenylhydrazine hydrochloride, secondary and tertiary amines, amino acids, thiourea and its derivatives, thiocyanate ion, and dicarbonyl compounds, especially β-diketones[556] could be used. A series of dyes was found to be effective, e.g., rose bengal, tetrabromofluorescein (eosin), acridine orange, 3,6-diaminoacridine (acriflavine), riboflavin-5′-phosphate, rhodamine B, thionine, or methylene blue. With certain combinations of dye and reducing agent, pure liquid monomers and concentrated solutions of monomers in water, methanol, or acetone were photopolymerized. Photopolymerization was possible with monomers of acrylic acid arylamide, methacrylic acid, vinyl acetate, methyl methacrylate, styrene, and others. Dye-sensitized photopolymerization offers a convenient method of rapid and controllable polymerizations with which extremely high molecular weights can be obtained. Even high molecular weight copolymers of allyl alcohol and acrylonitrile are produced.[550]

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[549] C. H. Bamford and M. J. S. Dewar, Proceedings of the Society of Dyers and Colourists: Symposium on Photochemistry in Relation to Textiles, *J. Soc. Dyers Colourists* **65,** 674 (1949).

[550] G. Oster and Y. Mizutani, *J. Polymer Sci.* **22,** 173 (1956).

[551] N. Uri, *J. Am. Chem. Soc.* **74,** 5808 (1952).

[552] G. Delzenne, W. Dewinter, S. Toppet, and G. Smets, *J. Polymer Sci.* **A2,** 1069 (1964).

[553] S. Chaberek, A. Shepp, and R. J. Allen, *J. Phys. Chem.* **69,** 641 (1965).

[554] G. Delzenne, S. Toppet, and G. Smets, *J. Polymer Sci.* **48,** 347 (1960).

[555] S. Chabereck and R. J. Allen, *J. Phys. Chem.* **69,** 647 (1965).

[556] S. Chabereck, R. J. Allen, and G. Goldberg, *J. Phys. Chem.* **69,** 2834 (1965).

[557] S. Chabereck, R. J. Allen, and A. Shep, *J. Phys. Chem.* **69,** 2842 (1965).

[558] C. S. H. Chen, *J. Polymer Sci.* **B2,** 891 (1964).

[559] Cr. Simionescu and C. Ungureanu, *Studii Cercetari Chim.* **13,** 757 (1964).

[560] A. I. M. Sheriff and M. Santappa, *J. Polymer Sci.* **A3,** 3131 (1965).

As photopolymerization has been observed either in the presence of oxygen during irradiation or by the introduction of oxygen after the photoreduction of the dye Oster[102] concluded that the free radicals which initiate polymerization result from the reaction between oxygen and the photoreduced dye. According to Delzenne *et al.*[554] these free radicals may be $HO_2\cdot$ radicals or may result from the decomposition of hydrogen peroxide which can be formed during the reoxidation of the reduced dye (i.e., the leuco derivate or the semiquinone). On the other hand, by kinetic studies on the anaerobic, thionine-sensitized photopolymerization of acrylamide in the presence of 2,4-pentanedione and other reducing agents, Chaberek *et al.*[553,557] showed that the polymerization-initiating free radicals appear to be semithionine or semimethylene blue. Therefore, for the formation of initiating radicals the following sequence of reactions can be discussed:

$$\begin{aligned} D + h\nu &\rightarrow D(S_1) \rightarrow D(T_1) \\ D(T_1) + RH &\rightarrow DH\cdot + R\cdot \\ DH\cdot + M &\rightarrow M\cdot + D + H^+ \\ M\cdot + M &\rightarrow 2M\cdot \rightarrow \text{Polymer} \end{aligned}$$

It is interesting to note that the dye-sensitized polymerization, e.g., the polymerization of acrylamide by methylene blue, has also been observed in the solid state.[558]

3. *Sensitized Photo-cross-linking of Polymers*

Polymer crosslinking reactions had been used as a first form of successful photography in the early 19th century by Niepce and Talbot. Because of the restrictions of cross-linking reactions of polymers to the ultraviolet region the practical use in photography, e.g., for photochemical processes such as photoengraving, was severely restricted.

Oster and co-workers[561–564] showed that the cross-linking of polyethylene, i.e., carbon–carbon crosslink in which hydrogen abstraction from two adjacent saturated hydrocarbon chains occurred, can be sensitized for the near ultraviolet range by benzophenone and 2-methylanthraquinone. With these compounds a series of polymers, e.g., nylon copolymers, poly(cellosolve methacrylate) Vinalak 5630 or poly(vinyl butyral), could be sensitized for crosslinking up to 400 nm.[565]

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[561] G. Oster, *J. Polymer Sci.* **22,** 185 (1956).

[562] G. Oster, G. K. Oster, and H. Moroson, *J. Polymer Sci.* **34,** 671 (1959).

[563] G. Oster, *Polymer Letters* **2,** 1181 (1964).

[564] G. K. Oster and G. Oster, *J. Polymer Sci.* **48,** 321 (1960).

[565] G. Oster, *J. Polymer Sci.* **B2,** 891 (1964).

Moreover, the cross-linking of polymers containing mercaptan groups as a result of the abstraction of labile hydrogens from sulfhydryl groups (which needs energies between 40 and 70 kcal/mole) can be extended to the visible region by the sensitizing action of dyes.[127] The primary step of these reactions was studied with dye–mercaptan systems, in which the sulfhydryl compound (e.g., glutathione, cysteine, or mercaptoethanol) reduced the excited dye to its leuco form, thereby being oxidized to the disulfide. In the presence of oxygen the leuco dye is reoxidized so that the dye can be reduced again. Oxidation of the mercaptan groups leads to cross-linking when these groups are residues of macromolecules.[564]

The ability of photoreduced dyes to reduce metal ions such as Hg^{2+}, or $Cr_2O_7^{2-}$ has been used for dye-sensitized cross-linking or de-cross-linking. Thus, the reduction of bichromate to Cr^{3+}, which cross-links polymers such as poly (vinyl alcohol), polyacrylamide, all proteins and many polysaccharides, can be extended from the ultraviolet region to the visible region by dyes. For example, the bichromate cross-linking process which is used in photoengraving becomes a visible light process by the addition of a photoreducible dye and an electron donor, e.g., the chelating agent ethylenediaminetetraacetic acid, to a gelatine–bichromate mixture.[548,564] On the other hand, metals which are cross-linking agents in their high valence state but not in their lower state bring about a de-cross-linking of metal cross-linked materials in the presence of an excited dye–donor system. For example, polyacrylamide which is cross-linked by mercuric ions becomes de-cross-linked by visible light absorbed by the dye–donor system (such as erythrosine and EDTA) so that a water-soluble polymer is produced.[564]

4. *Spectral Sensitization of the Photographic Process*

Formally, the spectral sensitization of silver halides discovered by H. W. Vogel in 1873 may be considered as a process in which silver ions are reduced by dyes which are photoreduced by an oxidation–reduction reaction between the light-excited dye and a reducing agent. By taking bromide ions, which can be rich in energy, in crystal dislocations, on the surface of the grains, and in other places,[566,567] as electron donors the simple scheme of Fig. 25 may describe the sensitization process.

It would be beyond the scope of this chapter to discuss the spectral sensitization of silver halides in detail; see, e.g., recent re-

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[566] J. Eggert, M. Biltz, and F. G. Kleinschrod, *Z. Wiss. Phot., Photophysik Photochem.* 39, 140, 155 (1941).

[567] W. F. Berg, *Rept. Progr. Phys.* 11, 264 (1946–1947).

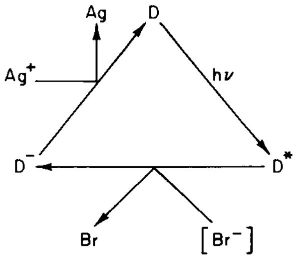

FIG. 25. Simple scheme of spectral sensitization of silver halides. $[Br^-]$ corresponds to energy-rich bromide ions in the Silver halide lattice (at surface points, etc.); see Eggert *et al.*[566] and Berg.[567]

views[6,457,475,568–570] and some special papers on the mechanism of this important process.[453,571–581] The process is more complicated than that discussed above because of the solid-state conditions and because of a variety of relationships (e.g., concerning the quantum efficiency,[582–584] the influence of dye-layer thickness,[585] the effect of temperature,[586,587] the

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[568] F. Dörr, *in* "Grundlagen der photographischen Prozesse mit Silberhalogeniden" (H. Frieser, G. Haase, and E. Klein, eds.), Vol. 3, pp. 603–663. Akad. Verlagsges., Frankfurt a.M., 1968.

[569] J. Bourdon, *J. Phys. Chem.* **69,** 705 (1965).

[570] E. Klein and R. Matejec, *in* "Optische Anregung organischer System. 2nd Internationals Farbensymposium" (W. Foerst, ed.), p. 698. Verlag Chemie, Weinheim, 1966.

[571] R. W. Gurney and N. F. Mott, *Proc. Roy. Soc.* **A164,** 151 (1938).

[572] W. Noddack and H. Meier, *Z. Elektrochem.* **63,** 971 (1959).

[573] J. Eggert, *Ann. Physik* [7] **4,** 140 (1959).

[574] R. C. Nelson, *J. Opt. Soc. Am.* **48,** 948 (1958).

[575] A. Terenin and I. Akimov, *J. Phys. Chem.* **69,** 730 (1965).

[576] W. West and B. H. Carroll, *in* "The Theory of the Photographic Process" (C. E. K. Mees and T. H. James, eds.), 3rd ed., p. 233. Macmillan, New York, 1966.

[577] J. Eggert and W. Noddack, *Naturwissenschaften* **15,** 57 (1927).

[578] G. Scheibe and F. Dörr, *Sci. Phot., Proc. 7th Intern. Colloq. Liege, 1959* p. 512. Pergamon Press, Oxford, 1962.

[579] W. Weigl, *Phot. Sci., 8th Symp., Zürich, 1961* p. 345. Focal Press, London, 1963.

[580] S. J. Dudkowski, A. G. Kepka, and L. I. Grossweiner, *J. Phys. Chem. Solids* **28,** 485 (1967).

[581] T. Tani, S. Kikuchi, and K. Honda, *Phot. Sci. Eng.* **12,** 80 (1968).

[582] B. Zuckerman, *Phot. Sci. Eng.* **11,** 156 (1967).

[583] J. P. Sage, *J. Phys. Chem. Solids* **26,** 1245 (1965).

[584] B. H. Carroll, *Sci. Phot., Proc. 7th Intern. Colloq., Liege, 1959* p. 427. Pergamon Press, Oxford, 1962.

[585] R. C. Nelson, *J. Opt. Soc. Am.* **46,** 13 (1956).

[586] W. West, *Phot. Sci. Eng.* **6,** 92 (1962).

[587] H. Frieser, A. Graf, and D. Eschrich, *Z. Elektrochem.* **65,** 870 (1961).

importance of the aggregated state of dyes,[288] the effects of desensitization,[457,588,589] the hypersensitization,[590] or the sensitization of the photoconductivity of different semiconductors such as ZnO, AgBr, CdS, etc.[457,591,591a,592]) which cannot be explained by the simple scheme given above.

The results obtained with photoelectric measurements on dye–silver halide and other model systems[478,479] show that the sensitization reaction may probably be attributed to two effects: Firstly to the formation and migration of electronic charge carriers which are produced in the dye by light absorption, and secondly to the formation of a junction potential difference in the zone which lies between the dye and the silver halide and which separates the charge carriers formed by the action of light.[457,593]

C. Sensitized Photooxidation

1. *Mechanism*

Dye-sensitized photooxidations can occur according to two different mechanisms, as an oxygen-transfer process or as a hydrogen-abstraction reaction.

a. Oxygen-Transfer Process. Different mechanisms have been discussed for this process in which oxygen is transferred to an oxidizable substrate. But, the excitation of the dye to the singlet state, which is followed by intersystem crossing to the triplet state, is common. In 1959, Oster and co-workers[320] using proflavine as sensitizer and *p*-toluenediamine as the substrate in their kinetic studies showed that usually dye molecules in the long-lived triplet state react in dye-sensitized photooxidations.

(1) According to the concepts of Schönberg, Schenck, and others[309,310,312,321,594–596] the reactive species is a metastable dye–oxygen complex produced between the triplet excited dye and oxygen, i.e.,

$$\begin{aligned} \mathrm{D} + h\nu &\rightarrow {}^1\mathrm{D} \rightarrow {}^3\mathrm{D} \\ {}^3\mathrm{D} + \mathrm{O_2} &\rightarrow [\mathrm{D} \cdot\cdot\cdot\cdot \mathrm{O_2}] \\ [\mathrm{D} \cdot\cdot\cdot\cdot \mathrm{O_2}] + \mathrm{A} &\rightarrow \mathrm{D} + \mathrm{AO_2} \end{aligned}$$

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[588] H. Wolff, *Fortschr. Chem. Forsch.* **3**, No. 3, 5031 (1955).

[589] H. Frieser and M. Schlesinger, *Phot. Sci. Eng.* **12**, 17 (1968).

[590] E. Inoue and T. Yamaguchi, *Bull. Chem. Soc. Japan* **36**, 1573 (1963).

[591] H. Gerischer and H. Tributsch, *Ber. Bunsenges. Phys. Chem.* **72**, 437 (1968).

[591a] H. Tributsch and H. Gerischer, *Ber. Bunsenges. Phys. Chem.* **73**, 850 (1969).

[592] S. W. Ing and Y. S. Chiang, *J. Chem. Phys.* **46**, 478 (1967).

[593] H. Meier, *Chimia (Aarau)* **18**, 179 (1964).

[594] A. Schönberg, *Ann. Chem.* **518**, 219 (1935).

[595] R. Livingston and V. Subba Rao, *J. Phys. Chem.* **63**, 794 (1959).

[596] T. Wilson, *J. Am. Chem. Soc.* **88**, 2898 (1966).

(2) As shown by Kautsky, Egerton, and others[350,356,357,375,431,597,598] photosensitized oxidation can occur in systems with separated dyes and substrates, indicating the production of an oxidizing volatile species, which seems to be in contradiction to the first concept. As discussed in Section II,B,3 this species may be either hydrogen peroxide (in the presence of water)[299,350] or a semireduced oxygen molecule $O_2\cdot^-$ which can act as an intermediate in the production of hydrogen peroxide ($O_2\cdot^- + H^+ \rightarrow HO_2\cdot$; $2\ HO_2\cdot \rightarrow H_2O_2 + O_2$).[308] The reaction between oxygen and dye leads to a semioxidized dye radical which is rereduced to the ground state by the oxidizable reactant.[352,599,600] Moreover, this semioxidized dye is also produced by an electron dismutation reaction between dye molecules in the excited triplet state and those in the ground state, so that the production of semioxidized dye radicals, e.g., of fluorescein,[110] can be appreciable. As in the dismutation process, a semireduced dye is formed which rapidly reacts with oxygen; the reduced $O_2\cdot^-$ also results from this indirect reaction. These reactions lead to the following simple scheme for photosensitized autoxidation reaction:

$$D + h\nu \rightarrow {}^1D \rightarrow {}^3D$$

$$\begin{array}{ll} {}^3D + O_2 \rightarrow D^+ + O_2\cdot^- & {}^3D + D \rightarrow D^+ + D^- \\ D^+ + A \rightarrow D + A_{ox} & D^- + O_2 \rightarrow D + O_2\cdot^- \\ O_2\cdot^- + H^+ \rightarrow HO_2\cdot & 2HO_2\cdot \rightarrow H_2O_2 + O_2 \end{array}$$

(3) As another possibility the production of an activated oxygen species by the excitation of the dye has been discussed by Kautsky, Egerton, and others.[37,350,353,354,601,602] This activated oxygen reacts with organic compounds, thereby producing peroxide, i.e.,

$$D + h\nu \rightarrow {}^1D \rightarrow {}^3D$$

$$({}^1D \text{ or}) \ {}^3D + O_2 \rightarrow D + O_2^* \qquad O_2^* + A \rightarrow AO_2$$

The oxidation products should be the same as in the first mechanism. However, instead of the dye–peroxide complex oxygen eventually, after diffusing over relatively large distances, reacts as active species. This activated oxygen may be vibrationally excited oxygen O_2^*, i.e., ${}^3\Sigma_g{}^-$.[356,357]

According to a hypothesis of Kautsky[354,601] proposed in 1931 oxygen reacts as a metastable species which is produced by an energy transfer from a dye molecule in a long-lived metastable state. Nowadays, the formation of dyes in their excited triplet state with high efficiency is known. Moreover, triplet–triplet transfer processes are proven (see Sec-

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[597] R. F. Weiner and H. H. Seliger, *Photochem. Photobiol.* **4,** 1207 (1965).

[598] L. Bourdon and B. Schnuriger, *Photochem. Photobiol.* **5,** 507 (1966).

[599] R. Livingston, *J. Phys. Chem.* **46,** 233 (1942).

[600] V. Kasche, *Photochem. Photobiol.* **6,** 643 (1967).

[601] H. Kautsky and H. De Bruyn, *Naturwissenschaften* **19,** 1043 (1931).

[602] H. Kautsky, *Biochem. Z.* **291,** 271 (1937).

tion I). Because of these facts Kautsky's mechanism can be discussed as a spin-allowed energy-transfer process from triplet dye molecules to triplet oxygen in which singlet oxygen is produced.[254,355,603-605] In Fig. 26 the different lowest states of oxygen are represented[16,355] which have been produced (and spectroscopically identified) by electrodeless discharge,[606,607] by the chemiluminescent hypochlorite–hydrogen peroxide reaction ($NaOCl + H_2O_2 \rightarrow O_2^* + H_2O + NaCl$),[603,608] and by other processes.[609,610]

Foote and co-workers[603,611] showed that by the oxidation of olefinic dienoid and aromatic compounds with singlet oxygen generated by the hypochlorite–hydrogen peroxide reaction the same products are obtained as those which are formed by dye-sensitized photooxygenation. The product distributions of reactions which result in several oxidation products have shown identity in both photosensitized and chemical oxygenation.[612] For instance, the product distribution in the oxygenation of limonene is the same when the reaction is photosensitized by rose bengal (riboflavin) in methanol (aqueous *tert*-butyl alcohol), or when a hypochlorite–hydrogen peroxide mixture is the oxidizing agent. It is interesting to note that, e.g., the stability to sensitized photooxygenation of α-pinene is also found in chemical oxygenation with singlet oxygen. From detailed studies of stereoselectivity with different acceptors and by ki-

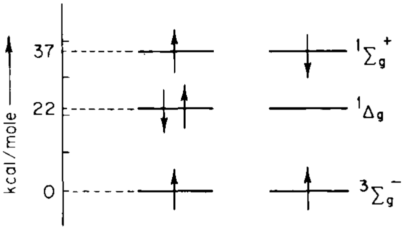

FIG. 26. Different lowest states of oxygen (see text).

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[603] C. S. Foote and S. Wexler, *J. Am. Chem. Soc.* **86,** 3879 (1964).

[604] D. R. Kearns, R. A. Hollins, A. U. Khan, R. W. Chambers, and P. Radlick, *J. Am. Chem. Soc.* **89,** 5455 (1967).

[605] E. J. Corey and W. C. Taylor, *J. Am. Chem. Soc.* **86,** 3881 (1964).

[606] S. N. Foner and R. L. Hudson, *J. Chem. Phys.* **25,** 601 (1956).

[607] J. Arnold, R. J. Browne, and E. A. Ogryzlo, *Photochem. Photobiol.* **4,** 963 (1965).

[608] A. U. Khan and M. Kasha, *J. Am. Chem. Soc.* **88,** 1574 (1966).

[609] E. McKeown and W. A. Waters, *Nature* **203,** 1063 (1966).

[610] H. H. Wasserman and J. R. Scheffer, *J. Am. Chem. Soc.* **89,** 3073 (1967).

[611] C. S. Foote, S. Wexler, W. Ando, and R. Higgins, *J. Am. Chem. Soc.* **90,** 975 (1968).

[612] C. S. Foote, S. Wexler, and W. Ando, *Tetrahedron Letters* **46,** 4111 (1965).

netic measurements Foote[355] concluded that the reactive intermediate in both the dye-photosensitized and chemical oxygenation is $O_2(^1\Delta_g)$. This $^1\Delta_g$ state is characterized by an energy of 22 kcal above the ground state, a longer lifetime than the $^1\Sigma_g^+$ state, an electrophilic character, and the possibility of two-electron reactions because of a vacant orbital. The transition $[O_2(^1\Delta_g)]_2 \rightarrow [O_2(^3\Sigma_g^-]_2$ can be seen from the red chemiluminescence ($\lambda = 6340$ Å corresponding to the combined energy of 22.5×2 kcal/mole, and $\lambda = 7030$ Å) in the $HOCl/H_2O_2$ reaction.[254,613]

From these results the following reaction scheme can be arrived at for dye-sensitized photooxidations:

$$D + h\nu \rightarrow {}^1D \rightarrow {}^3D$$

$$^3D + {}^3O_2 \rightarrow D + {}^1O_2(^1\Delta_g) \qquad {}^1O_2(^1\Delta_g) + A \rightarrow AO_2$$

Dyes which are sensitizers in such photooxygenation reactions (belonging above all to Class I) are very reactive toward oxygen, e.g., acridines, thiazines, xanthene-type dyes (see Section II,B,3).

b. Hydrogen-Abstraction Reaction. In the case of dyes with strong electron- or hydrogen-abstracting groups (i.e., dyes of the photochemical Class II discussed in Section II,B,3,b such as derivatives of anthraquinone, flavanthrone, etc.) which are in contact with compounds containing removable hydrogen, another type of sensitized photooxidation is possible. According to this mechanism, first discussed by Bäckström,[346] the photoexcited dye [in the (n, π^*) triplet state, see Section II,C,2] is reduced by the oxidizable reactant by a transfer of electrons or hydrogen. Then, the resulting semireduced dye radical is reoxidized to the ground state by oxygen,[93,109,242,614-616] i.e.,

$$D + h\nu \rightarrow {}^1D \rightarrow {}^3D$$

$$^3D + RH \rightarrow DH\cdot + R\cdot \qquad R\cdot + O_2 \rightarrow RO_2\cdot \rightarrow \text{Oxidation products}$$

$$DH\cdot + RO_2\cdot \rightarrow D + ROOH \qquad DH\cdot + O_2 \rightarrow D + HO_2\cdot$$

$$DH\cdot + HO_2\cdot \rightarrow D + H_2O_2 \qquad DH\cdot + DH\cdot \rightarrow D + DH_2$$

In the absence of oxygen the semireduced dye is not regenerated but is transformed to the leuco dye, i.e., photobleached. This sensitized oxidation can also lead to a sensitized photodestruction of a dye without any special substrate. In these cases the dye serves as oxidizable substrate, as in the bleaching of aerated chlorophyll by high intensities of light.

The products obtained with this type of sensitized photooxidation must not be the same as in the oxygen-transfer process. For example, isopropyl

[613] S. Arnold, E. A. Ogryzlo, and H. Witzke, *J. Chem. Phys.* **40,** 1769 (1964).

[614] G. O. Schenck, W. Müller, and H. Pfennig, *Naturwissenschaften* **41,** 374 (1954).

[615] J. S. Bellin and G. Entner, *Photochem. Photobiol.* **5,** 251 (1966).

[616] G. S. Egerton and N. E. N. Assaad, *Chem. & Ind.* (*London*) p. 2112 (1967).

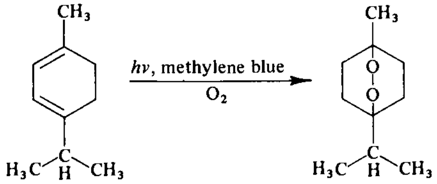
alcohol may be very intensely oxidized by the abstraction mechanism, but is not changed in dye-sensitized photooxygenations.[617]

2. *Examples of Dye-Photosensitized Oxidations*

a. Technical Importance of the Reaction

i. Phototendering. As discussed in detail in Section III the dye-photosensitized degradation of cotton and other textile fibers is the result of a sensitized oxidation of the substrate. Dyes with reactive π,π^* triplet states, such as acriflavine, thioflavine, eosine, fluorescein (i.e., dyes of Class I and III) usually react in the presence of air according to the oxygen-transfer mechanism. Vat dyes and other dyes with reactive n,π^* triplet states act as sensitizers according to the hydrogen-abstraction process. In both reactions the substrate can be destroyed without appreciable bleaching of the dye. In practice, this tendering and breakdown of the fiber is observed above all with certain fast vat dyes and many fugitive dyes. Severe tendering of cotton may already be possible after a short illumination.[618]

ii. Preparative use. With the dye-sensitized photooxygenation reaction oxygen can be highly specifically and smoothly introduced into organic compounds. In one reaction class the oxygenation of cyclic dienes and polycyclic aromatic and heterocyclic compounds leads to cyclic peroxides analogous to the adducts which are formed with dienophiles in the Diels-Alder reaction. For example, the synthesis of ascaridole from α-terpinene belongs to this class.[619,620]



(XIX)

In another reaction class olefins containing allylic hydrogen atoms are oxidized to allylic hydroperoxides with a shifting of the double bond analogous to the ene reactions. As examples of this type, schematically

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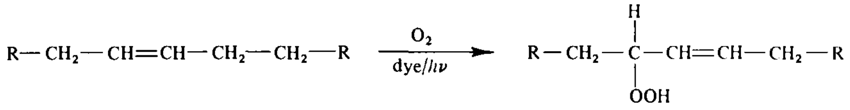
[617] G. O. Schenck, H. D. Becker, K. H. Schulte-Elte, and C. H. Krauch, *Chem. Ber.* **96,** 509 (1963).

[618] E. H. Daruwalla, A. P. D'Silva, and G. N. Tandon, *Textile Res. J.* **37,** 160 (1967).

[619] G. O. Schenck and H. Schulze-Buschoff, *Deut. Med. Wochschr.* p. 341 (1948).

[620] G. O. Schenck and K. Ziegler, *Naturwissenschaften* **38,** 356 (1951).



$$\mathrm{R{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}R} \xrightarrow[\mathrm{dye}/h\nu]{\mathrm{O_2}} \mathrm{R{-}CH_2{-}}\overset{\mathrm{H}}{\underset{\mathrm{OOH}}{\mathrm{C}}}\mathrm{{-}CH{=}CH{-}CH_2{-}R}$$

(XX)

given by (XX), the oxidations of β-pinene to mirtenyle hydroperoxide[621] or of (—)-caryophyllene to 4-allyl hydroperoxides,[622] which are highly sterically controlled,[623-627] should be mentioned.

For photosensitized oxygenations a series of dyes can be used (Class I or III), e.g., fluorescein derivatives such as eosin, rose bengal, etc., porphyrins, methylene blue and others, especially by irradiation with visible light. Further examples of these reactions are given by Schönberg, Schenck, Foote, and others.[6,355,628-632] In discussing the mechanisms of the reaction the fact stressed by Foote,[355] that the electrophilic singlet oxygen can be visualized as a reactive dienophile, analogous to maleic anhydride, which can undergo the Diels-Alder reaction with suitable dienes and the ene reaction with suitable olefins, must be taken into account.

b. Biologically Important Photodynamic Action. Marcacci (1888)[633] and Raab (1900)[634] discovered that biological systems which are sensitized by dyes can be damaged by visible light in the presence of oxygen.[635,636] Such dye-sensitized photoautoxidations, first demonstrated by the rapid killing of paramecia dyed with acridine and other dyes in the

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[621] G. O. Schenck, W. Eggert, and W. Denk, *Ann. Chem.* **584**, 177 (1953).

[622] K. H. Schulte-Elte and G. Ohloff, *Helv. Chim. Acta* **51**, 494 (1968).

[623] G. O. Schenck, K. Gollnick, G. Buchwald, S. Schroeter, and G. Ohloff, *Ann. Chem.* **674**, 93 (1964).

[624] W. Klein and W. Rojahn, *Tetrahedron* **21**, 2173 (1965).

[625] A. Nickon and F. Bagli, *J. Am. Chem. Soc.* **81**, 6330 (1959); **83**, 1498 (1962).

[626] W. H. Schuller and R. V. Lawrence, *J. Am. Chem. Soc.* **83**, 2563 (1962).

[627] H. D. Dässler, *Ann. Chem.* **622**, 194 (1959).

[628] A. Schönberg, "Preparative Organic Photochemistry," 2nd. ed. Springer, Berlin, 1968.

[629] K. Gollnick and G. O. Schenck, *in* "1,4 Cycloaddition Reactions" (J. Hamer, ed.), p. 255. Academic Press, New York, 1967.

[630] K. Gollnick, and G. O. Schenck, *Pure Appl. Chem.* **9**, 507 (1964).

[631] E. J. Bowen, *Advan. Photochem.* **1**, 23 (1963).

[632] G. O. Schenck, *Angew. Chem.* **69**, 579 (1957).

[633] A. Marcacci, *Arch. Ital. Biol.* **9**, 2 (1888).

[634] O. Raab, *Z. Biol.* **39**, 524 (1900).

[635] H. von Tappeiner and A. Jodlbauer, *Deut. Arch. Klin. Med.* **80**, 427 (1904).

[636] H. von Tappeiner and A. Jodlbauer, "Die sensibilisierende Wirkung fluorescierender Substanzen. Gesammelte Untersuchungen über die photodynamische Erscheinung," Vogel, Leipzig, 1907.

light,[634] have been observed in the chief chemical compounds of cells, such as amino acids (e.g., tryptophan,[637-639] L-tyrosine[240,600]), peptides,[637] proteins, nucleic acids (i.e., RNA,[640,641] DNA[642-645]) and enzymes,[646-649] in microorganisms, such as bacteria, viruses,[650] in green plants and mammals. In mammals photodynamic action can lead to different symptoms such as sensory stimulation, skin damage, and also death; see Blum *et al.*[6,651-653] Photodynamic action in man resulting from ingestion or contact with dyes or other sensitizing compounds,[6,651,654,655] or from porphyrin metabolism,[656] is often observed as an immediate phototoxic reaction or as a delayed photoallergic reaction.[657,658] This effect, which is sensitized by a series of dyes,[6,648] such as eosine, rose bengal, methylene blue, chlorophyll, uroporphyrin, trypaflavine, and others, can also lead to cancer, mutations, hemolysis, division anomalies, and other damage; see the reviews in references 6, 150, 651, 659, and 660. However, photosensitized inactivation may also be used as a means of eliminating harm-

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[637] L. Weil, *Arch. Biochem. Biophys.* **110,** 57 (1965).

[638] D. A. Boroff and B. R. Dasgupta, *J. Biol. Chem.* **239,** 3694 (1964).

[639] S. Gurnani, M. Arifuddin, and K. T. Augusti, *Photochem. Photobiol.* **5,** 495 (1966).

[640] E. R. Lochmann and W. Stein, *Biophysik* **4,** 243 (1968).

[641] E. R. Lochmann, *Z. Naturforsch.* **22b,** 196 (1967).

[642] A. Knowles and E. M. F. Roe, *Photochem. Photobiol.* **7,** 421 (1968).

[643] K. Uehara, T. Mizoguchi, Y. Okada, and J. Umemoto, *J. Biochem.* (*Tokyo*) **59,** 556 (1966).

[644] M. I. Simon and H. Van Vunakis, *Arch. Biochem. Biophys.* **105,** 197 (1964).

[645] M. I. Simon and H. Van Vunakis, *J. Mol. Biol.* **4,** 488 (1962).

[646] E. W. Westhead, *Biochemistry* **4,** 2139 (1965).

[647] D. B. S. Millar and G. W. Schwert, *J. Biol. Chem.* **238,** 3249 (1963).

[648] D. Robinson, D. Stollar, S. White, and N. O. Kaplan, *Biochemistry* **2,** 486 (1963).

[649] S. Yamagata, K. Takahashi, and F. Egami, *J. Biochem.* (*Tokyo*) **52,** 261 (1962).

[650] C. Wallis and J. L. Melnich, *J. Bacteriol.* **89,** 41 (1965).

[651] H. F. Blum, "Photodynamic Action and Diseases Caused by Light." Reinhold, New York, 1941.

[652] W. Hausmann, *Biochem. Z.* **30,** 276 (1911).

[653] C. E. Cornelius, I. M. Arias, and B. I. Osburn, *J. Am. Vet. Med. Assoc.* **146,** 709 (1965).

[654] M. M. Cahn, *J. Soc. cosmetic Chemists* **17,** 81 (1966).

[655] B. A. Kirshbaum and H. Beerman, *Am. J. Med. Sci.* **248,** 445 (1964).

[656] M. Borst and H. Koenigsdoerfer, "Untersuchungen über die Porphyrine mit besonderer Berücksichtigung der Porphyrin congenita," Hirzel, Leipzig, 1929.

[657] R. L. Baer and L. C. Harber, *Federation Proc.* **24,** Suppl. 14, 15 (1965).

[658] S. Epstein, *in* "Dermatoses Due to Environmental and Physical Factors" (R. B. Rees, ed.), pp. 119–135. Thomas, Springfield, Illinois, 1962.

[659] J. D. Spikes and B. W. Glad, *Photochem. Photobiol.* **3,** 471 (1964).

[660] J. D. Spikes, *in* "Photophysiology" (A. C. Giese, ed.), Vol. 3. pp. 33–64. Academic Press, New York, 1968.

ful organisms (because of the different resistance to photodynamic action of microorganisms), e.g., from live polio vaccines.[661]

Photodynamic action can be considered as a dye-sensitized photooxidation of the substrate, such as an oxidative destruction of certain amino acid side chains of the protein,[639] in which the dye is not consumed.[320,651] The biological effect of this action is different from that which results from an absorption of ultraviolet radiation and which can be photoreactivated.[662–665] In the last-mentioned reaction, e.g., in the bactericidal action of UV light, photodimerization [i.e., cross-linking of two identical or similar chemical subunits, such as the formation of thymine dimers in ultraviolet ($\lambda = 280$ nm) inactivation of DNA[665,666]] is implicated.[103,667] Therefore, for explaining the different photodynamic effects those mechanisms which have been discussed in Section IV,C,1,a, as, e.g., oxygen-transfer mechanisms, can be quoted. In the absence of oxygen, the photooxidation may also result from a hydrogen abstraction so that semiquinone dye radicals and radicals of the substrate are produced.[237]

D. ENERGY-TRANSFER PROCESSES

1. *Mechanisms*

The radiationless transfer of electronic energy occurring in the gas phase, in solutions, and in crystals is of great importance in many photochemical and biological processes. There are two different mechanisms which are responsible for this transfer (see reviews in 2 and 668):

The *resonance-excitation transfer* over distances up to 60 Å results from a dipole–dipole interaction of the oscillating electric charges between an excited molecule and an acceptor molecule. This radiationless energy transfer mostly observed between singlet states by measurement of the sensitization quenching and depolarization of fluorescence, has been discussed above all by Förster[14,669,670] and recently has clearly been

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[661] C. Hiatt, *Bacteriol. Rev.* **28,** 150 (1964).

[662] A. D. McLaren and S. Shugar, "Photochemistry of Proteins and Nucleic Acids." Pergamon Press, Oxford, 1964.

[663] J. Jagger, *Bacteriol. Rev.* **22,** 99 (1958).

[664] J. A. Duine and W. Berends, *Biochem. Biophys. Res. Commun.* **24,** 888 (1966).

[665] D. Shugar, *Israel J. Med. Sci.* **1,** 1347 (1965).

[666] C. S. Rupert, *in* "Photophysiology" (A. C. Giese, ed.), Vol. 2, pp. 283–327. Academic Press, New York, 1964.

[667] R. Beukers and W. Berends, *Biochim. Biophys. Acta* **49,** 181 (1961).

[668] R. G. Bennett and R. E. Kellogg, *Progr. Reaction Kinet.,* **4,** 215–238 (1967).

[669] T. Förster, *Ann. Physik* [6] **2,** 55 (1948).

[670] T. Förster, *U. S. At. Energy Comm., Div. Biol. Med.* **18,** (1965).

demonstrated by Kuhn and co-workers[671–673] on systems built up of dye monolayers kept at different distances by arachidic acid salt layers.

The *exchange energy transfer* occurs in cases in which the excited molecule is close to an acceptor molecule (< 15 Å), so that the electron clouds of the molecules interact.[674] Because of the independence of the exchanging electronic systems the triplet–triplet energy transfer which is forbidden by the resonance mechanism is possible, i.e.,

$$D(T) + A(S_0) \rightarrow D(S_0) + A(T) \tag{59}$$

The triplet–triplet energy transfer was discovered by Terenin and Ermolaev[675] by observing sensitized phosphorescence in rigid media at 77°K (e.g., with carbonyl compounds as donor and naphthalene and its halogen derivatives as acceptors) and confirmed by many studies.[42,676–679] The importance of this transfer results from the fact that triplets have a relatively long lifetime so that the probability of transferring the energy to a colliding acceptor may be very high. Moreover, by flash photolysis, sensitization or quenching studies of biacetyl phosphorescence,[680–682] delayed fluorescence measurements resulting from a triplet–triplet transfer followed by triplet–triplet annihilation[4], and chemical sensitization techniques,[260,261] it has been shown that the triplet–triplet excitation transfer can occur in fluid solutions with high efficiency at a diffusion-controlled rate ($k_{TT} \approx 10^9$ liter mole^{-1} sec^{-1}). That is, the triplet state of organic molecules in solution can be formed in solution without an intermediate excitation of their singlet state by the excitation of a sensitizing compound provided that the triplet energy of the donor is greater than that of the acceptor. The analogous energy condition holds also for intra-

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[671] K. H. Drexhage, M. M. Zwick, and H. Kuhn, *Z. Elektrochem. Chem.* **67,** 62 (1963).

[672] H. Bücher, K. H. Drexhage, M. Fleck, H. Kuhn, D. Möbius, F. P. Schäfer, J. Sondermann, W. Sperling, P. Tillmann, and J. Wiegand, *Mol. Cryst.* **2,** 199 (1967).

[673] H. Kuhn, *Naturwissenschaften* **54,** 429 (1967).

[674] D. L. Dexter, *J. Chem. Phys.* **21,** 836 (1953).

[675] A. Terenin and V. L. Ermolaev, *Trans. Faraday Soc.* **52,** 1042 (1956).

[676] J. K. Roy and M. A. El-Sayed, *J. Chem. Phys.* **40,** 3442 (1964).

[677] S. Siegel and L. Goldstein, *J. Chem. Phys.* **43,** 4185 (1965).

[678] N. K. Chaudhuri and M. A. El-Sayed, *J. Chem. Phys.* **42,** 1947 (1965).

[679] J. T. Dubois and R. L. Van Hemert, *J. Chem. Phys.* **40,** 923 (1964).

[680] G. Porter and F. Wilkinson, *Proc. Roy. Soc.* **A264,** 1 (1961).

[681] J. T. Dubois and F. Wilkinson, *J. Chem. Phys.* **38,** 2541 (1963).

[682] H. L. Bäckström and K. Sandros, *Acta Chem. Scand.* **14,** 48 (1960).

[683] P. A. Leermakers, G. W. Byers, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.* **85,** 2670 (1963).

[684] D. E. Breen and R. A. Keller, *J. Am. Chem. Soc.* **90,** 1935 (1968).

molecular triplet–triplet transfer between chromophores which are separated by chains of carbon atoms[683,684] or for processes in which energy from an organic ligand is transferred to metal ions.[685,686]

2. *Importance of Energy Transfer in Dye Photochemistry*

a. General Energy-Transfer Mechanisms in Photochemical Processes. Energy transfer which involves the singlet or the triplet state of dyes takes place in many biological and photochemical reactions. In discussing such processes in which the transfer of energy is decisive in crystals or aggregates, the possibility of triplet or singlet exciton migration[687,688] or of a transport of electronic charge carriers[6] must also be taken into account.

As an example of discussion of both energy and electron-transfer mechanisms in the literature, the dye sensitization of the silver halides (discussed in Section IV,B,4) can be cited.[457] According to the energy-transfer mechanism impurity centers in silver halides should act as acceptors for energy transferred from dyes by resonance. In photosynthesis for transferring energy through chlorophyll aggregates, mechanisms involving the transfer of triplet energy,[283] excitons,[689] or of electronic charge carriers[6,690,691] (detected in chlorophyll[6,453]) have been discussed.

Probably, the inhibiting effect of carotenoids on the photocatalytic destruction action of chlorophyll results from a triplet–triplet transfer to energy-degrading carotenoids (see Section III,E). In this context it should be noted that also the second excited singlet state of chlorophyll a (415 nm) is quenched by β-carotene, probably by the resonance energy transfer, however, not the first singlet state (600 nm).[692] Therefore, the fluorescence quantum yield (and the course of photochemical processes?) may depend on the wavelength of the exciting radiation as a consequence of a different energy-transfer behavior of excited states.

b. Photochemical Application of Triplet Excitation Transfer. Triplet–triplet energy transfer has been used for deducing important data on

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[685] M. L. Bhaumik and M. A. El-Sayed, *J. Phys. Chem.* **68**, 275 (1965).

[686] J. McCarthy and J. D. Winefordner, *Anal. Chem.* **38**, 848 (1966).

[687] H. C. Wolf, *Advan. At. Mol. Phys.* **3**, 119–142 (1967).

[688] A. Schmillen, *J. Phys. Chem.* **69**, 751 (1965).

[689] S. S. Brody, *Z. Elektrochem.* **64**, 187 (1960).

[690] A. Szent-Györgyi, *Nature* **9**, 157 (1941).

[691] W. Arnold, *J. Phys. Chem.* **69**, 788 (1965).

[692] N. R. Mury and E. Rabinowitch, *J. Chem. Phys.* **41**, 602 (1964).

organic molecules[693-695] necessary for constructing state diagrams (see Section I,C,2,c). Examples are the locating of triplet energies, e.g., in azo compounds,[696,697] the establishing of the photoreactive state of dyes in solution such as the discussion of the n, π^* triplet as the probable reactive state in acridine[249] (but see also reference 392), and the determination of the intersystem crossing yield from the first excited singlet state to the triplet state.[2,260,261]

The observation of high quantum yields of triplet formation of a variety of excited compounds in solution[39] and of an efficient triplet excitation transfer has led to an increasing application of sensitization by triplet energy transfer in organic photochemistry. With the energy-transfer process a large number of reactions has been sensitized (e.g., cis–trans isomerization, dimerization of conjugated dienes, bond fission, and other reactions), leading in some cases to products which are not formed by direct excitation or which could only be synthesized with difficulty; see Hammond and others.[2,39,44,696,698-701] The general mechanism of these reactions, in which benzophenone, anthraquinone, and other compounds have been used as sensitizers, is given by

$$\mathrm{D} + h\nu \rightarrow {}^1\mathrm{D}, \qquad {}^1\mathrm{D} \rightarrow {}^3\mathrm{D}, \qquad {}^3\mathrm{D} + \mathrm{A} \rightarrow \mathrm{D} + {}^3\mathrm{A}$$

Photodimerization would, e.g., result from the following reaction

$${}^3\mathrm{A} + \mathrm{A} \rightarrow \mathrm{AA}$$

which, however, according to Schenck[702] should be the result of an interaction between the sensitizer and bound substrate ($\mathrm{D}^* + \mathrm{A} \rightarrow \cdot\mathrm{D} - \mathrm{A}\cdot$, $\cdot\mathrm{D} - \mathrm{A}\cdot + \mathrm{A} \rightarrow \cdot\mathrm{D} - \mathrm{A} - \mathrm{A}\cdot \rightarrow \mathrm{D} + \mathrm{AA}$). The triplet transfer may also be active in the spectral sensitization of photosensitive polymers, e.g., in the cinnamate polymers which become sensitive, i.e., insoluble, in the visible range by the addition of Crystal Violet carbinol

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[693] W. M. Moore and M. Ketchum, *J. Am. Chem. Soc.* **84,** 1368 (1962).

[694] G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.* **66,** 1144 (1962).

[695] F. Wilkinson, *J. Phys. Chem.* **66,** 2569 (1962).

[696] J. R. Fox and G. S. Hammond, *J. Am. Chem. Soc.* **86,** 4031 (1964).

[697] P. S. Engel, *J. Am. Chem. Soc.* **89,** 5731 (1967).

[698] G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. Org. Chem.* **28,** 3297 (1963).

[699] R. S. H. Liu, N. J. Turro, and G. S. Hammond, *J. Am. Chem. Soc.* **87,** 3406 (1965).

[700] G. S. Hammond, P. Wyatt, C. D. De Boer, and N. J. Turro, *J. Am. Chem. Soc.* **86,** 2532 (1964).

[701] L. Horner, G. Bauer, and J. Dörges, *Chem. Ber.* **98,** 2631 (1965).

[702] G. O. Schenck and R. Steinmetz, *Bull. Soc. Chim. Belges* **71,** 782 (1962).

and other sensitizers.[703-705] The knowledge of this mechanism, which is supported by a series of facts, e.g., an increase of sensitivity of the sensitizers by the introduction of heavy atoms, etc.,[706] allows an estimation of the limit of spectral sensitization. For example, in the case of poly(vinyl cinnamate) the energy of the lowest triplet state of sensitizers must not be smaller than that of the cinnamoyl group, which is 18315 cm^{-1} (545 nm).[707]

c. Triplet Energy Transfer in Photobleaching. The triplet excitation transfer may be efficient in many photobleaching processes of dyes, but only a few exact studies have been made so far.

As an example, the indirect reductive photobleaching of methylene blue ($\lambda = 665$ nm) to leucomethylene blue in the presence of triethanolamine and erythosine by irradiation of erythrosine into its absorption band at $\lambda = 535$ nm should be mentioned.[708] As the rate of energy transfer from erythrosine triplet to methylene blue triplet is more rapid than the rate of the photoreduction of erythrosine (E) by triethanolamine (A), the photobleaching of erythrosine is inhibited in the presence of methylene blue (MB), the photobleaching of methylene blue, however, occurs although not directly irradiated, i.e.,

$$\begin{aligned}
&\mathrm{E} + h\nu \rightarrow {}^1\mathrm{E} \rightarrow {}^3\mathrm{E} \\
&{}^3\mathrm{E} + \mathrm{AH_2} \rightarrow (\mathrm{E}\cdot^- + \mathrm{AH_2}\cdot^+) \rightarrow \mathrm{EH}\cdot + \mathrm{AH}\cdot \qquad k_{\mathrm{R}} = 7.5 \times 10^3\ \text{liter/mole sec} \\
&2\mathrm{EH}\cdot \rightarrow \mathrm{EH_2} + \mathrm{E} \\
&2\mathrm{AH}\cdot \rightarrow \mathrm{AH_2} + \mathrm{A}
\end{aligned}$$

with MB

$$\begin{aligned}
&{}^3\mathrm{E} + \mathrm{MB} \rightarrow \mathrm{E} + {}^3\mathrm{MB} \qquad k_{\mathrm{Tr}} = 4.5 \times 10^8\ \text{liter/mole sec} \\
&{}^3\mathrm{MB} + \mathrm{AH_2} \rightarrow \mathrm{MBH_2} + \mathrm{A}
\end{aligned}$$

After the complete photobleaching of methylene blue triplet erythrosine becomes photoreduced accompanied by an intense deactivation by leucomethylene blue.

In the fading of rhodamine B in aqueous acetone solutions, which occurs rapidly upon exposure to UV below 300 nm, a triplet–triplet transfer from the primary excited acetone to the dye seems to be essential.[709]

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[703] L. M. Minsk, J. G. Smith, W. P. Van Deusen, and J. F. Wright, *J. Appl. Polymer Sci.* **2**, 302 (1959).

[704] E. M. Robertson, W. P. Van Deusen, and L. M. Minsk, *J. Appl. Polymer Sci.* **2**, 308 (1959).

[705] J. Kirs and E. Kirs, *Zh. Nauchn. i Prikl. Fotogr. i Kinematogr.* **11**, 355 (1966).

[706] M. Tsuda, *J. Polymer Sci.* **B2**, 1143 (1964).

[707] M. Tsuda, *Intern. Congr. Phot. Sci., Tokyo, 1967* Sect. V.

[708] P. Walker, *Phot. Sci. Eng.* **9**, 55 (1965).

[709] B. Stevens and W. S. Bingham, *J. Soc. Dyers Colourists* **79**, 632 (1963).

Like fluorescein,[108] the photoactivated rhodamine B in the triplet state may react to form semioxidized and semireduced radicals ($^3D + D \rightarrow D\cdot^+ + D\cdot^-$), of which the semireduced radical undergoes hydrogen abstraction, producing the leuco dye.

E. PHOTOSENSITIZATION IN NATURE

1. *Photosynthesis*

By the excitation of chlorophyll chromophores which, within the photosynthesizing plant cells (chloroplasts), form units of about 500 molecules,[710] water is oxidized to oxygen and CO_2 reduced to carbohydrates (sugars, starches), i.e.,

$$CO_2 + H_2O \xrightarrow[\text{Chlorophyll}]{h\nu} \frac{1}{n}(CH_2O)_n + O_2$$

The *first step* after the absorption of visible light by the photosynthetic unit (which contains several kinds of chlorophylls with different side groups, carotenoids, and other pigments) consists in a transfer of energy to two reaction centers. This energy migration has been concluded from measurements of quantum yield[711] or of fluorescence polarization[546,712–714] and is discussed in references 6 and 715–719.

In the *second step* by direct or indirect excitation of two chlorophyll-a-containing reaction centers, the far red System I ($\lambda < 730$ nm) and the short wave System II ($\lambda < 700$ nm) which have been detected and proved by Emerson, Kok, Witt, and others,[720–726] oxygen is evolved by oxidation of water, and hydrogen (or an electron and a hydrogen ion) is

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transferred to triphosphopyridine nucleotide (TPN or NADP). This mechanism, in which two systems cooperate in the primary process, is in contrast with Warburg's hypothesis[727,728] of the splitting of activated carbonic acid. However, studies on light-induced absorbancy changes,[724,725] the quantum yield,[721] fluorescence,[723] and tracing of the carbon sequence by radiocarbon,[719,729] points at the correctness of the water-splitting concept.

In principle, the photochemical primary process in photosynthesis can be described as an oxidation–reduction reaction, in which electrons (or hydrogen atoms) are transferred from a donor (H_2O) to an acceptor (ferredoxin or TPN which carries over hydrogen to CO_2). As the difference between the redox potentials of the couples O_2/H_2O ($E = +0.8$ eV; see Section II,B,2,b) and $CO_2/1/n(CH_2O)_n$ or TPNH/TPN ($E = -0.4$ eV) amounts to 1.2 eV, for the transfer of four electrons (or four hydrogen-atoms), i.e., for the reduction of one CO_2 molecule or evolving of one O_2 molecule, 4.8 eV ($\Delta G = 110$ kcal/mole) are necessary.[730,731] Corresponding to the Hill reaction[732] the capacity for photooxidation of water also remains intact in isolated chloroplasts in the presence of suitable hydrogen acceptors such as ferric salts, dyes, or quinones. By a special preparing of the chloroplasts also the reduction of CO_2, besides the evolution of O_2, could be realized by Calvin.[719]

Without the environment of the photosynthetic unit (enzymes, etc.), however, chlorophyll molecules are not able to bring about an analogous photosensitized redox reaction with H_2O as donor and Hill reagents as acceptors. On the other hand, a series of oxidation–reduction reactions sensitized by chlorophyll have been studied in solution with either an oxidation of a reducing substrate (e.g., allylthiourea) by molecular oxygen,[733] or the transfer of electrons (and hydrogen) from certain reducing compounds (such as ascorbic acid, phenylhydrazine) to certain acceptors (e.g., safranin, methyl red).[546,734–738] These sensitized redox reactions and

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the reversible photoreduction of chlorophyll, e.g., by ascorbic acid yielding a pink intermediate (Krasnovsky reaction[233]), or the reversible photooxidations with quinones or ferric salt[739-741] are analogous to the photoreactions exhibited by synthetic dyes[742] (see Section II,B). Probably, in many cases the photoreactions proceed via the triplet state of chlorophyll molecules, as has been shown by flash studies.[743-745] Moreover, by binding to high polymers the photochemical activity may be enhanced, as shown by observations with a series of dyes including chlorophyllin a.[232,248] It is interesting to note that some chlorophyll-sensitized redox reactions could be initiated which take part in photosynthesis, e.g., the photoreduction of cytochrome c,[746] the photooxidation of reduced cytochrome c coupled to the photoreduction of ubiquinone,[743,747] or the photoreduction of pyridine nucleotide in aqueous media.[748-750] Recently, the chlorophyll-sensitized oxidation–reduction photolysis of silver chloride crystals (i.e., spectral photographic sensitization; see Section IV,B,4) normally yielding silver and chlorine atoms has also been used for a continuous water splitting (i.e., oxygen development) by oxidizing the photolytically produced silver atoms with electron-accepting dyes and introducing the photolytically produced chlorine atoms into water [corresponding to $Cl + H_2O \rightleftarrows \frac{1}{2}\ HCl + \frac{1}{2}\ HOCl$ $(\rightarrow \frac{1}{2}\ HCl + \frac{1}{4}\ O_2)$].[751] In this interesting experiment a light-induced reaction between the excited chlorophyll and Cl^-/Ag^+ as the crystallized donor–acceptor couple occurs which, in a subsequent secondary reaction, leads to the splitting of water.

In chloroplasts the electrons of water (OH^-) seem to be immediately transferred along a transport chain which includes manganese[752-754] to

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the excited chlorophyll System II, leaving oxygen behind. While System II is at the potential of water (i.e., +0.8 V) the far red System I has a potential of (+0.4 V). As a consequence, electrons which are lifted from +0.8 V to about 0 V by the excitation of System II fall through a chain of electron carriers (including plastoquinone and cytochromes) to the lower energy of System I, whereby producing adenosine triphosphate (ATP) by photophosphorylation. The excited System I can lift the transferred electrons to a potential of —0.4 V, which is sufficient for forming a strong reductant, such as TPNH[726,755-757]; see the scheme of Fig. 27.

In the *third step* the photochemically formed energy-rich ATP and the reductant TPNH are used for the reduction of carbon dioxide to carbohydrate in a complicated dark process, the Calvin cycle.[719]

2. *Vision Process*

As discussed in Section II,B,1, by the excitation of the vision chromophore 11-*cis*-retinal, a photoisomerization to the trans form occurs which results in a dissociation of the chromophore from its protein, i.e., the visual pigment rhodopsin is converted in a sequence of successive reaction steps into *trans*-retinal and the protein opsin. According to the Wald cycle[758] in a dark reaction rhodopsin is again synthesized.

The question why a stimulation of the nerve ending results from rhodopsin excitation still remains. Perhaps, the photoelectric phenomena of the dye can give an answer.[6]

V. Conclusion

This review shows that by irradiation of organic dyes a variety of photochemical reactions can be produced. Nowadays, these reactions are no longer obscure as in the past, but can be discussed in the light of the findings of modern organic photochemistry. With this knowledge further important methods for the inhibition of technically and biologically interesting destructive effects of illuminated dye systems can be worked

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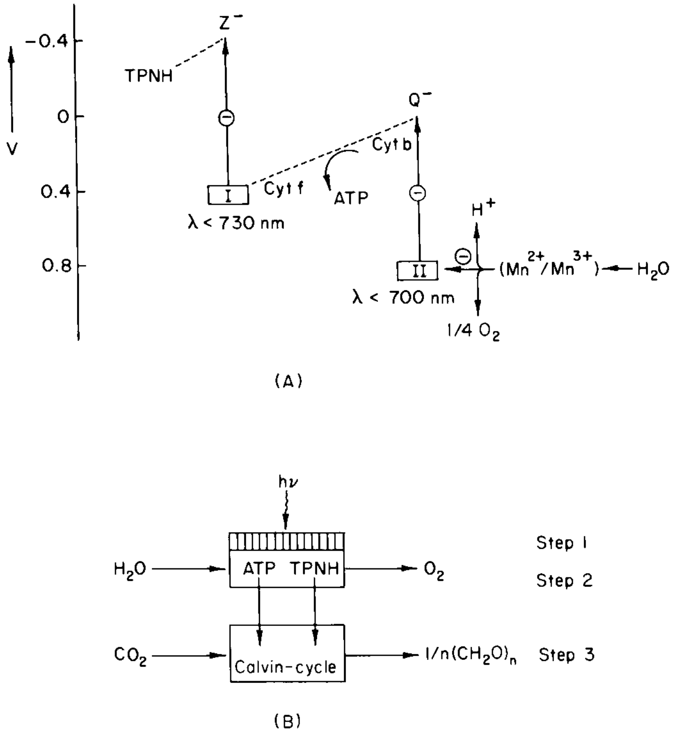

FIG. 27. (A) Scheme of the primary photoprocess in photosynthesis. (B) Simple block diagram of the overall process of photosynthesis.

out. Moreover, further areas of practical use can be detected. Besides the examples given above, we can cite experiments in which already an application of dyes has been proven, such as laser passive Q-switches,[759-762] liquid lasers,[763-766a] chemical dosimetry systems,[767-770] an oxygen-evolving

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system for astronautical crafts,[751] a means of providing flash blindness protection or a memory in computers,[209,771] the basis for a new kind of photography,[103] photochemically regenerative electrochemical systems,[772] fuel cell cathodes,[773,774,775] detectors for gases,[6,776] or light-sensitive targets in vidicon camera tubes for television.[777]

ACKNOWLEDGMENTS

The author is indebted to Dr. W. Albrecht and Dipl. Phys. U. Tschirwitz for their valuable assistance in experimental work, and to the Fonds der Chemischen Industrie, Düsseldorf, and the Deutsche Forschungsgemeinschaft for financial support.

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