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The Chemistry of
SYNTHETIC DYES

VOLUME VIII

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Edited by
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The eight volumes of this treatise are dedicated to Shakuntala, Dharma, and Radha

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GENERAL 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 in 1967 that the urgent need was not for a revision, because very little of the contents of the 1952 publication had become obsolete, but for a review of the subsequent developments.

The progress made in the chemistry of synthetic dyes in the last twenty years has been amazing. The discovery of reactive dyes is one major advance. There has also been extensive research on intermediates, disperse dyes, cationic dyes, cyanine dyes, pigments, and metal complexes, all of which have 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 fortunate in the response I have had to my invitations to contribute to the additional volumes. All the chapters have been written by acknowledged authorities, whose names are associated with many patents and papers, and who have worked for many years on the topics they have covered.

In addition to the synthesis and application of dyes of all types, fluorescent brightening agents and such fundamental topics as color and electronic states of organic molecules, photochemistry of dyes, physical chemistry of dyeing, and the relation between structure and technical properties are covered.

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 directions of future research.

I am indebted to the authors for accepting my invitation and to the companies who made it possible for their leading scientists to spare the necessary time. The plan for this international multiauthor effort took concrete shape during ten days I spent in the Research Department of Farbenfabriken Bayer. I am grateful to Professor Petersen, Dr. Delfs, and their colleagues, and also to Dr. R. R. Davies (Imperial Chemical Industries, Dyestuffs Division) for their help in the organization of this series. My thanks are due to Mr. J. V. Rajan, Mr. G. V. Kulkarni, and Mr. S. A. Nair for preparing the Subject Indexes, checking literature references, and dealing with the heavy correspondence. Academic Press has handled production problems 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, the Director-General of Scientific and Industrial Research, Dr. Y. Nayudamma, and his predecessor Dr. Atma Ram, without which I could not have undertaken this project.

K. VENKATARAMAN

PREFACE TO VOLUME VIII

Volume VIII, the last in this multivolume treatise, stresses the relation between the chemistry of synthetic dyes and their application properties, although this aspect was indeed not ignored in Volumes I and II and in the subsequent volumes. Dyes for leather, synthetic carotenoids as food colorants, and solvent dyes constitute the themes of three of the chapters in this volume. Although Volume VI was devoted solely to reactive dyes, additional data on the dye–fiber bond are discussed in a new chapter. One of the two chapters on new developments in textile coloration reviews the phenomenal progress made in transfer printing, for which the first commercial process became available as recently as 1968. The influence of structural factors on the lightfastness of dyed fibers is discussed in Chapter VI and is followed by a more general treatment correlating the structures of dyes with their technical properties. The fascinating story of the transformation of "a simple but revolutionary concept, the dye developer," into a commercially successful instant color photographic process is told in Chapter VIII.

In addition to its own Subject Index, Volume VIII contains a consolidated Dyestuff Index for Volumes III–VIII. An 18-page Dyestuff Index for Volumes I and II is provided in Volume II.

K. Venkataraman

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Volume I

Volume II

VOLUME III

VOLUME IV

Volume V

Volume VI

Volume VII

LIST OF ABBREVIATIONS

Manufacturing companies (CI abbreviations have generally been followed):

AAP	Koppers Co. Inc., Pittsburgh, Pennsylvania (American Aniline Products, Inc.)
Acna	Aziende Colori Nazionali Affini A.C.N.A., Milan, Italy
ACY	American Cyanamid Co., Bound Brook, New Jersey
Allied	Allied Chemical Corporation, Morristown, New Jersey
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
CGY	Ciba-Geigy Ltd., Basel, Switzerland
CIBA	CIBA Ltd., Basel, Switzerland
CN	Compagnie Nationale de Matières Colorantes et de Produits Chimiques du Nord Réunies Etablissements Kuhlmann, Paris, France
Dainippon	Dainippon Printing Co. Ltd., Tokyo, Japan
DuP	E. I. Du Pont de Nemours & Co., Wilmington, Delaware
EKCo	Eastman Kodak Co., Rochester, New York
FBy	Farbenfabriken Bayer A.G., Leverkusen, Germany
FH	Farbwerke Hoechst A.G., Frankfurt / Main-Hoechst, Germany
Fran	Compagnie Française des Matières Colorantes, Paris, France
FW	Farbenfabrik Wolfen, Kr., Bitterfeld, Germany
G(GAF)	General Aniline & Film Corporation, New York, New York
Gy	J. R. Geigy S. A., Basel, Switzerland
HCC	Hodogaya Chemical Co., Ltd., Tokyo, Japan
IBM	International Business Machines, Princeton, New Jersey
ICI	Imperial Chemical Industries, Ltd., Manchester, England
IG	I. G. Farbenindustrie A. G., Frankfurt a. Main, Germany
KYK	Nippon Kayaku Co., Ltd., Tokyo, Japan
LBH	L. B. Holliday & Co., Huddersfield, England
MCI	Mitsubishi Chemical Industries, Ltd., Tokyo, Japan
MDW	Mitsui Toatsu Chemicals, Tokyo, Japan
NSK	Sumitomo Chemical Co., Ltd., Osaka, Japan
S	Sandoz Ltd., Basel, Switzerland

Sublistatic	Sublistatic Holding S. A., Geneva, Switzerland
Toppan	Toppan Printing Co., Ltd., Tokyo, Japan
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, 3rd edition, 1971
CSD	The Chemistry of Synthetic Dyes, Vols. I–VII, Academic Press, 1952–1974
FIAT	Field Intelligence Agency Technical Report

Patents:

BeP	Belgian Patent
BP	British Patent
DAS	Deutsche Auslegeschrift
DBP	Deutsche Bundespatente
DOS	Deutsche Offenlengungschrift
DRP	Deutsche Reichspatente
EGP	East German Patent
FP	French Patent
Ger. Offen	German Offentlichung
JP	Japanese Patent
RP	Russian Patent
SP	Swiss Patent
USP	United States Patent

CHAPTER I

REACTIVE DYES—PHYSICOCHEMICAL ASPECTS OF DYE FIXATION AND DYE–FIBER BOND HYDROLYSIS

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I. Introduction

The concept of achieving fastness in dyeings on textile fibers by covalently binding chromogens to the polymer chains is a fairly obvious one and was demonstrated over eighty years ago to be valid in principle.[1] The synthesis of such reactive dyes involves well-established principles of acylation, etherification, and addition reactions using the hydroxyl, amino, thiol, and similar groups offered by textile fibers for dye binding.

However, the possibility of making reactive dyes and the demonstration of the effectiveness of covalent dye binding was not sufficient to establish dyeing with fiber-reactive dyes, because the presence of water during the dyeing operation leads under normal circumstances to an excessive degree of competition from the expected hydrolysis reaction and consequent low fixation efficiency. The development of fiber-reactive dyes in the period 1953–1956[2] was a result of the successful application of physicochemical principles to the problem of achieving

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[1] C. F. Cross and E. J. Bevan, "Researches on Cellulose," p. 34, 1895.

[2] I. D. Rattee and W. E. Stephen, *BP* 772,030; 774,925; 781,930.

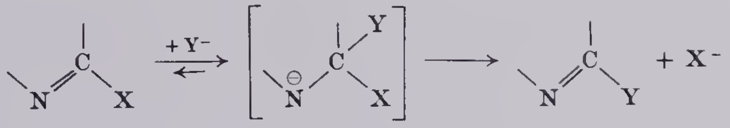
a selective reaction of a hydrolyzable dye to a hydrophilic substrate in the presence of water. The close involvement of the physical chemist in the development of fiber-reactive dyes from the outset has imposed a unique pattern on the rate and extent to which this range of dyes has developed. It has proved possible to apply experience gained in dye application directly to the planning of programmes of dye synthesis. Similarly, dyeing methods have been developed more rapidly and more precisely than the traditional empirical approach would allow. It is unlikely that the behavior of any other range of dyes is understood so well by the users and the synthesisers. The experience and economies in research that have thus been gained are such that the pattern of future developments is likely to follow a similar path. This being said, it would be a gross oversimplification to forget that many serious problems remain and are the concern of present research.

The physicochemical analysis of the fiber-reactive dyeing system is most simply considered in the first instance in terms of the hydrolysis reaction and in the second by taking into account a competing alcoholysis (or aminolysis) reaction in the same phase. The principles thus established may then be applied to the dyeing situation involving two phases (fiber and aqueous solvent). This approach provides a basis for the discussion of fixation. However, the properties of fiber-reactive dyes are important not only in relation to fixation. The fastness of the dyeing depends upon both the efficiency with which the dyer removes unfixed dye from the fabric and also the stability of the dye fiber bonds to subsequent attack during washing and related wet treatments. Thus, the consideration has to extend beyond the dyeing process and consider postdyeing treatments in a way that is not normally so important with physically (as opposed to chemically) bound dyes because of the reversibility of their attachment to fibers.

II. Hydrolysis

The hydrolysis behavior of reactive dyes has several important technical repercussions: (1) stored dye powders may decompose in the presence of atmospheric moisture; (2) solutions and print pastes containing reactive dyes may deteriorate on standing; (3) hydrolysis may compete excessively with the very similar dye fixation reactions, i.e., with OH, SH, or NH_2 groups. Consequently, the consideration of hydrolysis kinetics is of primary importance. The majority of reactive dyes fall into one of two categories distinguished by their reaction modes:

1. nucleophilic addition–elimination dyes



2. nucleophilic addition dyes

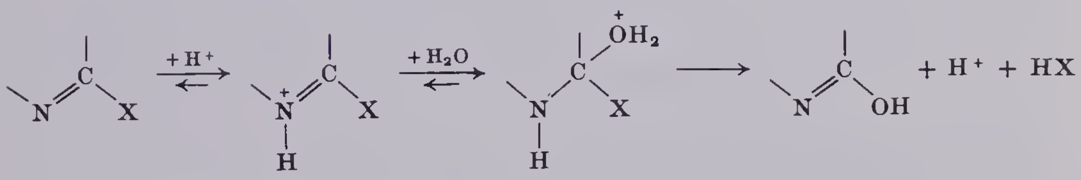
$$\text{—CH═CH}_2 \underset{\leftarrow}{\xrightarrow{+Y^-}} \text{—}\overset{\ominus}{\text{C}}\text{H—CH}_2\text{—Y} \underset{\leftarrow}{\xrightarrow{+H^+}} \text{—CH}_2\text{—CH}_2\text{—Y}$$

Zollinger[3] has indicated the existence of other categories that are fairly specialized, e.g., the Lanasol, Calcobond, or Dykolite dyes. Of these, the first involves several addition–elimination steps, the second is very different from all other reactive dyes in technical use involving an acid-catalyzed condensation with water elimination, and the third is as much in the ingrain as the reactive dye class. With the exception of dyes of the Lanasol and related ranges, all reactive dyes of current technical interest fall into the two main classes. The nucleophilic reagent shown as Y^- in the two categories above may be, in the case of hydrolysis, $—OH^-$ or H_2O. The hydroxyl ion is a strong nucleophile, so that the hydrolysis reaction would be expected to proceed with increasing rapidity with increasing pH and the rate of disappearance of reactive dye ($^-dD/dt$) to be given by Eq. (1), in which $[D]_t$ and $[OH^-]_t$

$$^-dD/dt = k[OH^-]_t[D]_t \tag{1}$$

are the concentrations of dye and hydroxyl ions at time t.

Water is itself a very weak nucleophile, and the reaction rate with dyes of technical interest is very slow indeed. However, the reaction rate may be increased if the electrophilic nature of the active carbon atom is increased, and this can occur when protonation of a nearby atom occurs, e.g.,



Thus, the hydrolysis reaction may in appropriate cases be acid-catalyzed, particularly when a proton accepting heteroatom is present in the reactive system. This effect has important technical repercussions with, for example, the highly reactive dichlorotriazinyl dyes (i.e.,

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[3] H. Zollinger, *in* "Theory of Coloration of Textiles" (C. L. Bird and W. S. Boston, eds.), Chapter 7. Dyers Company Publications Trust, 1975.

Procion MX dyes of ICI). In the dry powders, these hydrolyze extremely slowly due to ambient atmospheric water. However, such hydrolysis as does occur leads to the liberation of hydrochloric acid. This can act as an acid catalyst by protonation, leading to an increasingly autocatalyzed hydrolysis rate. Much depends upon the "regain" of the powder, the particle size, the crystal habit, etc., so that some dye powders are very stable and others are not. W. E. Stephen[4] observed in the early days of the reactive dye development work that the presence of buffers absorbed the protons and prevented autocatalysis. Less reactive dyes such as monochlorotriazinylamino or trichloropyrimidinylamino dyes are not sufficiently activated by protonation for the storage effect to be significant. However, their hydrolysis is nevertheless subject to proton catalysis. The nucleophilic groups involved in dye fixation onto fibers are not sufficiently active under acidic conditions in the overwhelming majority of cases for acid-catalyzed fixation to be important. The only technical acid-catalyzed system is the Calcobond system previously mentioned. Thus, apart from the important question of powder storage stability, the main conditions of hydrolysis that have to be considered involve alkaline solutions.

It is clear from Eq. (1) that in a buffered system in which $[\mathrm{OH}]_t$ is a constant, then the second-order rate constant K may be replaced by a pH-dependent pseudo-first-order rate constant k^1 (Eq. 2). From Eq. (2)

$$-dD/dt = k[\mathrm{OH}]_t[\mathrm{D}]_t = k^1[\mathrm{D}]_t \tag{2}$$

it can be seen that if k^1 is determined by appropriate standard means from experimental data, then since

$$k^1 = k[\mathrm{OH}] \tag{3}$$

$$\log k^1 = \mathrm{pH} + \log k \cdot \bar{K} \tag{4}$$

where $\bar{K}$ is the ionic product of water. The slope of the relationship should be unity. The extensive investigation of the hydrolysis kinetics of reactive dyes by numerous investigators springs from the fact that in the majority of cases this simple classic relationship is not observed.[5–16]

[4] W. E. Stephen, *Chimia* **19**, 261 (1965).

[5] P. Rys and H. Zollinger, *Helv. Chim. Acta* **49**, 749 (1966).

[6] A. Datyner, P. Rys, and H. Zollinger, *Helv. Chim. Acta* **49**, 755 (1966).

[7] P. Rys and H. Zollinger, *Helv. Chim. Acta* **49**, 761 (1966).

[8] P. Rys, *Textilveredlung* **2**, 95 (1967).

[9] P. Rys, A. Schmitz, and H. Zollinger, *Helv. Chim. Acta* **54**, 163 (1971).

[10] H. Ackermann and P. Dussy, *Melliand Textilber.* **42**, 1167 (1961).

[11] H. Ackermann and P. Dussy, *Helv. Chim. Acta* **45**, 212 (1962).

[12] S. Horrobin, *J. Chem. Soc.* p. 4130 (1963).

[13] R. Aspland and A. Johnson, *J. Soc. Dyers Colour.* **81**, 425, 477 (1965).

[14] W. Ingamells, H. Sumner, and G. Williams, *J. Soc. Dyers Colour.* **78**, 274 (1962).

Two main experimental methods have been employed for the study of hydrolysis in the case of reactive heterocyclic dyes containing chlorine as the leaving group. The first and most obvious one is to analyze the system for chloride ion released by hydrolysis using standard electrometric titration techniques. This presents some difficulties due to the small amounts involved, but with great care, reliable results can be obtained. Two approaches are possible. One involves the measurement of chloride released in a system, which may be buffered if pseudo-first-order conditions are desired, or the alkali may be consumed in a pH-stat titration of the system may be measured. The latter procedure inevitably gives rise to pseudo-first-order conditions. The second and very convenient method of analysis utilizes the observation by Sause[17] that in the presence of alkaline pyridine, halogenotriazines develop a complex with an absorption in the 450–460 nm region of the spectrum. The same effect is shown by other halogeno heterocyclic systems used in reactive dyes. The optical density at the appropriate wavelength achieved is proportional to the amount of reactive dye present, and the technique is quick and particularly convenient when numerous samples must be analyzed.

Different investigators have shown that in only a minority of cases does Eq. (4) lead to a rectilinear relationship. Instead, five general kinds of relationship are observed, as illustrated in Fig. 1. The rectilinear relationship shown by the line a, with constant unit slope, is the expected one. It is found to apply only to triazinyl and diazinyl dyes in which the reactive group is linked to the chromogens through an alkyl- or arylimino bridging group. The relationship in the majority of cases (i.e., where the bridging group is an imino group) follows curves b and c. A curve of type d was observed for the copper-containing dichlorotriazinyl dye C.1. Reactive Red 6 by Ingamells, Sumner, and Williams.[14] It was at one time thought the presence of traces of copper ions was responsible for the effect. Rys, however, has put forward an alternative explanation based on a complex situation involving dye aggregates. Rate dependences of type e have been observed by Datyner, Rys, and Zollinger[6,8] and have been ascribed to the presence of low-activity aggregates at the lower pH values. Ionization of appropriate substituents (e.g., naphtholic hydroxyl groups) as the pH is raised leads to a break down of the aggregates and higher reactivity. Most attention has been paid to dyes behaving in accordance with curves b and c, since these are the majority of available dyes.

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[15] D. Hildebrand and W. Beckmann, *Melliand Textilber.* **45**, 1138 (1964).

[16] K. S. Murthy and I. D. Rattee, *J. Soc. Dyers Colour.* **85**, 368 (1969).

[17] R. Sause, unpublished work.

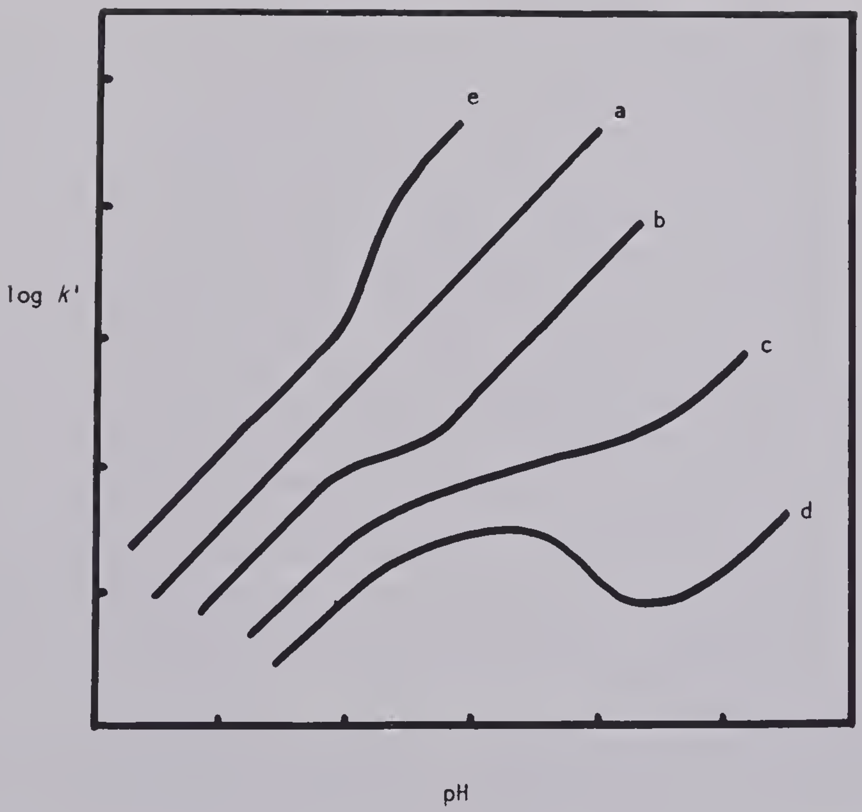
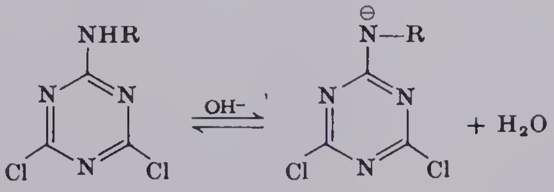


FIG. 1. General forms of log k^1 versus pH relationship observed with tri- and diazinyl reactive dyes.

Horrobin[12] observed behavior in accordance with curve c when studying the hydrolysis of model compounds and suggested that the cause lay in the loss of a proton by the imino bridging group to form a less reactive species. The reaction kinetics may be analyzed as follows:



(I) (II)

If the dye (I) above is represented as D and (II) as D⁻, then the stoichometric equations for the process may be written as in Eq. (5).

$$\begin{tikzcd} D + OH^- \arrow[rr, shift left, "K"] \arrow[dr, "OH^-"', "k_1"] & & D^- + H_2O \arrow[ll, shift left] \arrow[dl, "OH^-", "k_2"'] \\ & \text{products} & \end{tikzcd} \tag{5}$$

In Eq. (5), k_1 and k_2 are the bimolecular hydrolysis constants for dyes (I) and (II). Since the total dye present at any time is the sum of the quantities of dyes (I) and (II), then,

$$[\bar{D}] = [\mathrm{D}] + [\mathrm{D}^-] \tag{6}$$

in which the brackets signify concentrations, and $[\bar{D}]$ is the total dye concentration. Combining Eq. (6) with the relationship governing the acid–base equilibrium proposed by Horrobin,

$$[\mathrm{D}^-][\mathrm{H_2O}]/[\mathrm{D}][\mathrm{OH}^-] = K \tag{7}$$

equations for [D] and $[\mathrm{D}^-]$ are obtained in terms of $[\bar{\mathrm{D}}]$,

$$\mathrm{D} = \frac{K^1[\bar{\mathrm{D}}]}{K^1 + [\mathrm{OH}^-]} \tag{8}$$

$$\mathrm{D}^- = \frac{[\bar{\mathrm{D}}][\mathrm{OH}]}{\mathrm{K}^1 + [\mathrm{OH}^-]} \tag{9}$$

in which $K^1 = [\mathrm{H_2O}]/K$.

The observed hydrolysis rate is the rate of disappearance of the total reactive dye, which is given by

$$\begin{aligned} -\frac{\mathrm{d}\bar{\mathrm{D}}}{\mathrm{dt}} &= -\frac{\mathrm{dD}}{\mathrm{dt}} - \frac{\mathrm{dD}^-}{\mathrm{dt}} \\ &= k_1[\mathrm{OH}^-][\mathrm{D}]_t + k_2[\mathrm{OH}^-][\mathrm{D}^-]_t \end{aligned} \tag{10}$$

Combining Eq. (8)–(10) gives

$$\begin{aligned} -\frac{\mathrm{d}\bar{\mathrm{D}}}{\mathrm{dt}} &= \frac{k_1[\mathrm{OH}^-]K^1[\bar{\mathrm{D}}]_t}{K^1 + [\mathrm{OH}^-]} + \frac{k_2[\mathrm{OH}^-]^2[\bar{\mathrm{D}}]_t}{K^1 + [\mathrm{OH}^-]} \\ &= [\bar{\mathrm{D}}]_t[\mathrm{OH}^-]\frac{k_1K^1 + k_2[\mathrm{OH}^-]}{K^1 + [\mathrm{OH}^-]} \end{aligned} \tag{11}$$

Equation (11) shows that bimolecular or pseudo-first-order kinetics will be observed according to whether $[\mathrm{OH}^-]$ is kept constant or not and that when $[\mathrm{OH}^-]$ is kept constant the bimolecular rate constant is pH-dependent and equal to expression (12). At lower pH values, when

$$\frac{k_1K^1 + k_2[\mathrm{OH}^-]}{K^1 + [\mathrm{OH}^-]} \tag{12}$$

$[\mathrm{D}^-] \to 0$, the constant will equal k_1 and, correspondingly, at higher pH values will tend toward k_2. The determination of the latter value will in practice depend upon a knowledge of K^1 unless the two values are distinctly different.

Horrobin[12], for the compounds he studied, gives values relating to K^1 that are stated to be based on very rapid titration experiments. The pK values are in the region of 10.5 for the compounds cited and attempts to repeat the experiments by Murthy[18] failed due to the dilution effect that makes titration difficult in this region. Values obtained by titration of halogenopyrimidine compounds have been given, and pK values quoted are of the order of 12.5.[11] Of course, it is not necessary to postulate an actual mechanism of the equilibrium reaction in Eq. (5). Precisely the same derivations follow if the equilibrium is expressed as

$$D_1 + OH^- \overset{K_d}{\rightleftharpoons} D_2 \tag{13}$$

without stating the nature of D_1 and D_2. This treatment leads to a slightly different equation for the observed hydrolysis constant k_h because K_d is not an acid–base equilibrium constant,

$$k_h = \frac{k_1 + k_2 K_d[OH^-]}{1 + K_d[OH^-]} \tag{14}$$

Equation (14) may be rearranged to give

$$\frac{1}{k_h - k_2} = \frac{K_d}{k_1 - k_2}[OH^-] + \frac{1}{k_1 - k_2} \tag{15}$$

or

$$\frac{1}{1 + K_d[OH^-]} = \frac{1}{k_1 - k_2} k_h - \frac{k_2}{k_1 - k_2} \tag{16}$$

from which the values of k_1, k_2, and 0_k can be abstracted by standard computational methods.

This analysis has been carried out by Murthy and Rattee[16] for four dihalogenotriazinylamino reactive dyes over a range of temperatures. Three of the dyes gave log k^1–pH curves of type c, while one gave a curve of type b. It was found that with the type c dyes, k_2 was negligible compared with k_1, and the reciprocal of k_h was proportional to $[OH^-]$ at all temperatures. The type b dye had a significant k_2 value about one-sixth of the k_1 value. A later study by Hughes[19,20] using dichloropyrimidinyl dyes with either a cyano group in the 5 position of the

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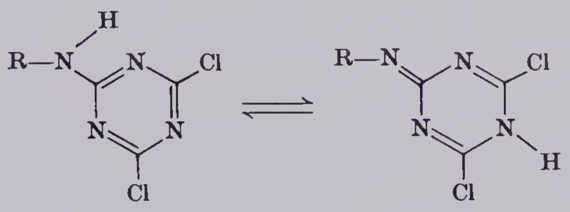
[18] K. S. Murthy, Ph.D. Thesis, University of Leeds, 1967.

[19] J. A. Hughes, Ph.D. Thesis, University of Leeds, 1970.

[20] I. D. Rattee and M. M. Breuer, "The Physical Chemistry of Dye Adsorption," p. 256. Academic Press, New York, 1975.

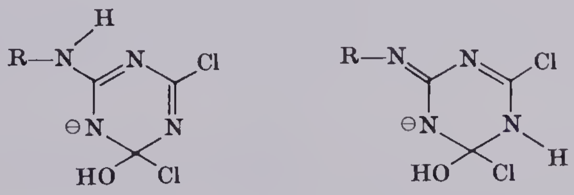
heterocyclic ring or a chlorine atom showed that the latter was similar to the type c dyes with a negligible k_2 value, while the more active 5-cyano dye had a small but significant k_2 value.

Arrhenius plots representing log k_1 against $1/T$ were prepared for three dichlorotriazinyl dyes by Murthy and Rattee, who found that the relationship was curved as might be expected if the dyes were aggregated or showed some variation in activity coefficient due to a change in hydration state. Moreover, the values of K_d were found to pass through a minimum as the temperature varied, whereas a maximum value would be expected if an acid–base equilibrium were involved. These results tend to show that the situation is highly complex and not explained adequately by Horrobin's hypothesis. This view is also that of Rys,[8] who showed that triazinyl reactive dyes with imino bridging groups exist in tautomeric forms with different reactivities.



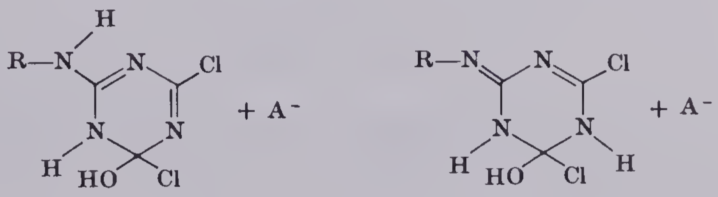
(17)

These form addition intermediates with the nucleophile (OH^-),



(18)

and these are involved in equilibria with a general acid (HA).



(19)

Clearly, variations in the relevant kinetic constants combined with any variations in the aggregation behavior of the different species produce a complex situation within which a very wide range of options exist, and any treatment of the competitive hydrolysis and dye fixation reactions, whether in a single solution phase or in a two-phase system involving fibers, perforce must be a greatly simplified one.

III. Competitive Alcoholysis and Hydrolysis in Solution

The following discussion, although concerned with competition between hydrolysis and alcoholysis in a single-phase system, is equally applicable if alcoholysis is replaced by reaction with amino or thiol groups. If the alcohol is designated AOH, then three reactions are involved at a given pH,

$$\begin{array}{rcll} \mathrm{AOH} & \rightleftharpoons & \mathrm{AO^- + H^+} & \text{(ionization)} \\ \mathrm{AO^- + D} & \longrightarrow & \mathrm{AOD} & \text{(alcoholysis)} \\ \mathrm{OH^- + D} & \longrightarrow & \mathrm{HOD} & \text{(hydrolysis)} \end{array} \tag{20}$$

Neglecting for the moment the problems of pH-dependent hydrolysis constants discussed above, the respective rates of the two fixation reactions will be given by Eq. (21) and (22), where df/dt and dh/dt refer

$$df/dt = k_\mathrm{f}[\mathrm{AO^-}][\mathrm{D}]_t \tag{21}$$

$$dh/dt = k_\mathrm{h}[\mathrm{OH^-}][\mathrm{D}]_t \tag{22}$$

to the alcoholysis and hydrolysis reactions respectively; k_f and k_h are the corresponding rate constants.

Thus, the rate of disappearance of reactive dye $-dD/dt$ is given by

$$-dD/dt = df/dt + dh/dt = \{k_\mathrm{f}[\mathrm{AO^-}] + k_\mathrm{h}[\mathrm{OH^-}]\}[\mathrm{D}]_t \tag{23}$$

Eq. (23), so that at a fixed pH and constant alcohol concentration, the reaction will be pseudo-first-order with an associated rate constant k^1_total that is the sum of the two subsidiary pseudo-first-order constants as in Eq. (24).

$$k^1_\mathrm{total} = k_\mathrm{f}{}^1 + k_\mathrm{h}{}^1 = k_\mathrm{f}[\mathrm{AO^-}] + k_\mathrm{h}[\mathrm{OH^-}] \tag{24}$$

The ionization of the alcohol is governed by

$$K_\mathrm{a} = [\mathrm{AO^-}][\mathrm{H^+}]/[\mathrm{AOH}] \tag{25}$$

$$= [\mathrm{A\bar{O}}]K_\mathrm{w}/[\mathrm{AOH}][\mathrm{OH^-}] \tag{26}$$

where K_w is the dissociation constant of water. Because the degree of ionization of the alcohol is normally very low, [AOH] is largely independent of $[\mathrm{AO^-}]$, so that

$$\frac{[\mathrm{AO^-}]}{[\mathrm{OH^-}]} = K_\mathrm{a}\frac{[\mathrm{AOH}]}{K_\mathrm{w}} \tag{27}$$

and combining (24) with (27),

$$k^1_\mathrm{total} = k_\mathrm{f}(K_\mathrm{a}/K_\mathrm{w})[\mathrm{AOH}][\mathrm{OH^-}] + k_\mathrm{h}[\mathrm{OH^-}] \tag{28}$$

Thus, despite the presence of the alcohol, the reaction behaves as a first-order reaction if $[\mathrm{OH}^-]$ is kept constant and there is an apparent bimolecular rate constant given by

$$k^1_{\mathrm{total}}/[\mathrm{OH}^-] = k_\mathrm{f}(K_\mathrm{a}/K_\mathrm{w})[\mathrm{AOH}] + k_\mathrm{h} \tag{29}$$

Equation (29) may be simplified by combining the constants relating to water and the alcohol so that

$$K_\mathrm{a}[\mathrm{AOH}]/K_\mathrm{w} = K_\mathrm{a}{}^1 \tag{30}$$

When a dye giving a constant bimolecular hydrolysis constant is considered, i.e., a dye giving curves of type c and being involved in no such equilibrium as Eq. (13) shows, k_f and k_h are constants as is the overall bimolecular rate constant so that

$$k_\mathrm{f}K_\mathrm{a}{}^1 + k_\mathrm{h} = k^1_{\mathrm{total}}/[\mathrm{OH}^-] \qquad \text{(i.e., a constant)} \tag{31}$$

$$\frac{k_\mathrm{f}}{k_\mathrm{h}} = \frac{1}{K_\mathrm{a}{}^1}\left[\frac{k^1_{\mathrm{total}}}{k_\mathrm{h}[\mathrm{OH}^-]} - 1\right] = \mathrm{R}_\mathrm{r} \tag{32}$$

The reactivity ratio can be seen to be a pH-independent constant depending on the value of k_h and the properties and the concentration of the alcohol.

For dyes behaving as shown in Eq. (5), allowance must be made for two species with two hydrolysis and fixation constants. Thus, there will be two versions of Eq. (15) to correspond with the hydrolysis or fixation reactions, i.e.,

$$\frac{1}{k_\mathrm{h} - k_2{}^\mathrm{h}} = \frac{K_\mathrm{d}}{\Delta k^\mathrm{h}}[\mathrm{OH}^-] + \frac{1}{\Delta k^\mathrm{h}} \tag{33}$$

$$\frac{1}{k_\mathrm{f} - k_2{}^\mathrm{f}} = \frac{K_\mathrm{d}}{\Delta k^\mathrm{f}}[\mathrm{OH}^-] + \frac{1}{\Delta k^\mathrm{f}} \tag{34}$$

in which $\Delta k^{\mathrm{h,f}}$ signify $k_1 - k_2$ for the hydrolysis or fixation reactions, respectively. Thus

$$\frac{k_\mathrm{f}}{k_\mathrm{h}} = \frac{k_1{}^\mathrm{f} + k_2{}^\mathrm{f}K_\mathrm{d}[\mathrm{OH}^-]}{k_1{}^\mathrm{h} + k_2{}^\mathrm{h}k_\mathrm{d}[\mathrm{OH}]^-} \tag{35}$$

Thus, the constancy of the reactivity ratio with pH will depend upon the magnitude of $k_2{}^\mathrm{f}$, or $k_2{}^\mathrm{h}$ and K_d. For many compounds, since they give type c hydrolysis curves, k_2 is small compared with k_1, the reactivity ratio is constant.[14,21] At high pH values, the ionization of the alcohol may become significant so that $K_\mathrm{a}{}^1$ is no longer a constant.

[21] A. S. Fern and C. Preston, *Chimia* **15**, 177 (1961).

The efficiency of the alcoholysis reaction in the competitive situation is governed by the ratio of the two reactions (d_f/d_h) and this gives Eq. (36) when alcohol ionization is proportionally small. For dyes

$$\frac{d_f}{d_h} = \frac{k_f[AO^-]}{k_h[OH^-]} = \frac{k_f}{k_h} K_a{}^1 \tag{36}$$

exhibiting equilibria of the type of Eq. (5),

$$\frac{d_f}{d_h} = \frac{k_1{}^f + k_2{}^f K_d[OH^-]}{k_1{}^h + k_2{}^h K_d[OH^-]} K_a{}^1 \tag{37}$$

so that even with these dyes the efficiency of fixation will be pH-independent when $k_2{}^h$ and $k_2{}^f$ are negligibly small. An important factor in any case is $K_a{}^1$. This is particularly so when different alcohols are being considered. This was neglected in the work of Dawson *et al.*[22] when comparing reactivity toward normal and isopropanol, and by Gardner and Purves[23] when determining the relative reactivity of different hydroxyl groups in cellulose.

The analysis of competitive kinetics is not significantly changed if reaction with an amine is considered. Instead of ionization of the hydroxyl group, protonation of the amino group and the possible effects of protonation of the reactive system in the dye have to be considered.

Having discussed some of the factors involved in single-phase reactions, attention may now be turned to the more complex multiphase situation that exists when dyes are reacting with fibers.

IV. Competitive Reaction with Adsorption and Diffusion

When the ionized alcohol or the amino group with which the dye is to react is part of a water-swollen polymer matrix, then new factors have to be taken into account that do not arise in the single-phase solution situation. First, there are three phases to consider: (1) the external solution phase, (2) the polymer matrix which the dye reacts, and (3) the internal aqueous phase in the polymer. When the dye and perhaps also the polymer are charged, then concentrations in the internal and external aqueous phases will not be the same due to surface potential effects. Second, the dye molecules must be transported to the site of reaction in the polymer matrix, and this raises the question of the

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[22] T. L. Dawson, A. S. Fern, and C. Preston, *J. Soc. Dyers Colour.* **76**, 21 (1960).

[23] T. S. Gardner and C. B. Purves, *J. Am. Chem. Soc.* **64**, 1539 (1942).

diffusion of a reacting species through a medium with which it can react.

Two ways of dealing with this complex problem have been advanced. The first uses an analysis of simultaneous diffusion and reaction of Danckwerts[24] combined with standard treatment of ionic distributions at the fiber–liquid interface. The second uses an analysis of the diffusion process based on the pore model of Weisz[25–28] combined with standard reaction kinetics. Each treatment is valuable and provides different kinds of information.

When a substance is diffusing in a medium with which it can react, then the net flux is the sum of the diffusional flux and the rate of reaction,

$$\frac{ds}{dt} = \frac{D\,dc}{dx} - kc \tag{38}$$

or

$$\frac{\partial c}{\partial t} = \frac{D\,\partial^2 c}{\partial x^2} - kc \tag{39}$$

where D is the diffusion coefficient, dc/dx is the concentration gradient, c is the concentration at the point in question, and k is a first-order reaction rate constant. Thus, two assumptions are implicit, (i) a constant diffusion coefficient that does not vary with t, x, or c and (ii) first-order kinetics. Danckwerts has produced solutions to Eq. (39) for a number of system geometries. For an infinite plane slab and a constant concentration at the slab–solution interface, the solution may be written,

$$Q_t = [\mathrm{D_f}](D/k_\mathrm{f}{}^1)^{0.5}(tk_\mathrm{f}{}^1 + 0.5)\,\mathrm{erf}\,(tk_\mathrm{f}{}^1)^{0.5} + (tk_\mathrm{f}{}^1/\pi)^{0.5}\exp(-tk_\mathrm{f}{}^1) \tag{40}$$

in which Q_t is the quantity of species reacting in time t; $[\mathrm{D_f}]$ is the adsorbed dye concentration at the interface; $k_\mathrm{f}{}^1$ is the (pseudo) first-order fixation constant, and D is the diffusion coefficient (assumed constant). Sumner and Weston[29] have shown that under appropriate limiting conditions Eq. (40) becomes

$$Q_t = [\mathrm{D_f}]\{t + (1/2k_\mathrm{f}{}^1)\}(Dk^1{}_\mathrm{f})^{0.5} \tag{41}$$

[24] P. V. Danckwerts, *Trans. Faraday Soc.* **46**, 300 (1950).

[25] P. B. Weisz, *Trans Faraday Soc.* **63**, 1801 (1967).

[26] P. B. Weisz and J. S. Hicks, *Trans. Faraday Soc.* **63**, 1807 (1967).

[27] P. B. Weisz and H. Zollinger, *Trans. Faraday Soc.* **63**, 1815 (1967); 168 (1968).

[28] P. B. Weisz and H. Zollinger, *Melliand Textilber.* **48**, 70 (1967).

[29] H. Sumner and C. D. Weston, *Am. Dyest. Rep.* **52**, 442 (1963).

Taking the simpler form, the rate of fixation is given by

$$dQ_{\mathrm{f}}/dt = [\mathrm{D_f}](Dk_{\mathrm{f}}{}^{1})^{0.5} \tag{42}$$

The total rate of hydrolysis is made up of that in the external and internal solutions, and this means that the efficiency E is given by

$$E = \frac{dQ_{\mathrm{f}}}{dh_{\mathrm{i}} + dh_{\mathrm{s}}} = \frac{[\mathrm{D_f}](Dk_{\mathrm{f}}{}^{1})^{0.5}}{k_{\mathrm{h}}[\mathrm{OH_s}][\mathrm{D_s}] + k_{\mathrm{h}}[\mathrm{OH_i}][\mathrm{D_i}]} \tag{43}$$

in which the suffixes s and i signify the internal and aqueous phases; k_{h} is the bimolecular hydrolysis constant. The difference between the internal and external concentrations arises because of the presence of a surface potential due to the presence of carboxyl groups and the ionization of hydroxyl groups in the cellulose. Signifying this potential by ψ, the relationship between internal and external concentrations is given by the Donnan distribution equations

$$\frac{[\mathrm{D_s}]}{[\mathrm{D_i}]} = \frac{[\mathrm{OH_s}]}{[\mathrm{OH_i}]} = \exp - \frac{e\psi}{kT} \tag{44}$$

for a monobasic dye. Combining Eq. (43) and (44) gives

$$E = \frac{[\mathrm{D_f}](Dk_{\mathrm{f}}{}^{1})^{0.5}}{k_{\mathrm{h}}[\mathrm{OH_s}][\mathrm{D_s}]\{1 + \exp(2e\psi/kT)\}} \tag{45}$$

The pseudo-first-order constant $\mathrm{k_f}{}^{1}$ may be written in terms of the bimolecular constant k_{f}, since

$$k_{\mathrm{f}}{}^{1} = k_{\mathrm{f}}[\mathrm{cello}^{-}] \tag{46}$$

The ionization of the cellulose is related to $[\mathrm{OH^-{}_i}]$ by

$$\frac{[\mathrm{cello}^{-}]}{[\mathrm{OH^-{}_i}]} = \frac{K_{\mathrm{cell}}[\mathrm{C}]}{K_{\mathrm{w}}} = K^{1}_{\mathrm{cell}} \tag{47}$$

in which K_{cell} is the ionization constant of cellulose and [C] is the cellulose concentration. Combining Eq. (45)–(47), using the fact of a constant reactivity ratio and rearranging, gives

$$\mathrm{E} = \frac{[\mathrm{D_f}]}{[\mathrm{D_s}]}\left(\frac{DR_{\mathrm{r}}K^{1}_{\mathrm{cell}}}{k_{\mathrm{h}}[\mathrm{OH_s}]}\,\frac{\exp(e\psi/kT)}{\{1 + \exp(2e\psi/kT\}^{2}}\right)^{0.5} \tag{48}$$

The exponential term decreases with ψ, providing that it is more negative than 14 mV (which is always the case with cellulose).

Equation (48) serves to demonstrate the main factors governing the efficiency of the fixation reaction. First, the dominating influence of the substantivity ratio can be seen. Second, the importance of surface charge effects is clear. Heavy depths of shade will be fixed with lower efficiency due to the strongly negative potential they induce. Added electrolyte is seen to affect both the substantivity ratio and the electrostatic factor leading to higher fixation. From the point of view of removing unfixed dye, however, it is desirable that $[D_s]/[D_i]$ be as high as possible, which is best done by maximizing the potential effect. Thus, a compromise must be reached. High reactivity can also be seen to be disadvantageous from the efficiency point of view.

If the analysis is desired to be applied to real fiber systems in a quantitative sense, then it is necessary to use a more appropriate solution to the diffusion equation and allow for concentration-dependent diffusion coefficients. This is not in principle difficult. The simpler situation has been used here for clarity. The predictions of this treatment have been substantiated experimentally by Sumner and Taylor[30] and in practice. Beckmann and Hildebrand[31] have produced data that follow the predicted trend.

The effects of the pH on the rate constants of fixation and hydrolysis are also factors that need to be taken into account in a full treatment. This particular abnormality of some reactive dyes is responsible for an important anomalous effect whereby the rate of fixation may be actually reduced by raising the pH. The effect of pH on the substantivity ratio can be very marked. A particular case is shown in Fig. 2.[32]

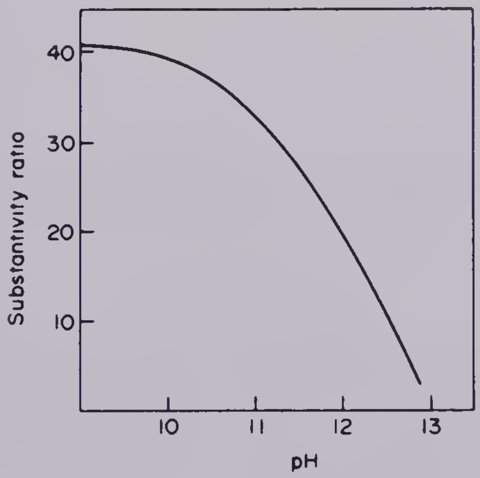

FIG. 2. The effect of pH on the substantivity ratio. (Reproduced with permission from Rattee and Breuer[32].)

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[30] H. Sumner and B. Taylor, *J. Soc. Dyers Colour.* **83**, 445 (1967).

[31] W. Beckmann and D. Hildebrand, *J. Soc. Dyers Colour.* **81**, 11 (1965).

[32] I. D. Rattee and M. M. Breuer, "The Physical Chemistry of Dye Adsorption," p. 251. Academic Press, New York, 1975.

Since a fall in substantivity ratio means a fall in $[D_f]$, then when increasing the pH produces relatively little increase in the reaction constants, it must rebuce both the rate and efficiency of fixation. If the water-swollen phase is regarded as the "more reactive" phase, then the desorption resulting from an increase in the pH means that the dye is tending to migrate to the "less reactive" phase with expected consequences.

The alternative analysis of the situation of Zollinger[3] takes into account the concentration dependence of the experimental diffusion coefficient from the outset. Thus, the diffusion coefficient is expressed as a function in a material balance equation (Eq. 49) in which $[D]_{\text{adsorbed}}$

$$\frac{\partial[D]_{\text{adsorbed}}}{\partial t} = \frac{\partial}{\partial x}\frac{D}{b}\frac{\partial[D_i]}{\partial x} = \frac{D}{b}\frac{\partial^2[D_i]}{\partial x^2} \tag{49}$$

is the total fixed and unfixed reactive dye and hydrolyzed dye in the fiber; D is the "real" diffusion coefficient (i.e., that relating to dye moving in water in the fiber pores), and b is a factor allowing for the tortuosity of the pores. Thus

$$[D]_{\text{adsorbed}} = [D_i{}^r] + [D_i{}^h] + ([D^f] + [D^a])/P \tag{50}$$

where $[D_i{}^r]$ is the concentration in the internal water of mobile reactive dye; $[D_i{}^h]$ is the corresponding amount of hydrolyzed dye; $[D^f]$ and $[D^a]$ are the concentration of immobilized reactive dye either fixed (f) or adsorbed (a); P is the porosity. Thus, combining Eqs. (49) and (50) gives Eq. (51).

$$\frac{D}{b}\frac{\partial^2[D_i]}{\partial x^2} = \frac{\partial[D_i{}^r]}{\partial t} + \frac{\partial[D^a]/P}{\partial t} + \frac{\partial[D^f]/P}{\partial t} + \frac{\partial[D_i{}^h]}{\partial t} \tag{51}$$

Due to the low affinity of most reactive dyes, it is a reasonable assumption that for the most part there is a linear isotherm inside the fiber so that

$$[D^a] = K[D_i{}^r] \tag{52}$$

where K is the internal partition coefficient. This enables $(\partial[D^a]/P)/\partial t$ to be eliminated from Eq. (51). Furthermore, $(\partial[D^f]/P)/\partial t$ can be replaced by a kinetic expression $k_f[\text{cello}^-][D^a]/P$ or $k_f K[\text{cello}^-][D_i{}^r]$. Also $\partial[D_i{}^h]/\partial t$ is given by a hydrolysis equation $k_h[OH^-{}_i][D_i{}^r]$. In a buffered system, and for normal degrees of reaction with the fiber $[\text{cello}^-]$ and $[OH^-{}_i]$ are constants. Combining all the factors gives Eq. (53). From

$$\frac{\partial[D_i{}^r]}{\partial t} = \frac{D}{1+K}\frac{\partial^2[D_i{}^r]}{\partial x^2} - \frac{k_f K[\text{cello}^-] + k_h[OH^-{}_i]}{1+K} \tag{53}$$

this equation, an appropriate expression for the concentration of reacted dye as a function of time can be derived. Zollinger has shown that using this treatment an efficiency expression can be derived for a constant dyebath concentration that may be divided into the factor E_r, which arises when reactivities are the only factors, and the factor E_d, which arises when fixation is diffusion controlled. Which factor determines the situation depends upon the magnitude of the ratio of relaxation times of the diffusion and fixation process. When this is much less than unity, the efficiency is dominated by the fixation factors and

$$E = E_r = \frac{k_f[\text{cello}^-]K}{k_h[\text{OH}^-{}_i]} \tag{54}$$

When the ratio of relaxation times greatly exceeds unity, the role of diffusion becomes dominant and

$$E = E_d = \frac{k_f[\text{cello}^-]KP[\text{D}_i{}^r]}{k_h[\text{OH}^-{}_s]V[\text{D}_s{}^r]}\left(\frac{D}{L^2(k_f[\text{cello}^-]K + k_h[\text{OH}^-{}_i])}\right)^{0.5} \tag{55}$$

in which V is the liquor-to-goods ratio, L is the radius of the cylindrical fiber, and the other terms have their previous significance.

Variation of the application conditions of the dye or changing the dye for another of different reactivity will cause the efficiency of fixation to vary between the limits of E_r and E_d. In order to maximize efficiency, application conditions are normally designed so as to achieve as much of the diffusion process as possible before fixation is allowed to occur and to maximize exhaustion so as to limit hydrolysis in the external phase.

In both treatments of fixation and hydrolysis kinetics in a two-phase system, hydrodynamic factors have been neglected. Their importance in dye adsorption kinetics has been argued by Peters,[33] and clearly they might be expected to affect the ratio of reaction rates in the two phases involved. The effect of the hydrodynamic boundary layer is particularly important in processes where the dyebath is not stirred, i.e., in continuous and pad–batch processes. In the former, the processes normally take the form pad–dry–fix, in which the intermediate drying stage ensures complete transfer of the dye to the fiber. However, in the pad–batch processes, the fabric is left in contact with an unstirred dyebath held in the interstices of the fabric. When there is no transport process other than diffusion, then a steady state must exist at the surface, so that

$$\bar{D}_s\bar{\nabla}_s = \bar{D}_f\bar{\nabla}_f \tag{56}$$

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[33] R. H. Peters and R. McGregor, *J. Soc. Dyers Colour.* **81**, 393 (1965).

in which $\bar{D}_s, \bar{D}_f$ are the diffusion coefficients in the solution and fiber phases; ∇_s, ∇_f are the corresponding concentration gradients. It is normally presupposed that $D_f \ll D_s$ and that the solution phase, i.e., the hydrodynamic boundary layer, is thin so that ∇_s tend to be large. These conditions, if they apply, mean that the rate-controlling process will be the flux in the fiber phase. These conditions are rarely met in practical dyeing machines, however, and are difficult to approach even in experimental conditions. Certainly, in an unstirred system the conditions are not met. One important factor in an unstirred system will be the volume of the entrained dyebath, since this will affect the value of ∇_s. Generally, in continuous dyeing, the volume is very low, but in pad–batch systems this is not so, with the consequence that completion of dyeings takes several hours under pH and temperature conditions that in a stirred system lead to rapid completion of the process. The effect is clearly shown for a reactive dye applied to cellulose in Fig. 3.[34]

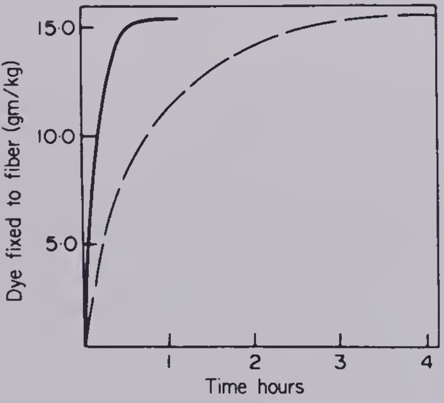

FIG. 3. A comparison between the fixation rates of C.I. Reactive Red 1 applied to cotton with or without liquor circulation. Broken line indicates data for dye applied by pad-batch procedure (0.8:1 liquor ratio), solid line for dye applied by circulation batch dyeing (5.0:1 liquor ratio). (Reproduced with permission from Rattee and Breuer[34].)

Whether there is control over the rate of dyeing by diffusion through the external phase or by the reactivity of the dye depends partly on the latter and partly on the composition of the dye padding solution. For example, in the bad–patch process for dyeing wool with reactive dyes, it is found that highly reactive dyes such as dichlorotriazinylamino dyes give poor results unless their reactivity is suppressed by the addition of complexing agents because of the slow wetting of the wool in the padded and batched material. The rate of fixation is entirely controlled by the diffusion of the dye in the entrained solution, and changes in the

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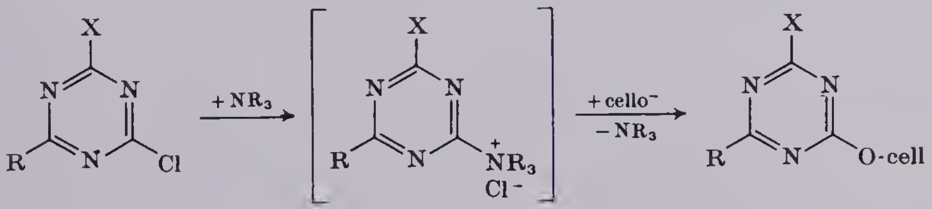
[34] I. D. Rattee and M. M. Breuer, "The Physical Chemistry of Dye Adsorption," p. 286. Academic Press, New York, 1975.

reactivity affect only quality and not the overall rate. When dyes of low reactivity are used, on the other hand, the fixation rates are almost entirely reactivity controlled.

Thus, three general kinds of rate-conditioning factor exist in the two-phase (solution–water-swollen fiber) system. When the dyebath is well stirred so as to minimize the hydrodynamic factor, reactivity will control the rate of fixation when dyes of low reactivity and relatively rapid diffusion are used. On the other hand, in such systems, when reactivity is high the rate of fixation will be modified by the rate of diffusion in the fiber. In practical systems, which generally are not well stirred, diffusion through the external aqueous phase may dominate the situation, particularly in unstirred systems such as the pad–batch systems much favored in reactive dye application, some continuous processes, and jig and winch dyeing.

V. Use of Reaction Catalysts

Among the reactive dyes, fixing by nucleophilic substitution–elimination mechanisms, the most favored leaving group is chlorine. The methoxy group has also been used. However, in systems of this kind, much higher reactivity can be achieved by using a more electronegative group such as $—NR_3^+$. This brings some stability and solubility problems when the group is incorporated into the dyestuff at the manufacturing stage, but these can be readily overcome to open up the possibility of many interesting dyes. However, the use of the quaternary ammonium group in dyes can be effected by catalytic quantities of tertiary amines in the dyebath to form the reactive compound as a transitory product.



The quantity of tertiary amine present to give an adequately accelerated rate of reaction depends upon the rate of quaternization and the rate of reaction of the quaternary product. The kinetics of fixation catalysis have been studied in detail by Dawson,[35] who showed that the main difficulty in using this apparently attractive method of producing

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[35] T. L. Dawson, *J. Soc. Dyers Colour.* **80**, 134 (1964).

a controlled degree of reactivity in reactive dyeing systems lay in the problem of achieving compatibility between dyes in mixture.

In the use of a catalyst system, the following rate processes and equilibria given in Eqs. (57)–(67) are involved.

$$\mathrm{D_1 + [OH^-]} \overset{K_d}{\rightleftarrows} \mathrm{D_2} \qquad \text{(cf. Eq. 13)} \tag{57}$$

$$\mathrm{D_1 + [OH^-]} \longrightarrow \text{hydrolysis product} \tag{58}$$

$$\mathrm{D_1 + cello^-} \longrightarrow \text{fixed dye} \tag{59}$$

$$\mathrm{D_2 + [OH^-]} \longrightarrow \text{hydrolysis product} \tag{60}$$

$$\mathrm{D_2 + [cello^-]} \longrightarrow \text{fixed dye} \tag{61}$$

$$\mathrm{D_1 + amine} \longrightarrow \text{quaternized dye } \mathrm{D_1{}^q} \tag{62}$$

$$\mathrm{D_1{}^q + [OH^-]} \longrightarrow \text{hydrolysis product} \tag{63}$$

$$\mathrm{D_1{}^q + [cello^-]} \longrightarrow \text{fixed dye} \tag{64}$$

$$\mathrm{D_2 + amine} \longrightarrow \text{quaternized dye } \mathrm{D_2{}^q} \tag{65}$$

$$\mathrm{D_2{}^q + [OH^-]} \longrightarrow \text{hydrolysis product} \tag{66}$$

$$\mathrm{D_2{}^q + [cello^-]} \longrightarrow \text{fixed dye} \tag{67}$$

Equations (61) and (64) relate to amine consumption, while equations (62), (63), and (66) relate to amine release. An analysis of the kinetics is more easily carried out if the equilibrium involving D_1 and D_2 is ignored so that five reactions are involved:

$$\begin{aligned}
\mathrm{D + A} &\xrightarrow{k_1} \mathrm{D^q} \\
\mathrm{D^q + F} &\xrightarrow{k_2} \text{fixed dye} + \mathrm{A} \\
\mathrm{D^q + OH^-} &\xrightarrow{k_3} \text{hydrolyzed dye} + \mathrm{A} \\
\mathrm{D + F} &\xrightarrow{k_4} \text{fixed dye} \\
\mathrm{D + OH^-} &\xrightarrow{k_5} \text{hydrolyzed dye}
\end{aligned}$$

The rate of formation of fixed dye is thus equal to

$$k_2[\mathrm{D^q}][\mathrm{F}] + k_4[\mathrm{D}][\mathrm{F}] \tag{68}$$

The rate of change of concentration of amine is equal to

$$k_1[\mathrm{D}][\mathrm{A}] - k_2[\mathrm{D^q}][\mathrm{F}] - k_3[\mathrm{D^q}][\mathrm{OH^-}] \tag{69}$$

The rate of loss of original reactive dye is equal to

$$k_1[\mathrm{D}][\mathrm{A}] + k_4[\mathrm{D}][\mathrm{F}] + k_5[\mathrm{D}][\mathrm{OH^-}] \tag{70}$$

The rate of loss of original reactive dye $(-dD/dt)$ is first order under certain conditions. Equation (70) can be written as

$$-dD/dt = [\mathrm{D}]\{k_1[\mathrm{A}] + k_4[\mathrm{F}] + k_5[\mathrm{OH^-}]\} \tag{71}$$

In a buffered system when $[OH^-]$ is constant and [F] is effectively constant, then because of Eq. (69), a steady state will be set up in which [A] is constant and the reaction will behave as first order. In the steady state condition,

$$k_1[D][A]_s = k_2[D^q][F] + k_3[D^q][OH^-] \tag{72}$$

so that

$$[A]_s = [D^q]\{k_2[F] + k_3[OH^-]\}/k_1[D] \tag{73}$$

where $[A]_s$ is the steady state concentration of the amine. Substituting from Eq. (73) into Eq. (71) gives

$$-dD/dt = [D]\{([D^q]/[D])(k_2[F] + k_3[OH^-]) + k_4[F] + k_5[OH^-]\} \tag{74}$$

Clearly, the higher the proportion of dye that is quaternized, the faster reactive dye will disappear. Also, from the steady state relationship, $[D^q]$ can be expressed in terms of $[A]_s$ and the rate of fixation written as

$$[F]\left(\frac{k_1[A]_s}{k_2[F] + k_3[OH^-]} + k_4\right) \tag{75}$$

Clearly, the higher the steady state concentration of amine the faster the rate of fixation, and from Eq. (73) it can be seen that this depends upon the ratio of the sum of the fixation and hydrolysis constants and the quaternization constant,

$$\{k_2[F] + k_3[OH^-]\}/k_1 \tag{76}$$

If a fixed ratio (R_r) is assumed to exist between the two reaction constants, then Eq. (76) can be rearranged and combined with Eq. (47) to give

$$(k_3[OH^-]/k_1)(R_r K'_{\text{cell}} \exp(e\psi/KT) + 1) \tag{77}$$

The kinetics of the quaternization reaction (k_1) involve different factors when compared with those of the hydrolysis of the quaternized dye (k_3). This is partly because quaternization involves a change in the charge density around the heterocyclic ring system. This must affect the structure of the solvent cage and lead to new effects. Thus, two dyes that react similarly as halogeno reactive dyes may quaternize at different rates to give products of similar reactivity. When the two dyes are present in mixture, the more rapidly quaternizing dye will tend to deplete the supply of amine available to quaternize the other dye, consequently, compatibility problems can arise. These are even worse in the case where the more rapidly quaternizing dye reacts more slowly, thus locking up the amine available for catalysis. Such an effect can arise not only from general charge and solvation factors, but also from the great propensity of quaternized dyes to form aggregates, which can show a much lower reactivity than expected.

An additional factor is that of exhaustion. Dyes possess much greater affinity for cellulose than do tertiary amines. Consequently, unless quaternization occurs very quickly, a situation is created in which the unquaternized dye is exhausted, leaving the tertiary amine in the dyebath. Clearly, this can produce considerable problems of compatibility in mixture. A rapidly exhausting but slowly quaternizing dye in mixture with a weakly exhausting dye that produces a quaternary dye of low reactivity will provide a completely incompatible mixture, for example.

The combination of the problem of multiple reactions, the differences between quaternization and fixation rates, deactivation due to aggregation, and factors associated with differences in substantivity creates the not altogether surprising situation that relatively few of the lower-reactivity dyes for cellulose are suitable for assistance with catalysts, and compatibility in mixture is the exception rather than the rule. Additionally, in many unstirred dyeing situations, the rate-controlling step in achieving fixation is not reactivity but diffusion, so that little benefit would be found in any case with many dyes.

It would certainly be possible to produce a range of low-reactivity dyes showing good compatible behavior in the presence of fixation catalysts, provided this criterion was part of the process of selection for development. It seems unlikely that any range of dyes selected for quite different reasons would provide a suitable basis.

VI. Removal of Unfixed Dye from Reactive-Dyed Materials

While the objective in designing the reactive dye and the application conditions has been to achieve maximum fixation, it is an unfortunate fact that when dyeing a water-swollen fiber, a certain amount of unfixed hydrolyzed dye must be retained due to the competitive hydrolysis reaction inside the fiber. This condition imposes an upper limit on achievable fixation between 80% and 90% of the total dye present. In order to achieve wet-fastness it is necessary to remove that unfixed dye. In the dyeing of cotton with fiber-reactive dyes, this is a fairly straightforward matter, although some interesting physicochemical features require discussion. In wool dyeing, on the other hand, unfixed dye removal is not a simple matter, and indeed, this is the factor that has meant that despite the preoccupation of early reactive dye research with wool, this fiber has seen the least extensive developments in the field as compared with other hydrophilic fibers.

Considering the dyeing of cellulosic fibers first, the problem of unfixed dye removal is one of reducing its substantivity to a minimum by raising the temperature and removing any electrolytes present. In practice, it has been shown by Sumner[36] that the actual adsorbed dye is readily removed, so that the bulk of the washing time in real dyeing machines is concerned with rinsing out carried over dye liquors. Many dyeing machines, for example, the jig machine, are among the most inefficient washing machines imaginable, and consequently the rinsing process can be expensive and time consuming. However in continuous dyeing operations where very short washing off times are employed, it is often the case that the rate of diffusion of unfixed dye through the dyed cellulose is a significant factor. It should be remembered that the dye is not diffusing through a regular cellulosic medium, but one modified by reaction with arylsulfonic acids and, consequently, one that has a much greater electronegative potential than usual. While the new fixed negative changes are uniformly distributed in the system, this will lead to a more rapid diffusion at low electrolyte concentrations due to the charge repulsion effect. However, if the changes are not uniform, then they can become a barrier to diffusion, making removal of dye difficult. This is the case where ring dyeing has occurred, and the effect is illustrated in Fig. 4.

The problem in wool dyeing arises from the fact that the unfixed dye normally possesses significant affinity for the wool fiber under conditions that may be used, bearing in mind the instability of wool to hot alkali. One solution to this problem that was found at one time was to employ dyes that possessed high washing fastness even in the unfixed state,[37] but this is clearly a solution of limited efficacy. A second problem that arises with wool is the fact that reaction occurs with both amino groups and thiol groups in the fiber. The latter have less stability for reasons that are discussed later. With many types of reactive dye, the effect is to produce significant bond breakage during the loose dye removal operation, thus giving rise to a continuing problem. By selecting dyes containing some of the few reactive systems that permit these difficulties to be resolved, fastness results have been optimized, but so far, the highest standards demanded remain unmet.

Very often, particularly in cotton package dyeing, hydrolyzed dye is completely removed from the dyeing during the washing stage only for sufficient decomposition or bond hydrolysis to occur during drying to recreate the problem. This is noticed most in cotton package dyeing systems, because drying occurs with migration of water from the center

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[36] H. Sumner, unpublished work.

[37] A. N. Derbyshire and G. R. Tristram, *J. Soc. Dyers Colour*, 81, 584 (1965).

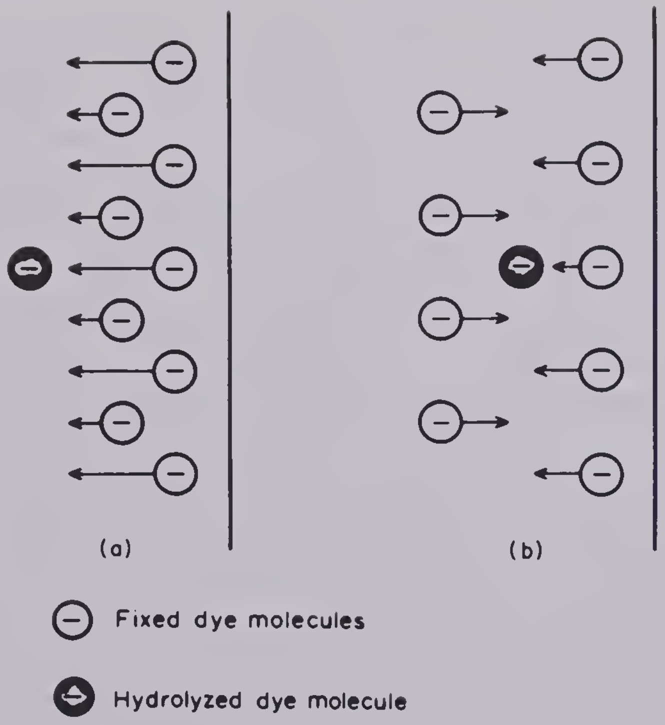


FIG. 4. The effect of ring dyeing on the removal of unfixed dye. (a) *Ring-dyed fiber:* Charge repulsion resists escape of hydrolyzed dye molecule (shaded symbol). (b) *Penetrated fiber:* Charge repulsion effects mutually neutralize.

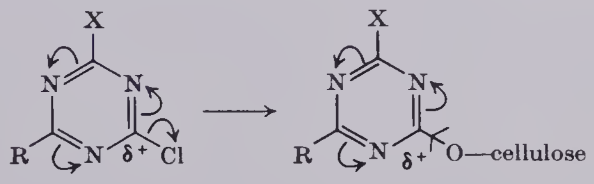
to the outside of the package, thus concentrating any loose dye present on the outside. Very few dye–fiber bonds need to be broken to have a serious effect under these conditions, but the problem can be avoided by reasonable care in selecting drying conditions. This problem and also that mentioned in the case of fiber-reactive dyes applied to wool emphasises the importance of dye–fiber bond stability in determining wet fastness, and it is to this question that attention may now be turned.

VII. Stability of Dye–Fiber Bonds

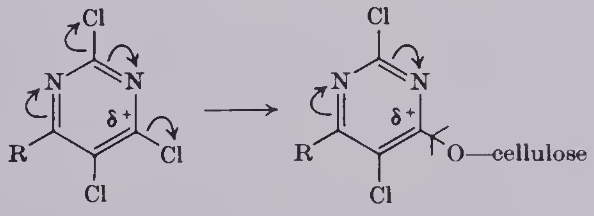
The bonds formed in the fixation of reactive dyes depend naturally enough on the substrate. In the case of cellulosic substrates, the reaction is always between the dye and a hydroxyl group, so that the product is invariably one that may be considered in the context of cellulose ethers and esters. Where polyamide or proteinaceous substrates, such as nylon, wool and silk, are being considered, the reaction is with amino, thiol, or hydroxyl groups, depending upon the pH, the nature of the dye, and the structure of the material. Thus, various kinds of product require their own consideration in the context of bond stability, and in addition, it must be remembered that the reactive moiety in the dye is a substituent of a chromogenic system, and the link between the reactive group and the color system makes at least as important a contribution to the stability as the dye–fiber bond itself.

It is well known that the reaction of cellulose with acylating or alkylating agents produces cellulose esters or ethers and that the former are less stable to acid and alkaline hydrolysis than the latter. Simple colored esterifying or etherifying agents consequently give dyeings of low stability to hydrolysis or bonds of high stability but difficult to produce. A practical reactive dye system demands high enough reactivity for ready fixation with low enough activation in a chemical sense to give bond stability. Thus, whether the starting point of a reactive dye system is a very active compound, such as acetyl chloride, or a relatively inert one, such as chloromethane, by the time a technically viable product has been achieved, it will have pretty much the same properties whichever the starting point.

The major result of this constraint in the cellulosic dye field is that all reactive dyes in use give rise to reactive alkali-hydrolyzable products when fixed. This is exemplified in Eqs. (78)–(80). It can be seen in the first two cases that while susceptibility to nucleophilic attack by hydroxyl ions has been lessened as a result of replacing the chlorine with a cellulosyl residue, it nevertheless remains so that the product is still, albeit less, hydrolyzable. In the third case, an intermediate vinylsulfone is formed, but the cellulose esterifying acid is only less readily removable



(78)



(79)

$$R{-}SO_2CH_2CH_2OSO_3Na \xrightarrow{OH^-} R{-}SO_2CH{=}CH_2 \underset{OH^-}{\rightleftharpoons} R{-}SO_2CH_2CH_2O{-}\text{cellulose} \qquad (80)$$

Before fixation

After fixation

to a degree by hydroxyl ion attack than the original esterifying sulfuric acid. Under acid conditions, hydrolysis will occur if protonation of the system is possible, so making the dye–fiber bond susceptible to attack by the weak nucleophile, water.

The similarity between the factors governing the hydrolysis of dye–fiber bonds in the case of the dyes for cellulosic fibers and of direct hydrolysis of the reactive dye is emphasized by the correspondence between the hydrolysis rate–pH relationships. These have been shown by Senn, Stamm, and Zollinger[38] for a wide variety of dye–fiber bonds to take the general form shown in Fig. 5. This is the same form as is shown in hydrolysis reactions, the pH region of maximum stability being that recommended by Stephen[4] for stabilization of dye powders.

Reactions with thiol groups in wool will produce much the same situation as the reaction with hydroxyl groups in cellulose, except that the bonds will be less stable. On the other hand, reaction with amino groups in wool or nylon would generally be expected to give rise to dye–fiber bonds resistant to acid or alkali as a result of the strong deactivating effect of the nitrogen atom.

Quite apart from the stability of the dye–fiber bond, consideration must be given to the stability of the bridging group between the chromogen and the reactive system. This has a decisive role to play in many cases. In the case of ω-chloroacetylamino dyes, for example,

$$\mathrm{RNHCOCH_2Cl} \xrightarrow{\mathrm{FNH_2}} \mathrm{R{\cdot}NH{\cdot}CO{\cdot}CH_2NHF} \xrightarrow[\mathrm{H_2O}]{\mathrm{H^+}} \mathrm{R{\cdot}NH_2} + \mathrm{HOOC{\cdot}CH_2NHF} \qquad (81)$$

Indeed, the amide bridging group is hazardous generally, although its reactivity can be modified to some extent by careful selection.

Benz[39] has discussed the behavior of a number of bridging groups in reactive dyes for cellulose and has substantiated the reasons for the general use of imino groups.

The stability of dye–fiber bonds on wool has always been a problem for the dye chemist that has been resolved only with difficulty. The physical chemistry of dye–fiber bond stability has not been studied as extensively on that fiber, however, as it has on cellulosic fibers. In wool dyeing, it is a fairly simple matter to produce a reaction product between a reactive dye and an amino group with adequate stability. The problem thus becomes one of preparing fiber-reactive dyes with sufficiently stable bridging groups, i.e., avoiding the kind of problem shown in Eq. (80) or dealing with the problem of the reactive products of reaction between the dye and thiol groups. Both aspects have been

[38] R. C. Senn, O. A. Stamm, and H. Zollinger, *Melliand Textilber.* **44**, 261 (1963).

[39] J. Benz, *J. Soc. Dyers Colour.* **77**, 734 (1961).

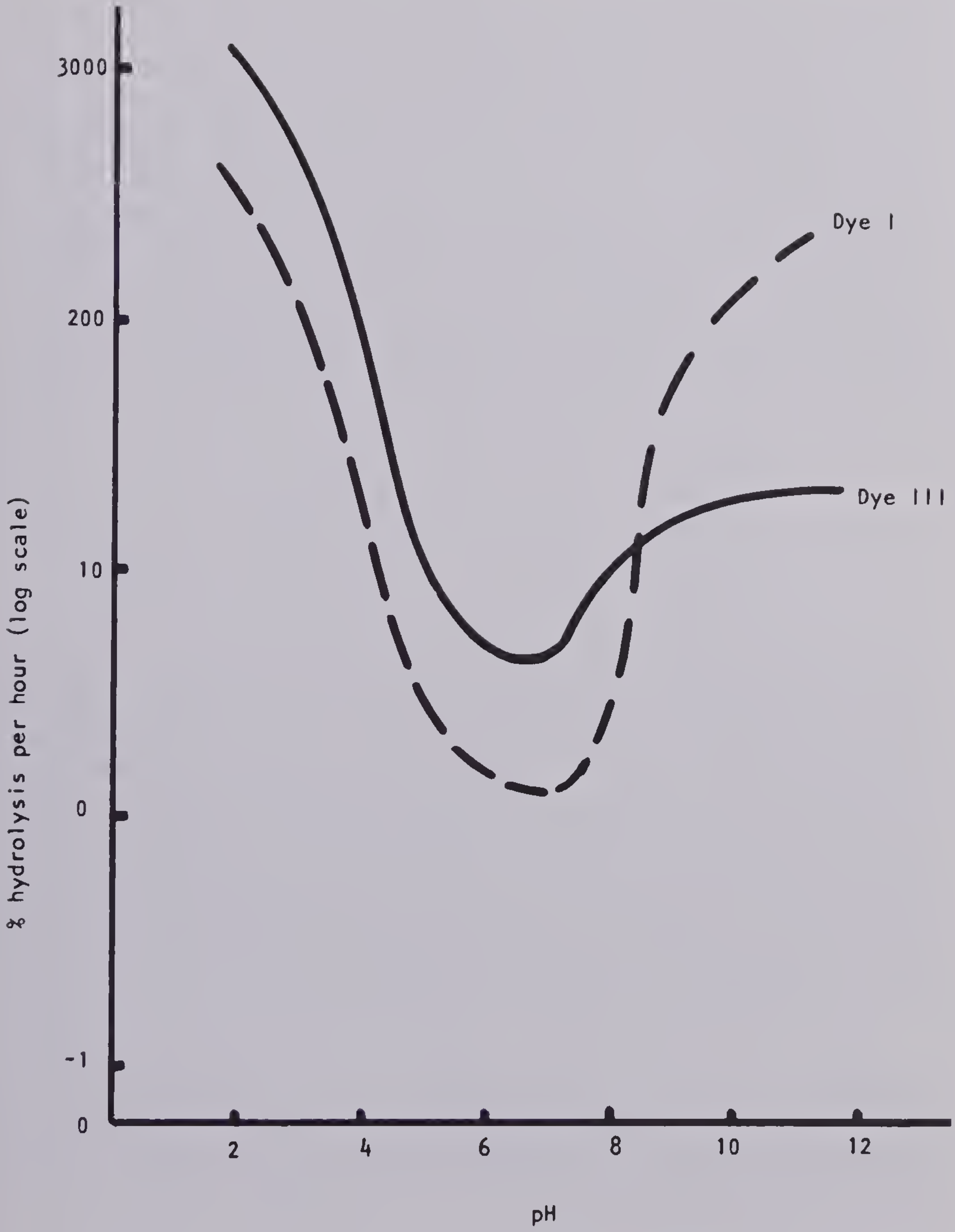


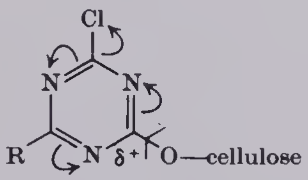
FIG. 5. The general form of the variation of dye–fiber bond hydrolysis rates with pH.

tackled in the same way, i.e., by the appropriate choice of dye structures and reactive systems that minimize undesirable side reactions.

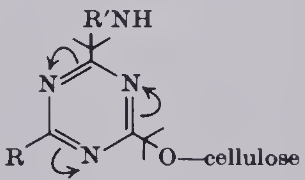
With regard to dye–fiber bond stability in the field of cellulosic fiber dyeing, there has been a great deal of investigation, partly because of the much greater technical importance of reactive dyes for cellulose as compared with other fibers, and partly because fastness standards on cellulose are the highest among dyed textiles.

Generally speaking, the problem of fastness to alkaline treatments, i.e., the alkaline hydrolysis of dye–fiber bonds, has been managed by dyestuff selection at the development stage. Even with an unchanging reactive system, dyes vary in reactivity due to the substituent effects of different chromogens. Consequently, dyes giving unacceptable reactive dye–fiber bonds can be selected out. However, certain intrinsic properties do exert an influence, and two examples may be considered here.

The chlorotriazinyl dyes are of two types, depending on the number of labile chlorine atoms present. Reaction with cellulose under alkaline conditions gives rise to two products (III and IV) in the first instance as

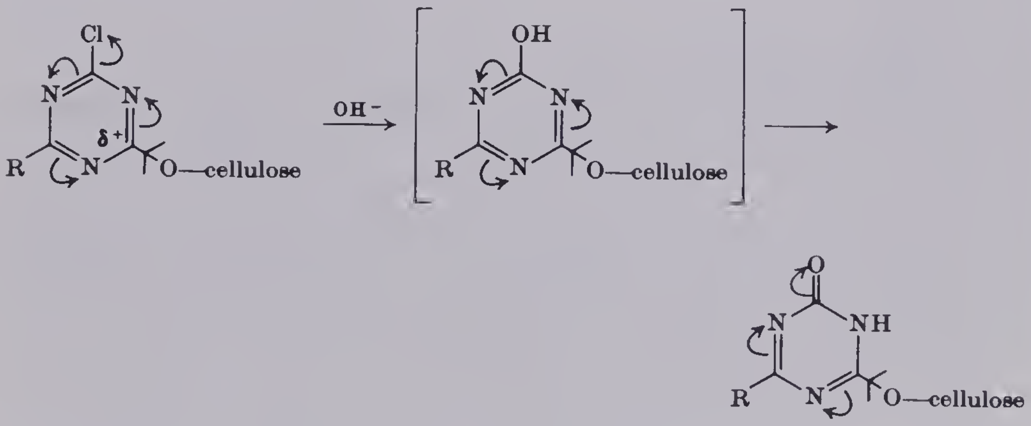


(III)



(IV)

a consequence. In both cases, the carbon atom attached to the cellulose residue is susceptible to nucleophilic attack by a hydroxyl ion. In the case of dye IV, such attack is much less ready due to the *deactivating* effect of the R′NH⁻ substituent as compared with the *activating* effect of the chlorine substituent in (III). Consequently, treatment with alkali is in both cases, but to different degrees, likely to break the dye–fiber bond. In the case of dye (III), however, such bond rupture has to compete with attack at the other active carbon position. This is the more reactive, so that the more probable reaction is to lose the chlorine atom. The product of this reaction rapidly isomerises,



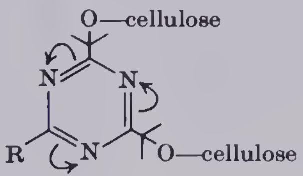
(V)

The dye (V) has lost a great deal of the activation provided by the conjugated heterocyclic ring system and is also deactivated by the keto group. The dye–cellulose bond in the case of dye (V) is therefore much more stable than in the cases of dyes (III) and (IV). The alternative reaction route also means that the bond in dye (III) appears more stable than that in dye (IV).

From the general standpoint of washing fastness, the differences discussed are not very important and can be minimized by dye selection at the development stage. However, monochlorotriazinyl dyes leading to products of the dye (IV) type must be applied under hot alkaline conditions in order to achieve fixation in technically reasonable dyeing times. Under these conditions, the dye–fiber bonds do show some reactivity, so that dye fixation passes through a maximum value with time. This can cause some problems in shade matching if the effect is unsuspected.

The vinylsulfonyl-reactive dyes exhibit some reversibility in fixation as shown in Eq. (79). The effect is put to good use in discharge printing. The disadvantageous consequences of the effect from the point of view of wash fastness are avoided by dye selection at the development stage, but this has important consequences in development costs. Since the dye resulting from hydrolysis of the dye–fiber bond is reactive, it is essential that it not be absorbed onto adjacent undyed material, since it will cause a permanent stain. Normally, a certain amount of adsorption of loose dye in wash liquors is acceptable, as it may be removed in rinsing. However, when the loose dye is reactive, this is not so, and consequently only dyes of low affinity may be used. The consequence this has in development work is to make it very difficult to devise dyes that may be applied by exhaustion methods. Thus, it can be seen that reversibility in dye–fiber bond formation is to be regarded as generally undesirable.

Stability to acid treatments is not generally important as far as cellulosic fabrics are concerned, but the general acid nature of urban atmospheres does have a potentially deleterious effect on reactive dyeings through acid-catalyzed hydrolysis of dye–fiber bonds. In practical terms, the effect is not sufficiently marked to cause concern



(VI)

with most reactive dyes for cellulose except for certain dichlorotriazinyl dyes based on H-acid and some dyes in which an imido bridging group is used.

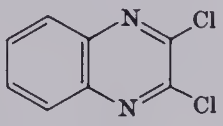
Considering first the dichlorotriazinyl dyes, it has been shown that two reaction products are possible, dyes (III) and (V). To these must be added a third, produced by the reaction of dye (III) with a cellulosyl group to give a doubly-bonded dye (VI). In all three cases, the heterocyclic ring can accept a proton, thus promoting considerable activation and, consequently, the possible attack by a water molecule to produce dye–fiber bond rupture. In the case of dye (III), the most probable result is the formation of a protonated dye (V). In the case of dye (VI), the result will be the rupture of one dye–fiber bond to form the same product. The reactivity of dye (VI) will be much less than that of dye (III). Dye (V) is capable of accepting more than one proton and showing considerably greater reactivity than dyes (III) or (VI) or, for that matter, dye (IV). Thus dyeings that are predominantly of the dye (V) type show significantly less stability to acids than those of dyes (III), (IV), or (VI). The effect is of potential technical significance only in the case of dyes based on H-acid.

The significant parameter is the internal pH of the fiber; so the hydrolysis reaction does not follow simple kinetics. The internal pH is dependent upon the amount of dye present, which introduces a complicating factor. A study by Johnstone and Rattee[40] has shown that the kinetics are described by Eq. (82), in which c is a system constant that

$$kct = \ln \frac{[\mathrm{D_f}]_0[\mathrm{H^+}_\mathrm{i}]_t}{[\mathrm{D_f}]_t[\mathrm{H^+}_\mathrm{i}]_0} \tag{82}$$

is a function of $[\mathrm{D_f}]$, the subscripts 0 and t signify the time t equals 0 and t, $[\mathrm{D_f}]$ is the fixed dye concentration, and $[\mathrm{H^+}_\mathrm{i}]$ is the internal hydrogen ion concentration. This equation rationalizes the anomalies that may be apparent through the use of different acids in determining pH and also the effects of different salts. It was shown that the dyes based on H-acid exhibit an unusually high reactivity as compared with other dyes at an internal pH of about 3.

Dyes based on the reactive system,



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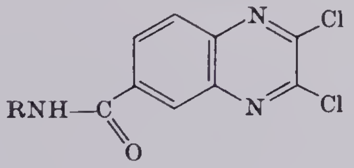
[40] J. E. Johnstone and I. D. Rattee, *J. Soc. Dyers Colour.* **89**, 89 (1973).

are normally attached to the chromogen through an amide group in the 6-position:



This bridging group is susceptible to acid-catalyzed hydrolysis, leading to a breakdown of dye–fiber bonding. Such sensitivity tends to vary little between one dye and another, producing a general deficiency with regard to storage stability in acid atmospheres among dyes of this type.

It should be stressed that instability problems of the type discussed are often not noticed in practice, since frequent washing renders the effect undetected in use; resin finishing prevents the occurrence, and dye selection at the development stage minimizes the problem.

VIII. Fixation of Reactive Dyes on Wool

Although much of the above discussion applies in principle to reactions with both wool and cellulose, the fixation of reactive dyes on wool does present special features that merit separate attention. The production of fast shades on wool by dye–fiber reaction appears on the face of it to be a much more simple proposition than the same target in cellulose dyeing due to the higher reactivity of wool toward chemical agents. The reaction of wool with iodoacetic acid or dinitrofluorobenzene is commonplace in wool chemistry, and the step from such reagents to actual reactive dyes does not seem a large one. Supramine Orange R (CI Acid Orange 30) introduced in the 1930s contained an ω-chloroacetamido group, and it showed significantly improved wet fastness as compared with its acetyl analog. Although it was not realized at the time, the improvement was due to dye–fiber reaction. Other dyes of improved fastness were also produced at the time bearing β-chloroethylsulfonamido groups, which became fast when dyeings were aftertreated with alkali. Neither of these approaches gave results of really good quality, and even after the concept of dye–fiber reaction became familiar to dye chemists after 1956, reexamination of these early systems failed to reveal satisfactory dyes. Some ω-chloroacetyl dyes were to be found in the early Cibalan Brilliant dyes introduced to supplement the 1:2 chromium complex dyes, but these did not exhibit particularly good results. The Remalan dyes of Hoechst, which predated the chemically similar Remazol reactive dyes for cotton, also gave good fastness as compared with acid dyes, but again were deficient as fast wool dyes.

The problem in all these cases is the residual staining of adjacent wool (or nylon) that occurs on washing. The effect is known to derive from two causes. The first is the difficulty of completely removing unfixed or hydrolyzed dye from the wool during the final clearing treatment due to the relatively high affinity that acid dyes have for wool. The second is the variety of reaction products that reactive dyes can provide with wool and the fact that not all of them are stable to washing treatments.

The groups present in wool that are capable of involvement in dye–fiber reactions using conventional reactive dyes are NH_2 of lysine and terminal amino acids, NH of histidine, SH of cysteine, and OH of threonine, serine, and tyrosine (cf. *CSD VI*, p. 341, Fig. 3).

Reaction products with all these reactive side chains have been observed in one investigation or another. Using vinylsulfonyl reactive dyes, Rouette and Zahn[41] found reaction products with lysine, histidine, and cysteine. Lewis[42] has observed reaction products of ω-chloroacetylamino dyes with the same residues. In his case, reaction with histidine residues occurred only when the pH was less than 7, while reaction with thiol groups occurred at all pH values. Hille,[43] using both halogenotriazinyl and vinylsulfonyl reactive dyes in high concentration, observed reaction products not only with the three residues mentioned, but also with serine and tyrosine. Asquith and Chan,[44] using rather lower and technically probable amounts of dye, found that reaction products with lysine and histidine were the most readily produced. Derbyshire and Tristram[45] obtained similar results using acryloylamino dyes. A detailed study by Corbett[46] established that the reactivity of vinylsulfonyl dyes toward reactive groups found in keratin shows an order thiols > amines > hydroxyl in an approximate ratio of $10^4:10^2:1$.

Of course, the relative concentrations of such groups in wool will also affect the proportion of reaction with a particular group. Amino groups predominate over thiol groups in wool that is not specially reduced, so that the proportion of reactive dyes reacting with the latter is less than might be expected on reactivity grounds, although it is generally significant.

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[41] P. Rouette and H. Zahn, *Textilveredlung* **3**, 241 (1968).

[42] D. M. Lewis, Ph.D. Thesis, University of Leeds, 1966.

[43] E. Hille, *Text.-Prax.* **17**, 171 (1962).

[44] R. S. Asquith and D. K. Chan, *J. Soc. Dyers Colour.* **87**, 181 (1971).

[45] A. N. Derbyshire and G. R. Tristram, *J. Soc. Dyers Colour.* **81**, 584 (1960).

[46] J. F. Corbett, *Proc. 3rd Int. Wool Text. Res. Conf.*, Vol. III, p. 321 (1965).

The reaction products with amino groups are in almost every case stable except in that ω-chloroacetylamino dyes tend to hydrolyze to produce carboxymethylamino compounds, so that high fastness cannot

$$\text{Dye—NHCOCH}_2\text{Cl} \xrightarrow{\text{W—NH}_2} \text{Dye—NHCO}\cdot\text{CH}_2\text{NHW} \xrightarrow[\text{alkali}]{\text{acid or}}$$

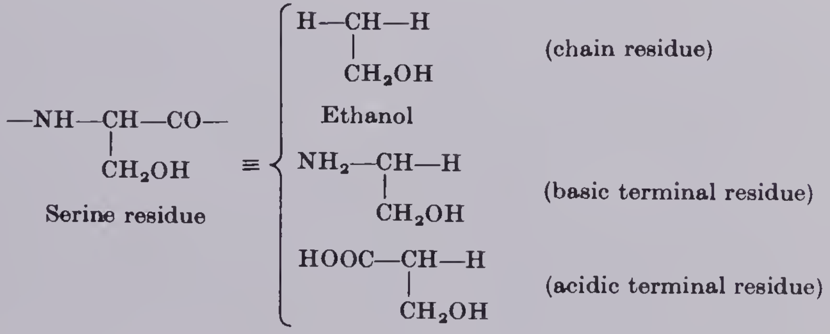
$$\text{Dye—NH}_2 + \text{WNH—CH}_2\text{COOH}$$

be achieved even if reaction with thiol groups were to be avoided.

When a halogenotriazinyl dye reacts with an alkylthio group, the result is a dye that is only marginally less reactive than the original one. Thus reaction of such groups with thiol groups in wool tends to give unstable products of low fastness.

Because of the difficulties of removing any exhausted hydrolyzed dye from wool at the end of the dyeing operation, it is necessary to avoid hydrolysis of dye as well as reaction with groups giving unstable products. Consequently, in the Hostalan dyes, the methyltaurine ethylsulfonyl group is present, which is converted only slowly to the reactive vinylsulfone. In the Verofix, Reactolan, and Drimarene F ranges, a difluoromonochloropyrimidinyl group is present, which has the unusual ability to resist hydrolysis but to react readily with amino groups.[47]

The physical chemistry of the reaction of dyes with wool has been studied extensively by Shore[48–51] using a dichlorotriazinyl dye in reaction with a series of model compounds bearing the same functional group as amino acids identified as significant in dye–fiber reactions. In effect, Shore replaced peptide links by hydrogen atoms (Scheme 1).



$$\underset{\text{Serine residue}}{\begin{array}{c}\text{—NH—CH—CO—}\\ |\\ \text{CH}_2\text{OH}\end{array}} \equiv \left\{\begin{array}{ll} \begin{array}{c}\text{H—CH—H}\\ |\\ \text{CH}_2\text{OH}\\ \text{Ethanol}\end{array} & \text{(chain residue)}\\ \begin{array}{c}\text{NH}_2\text{—CH—H}\\ |\\ \text{CH}_2\text{OH}\end{array} & \text{(basic terminal residue)}\\ \begin{array}{c}\text{HOOC—CH—H}\\ |\\ \text{CH}_2\text{OH}\end{array} & \text{(acidic terminal residue)} \end{array}\right.$$

Using such models for reactive side chains in proteins, Shore established rate constants on the basis of which overall reaction constants

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[47] D. Hildebrand and G. Meier, *Text.-Prax.* **26**, 499 (1971).

[48] J. Shore, *J. Soc. Dyers Colour.* **84**, 408 (1968).

[49] J. Shore, *J. Soc. Dyers Colour.* **84**, 413 (1968).

[50] J. Shore, *J. Soc. Dyers Colour.* **84**, 545 (1968).

[51] J. Shore, *J. Soc. Dyers Colour.* **85**, 11 (1969).

for proteins of known structure could be predicted as a function of pH and temperature. Excellent correlation was obtained for several soluble proteins and mixtures of the model compounds. The results confirmed in a general way results such as those of Lewis[42] relating to the reactivity of thiol and lysine groups.

The general approach for the kinetic analysis of the reaction of dyes with cellulose was applied then to wool. This presented some difficulty due to the fact that wool fibers rather than cellophane sheet had to be used. However, the form of the Danckwerts equation (83) applicable to semiinfinite cylinders[57] was found to be effective:

$$Qt = 4\pi D[\mathrm{D_f}] \sum_{n=1}^{\infty} \frac{k_{\mathrm{f}}^{1} + D\alpha_n^{2} \exp\{-t(k_{\mathrm{f}}^{1} + D\alpha_n^{2})\}}{(k_{\mathrm{f}}^{1} + D\alpha_n^{2})} \tag{83}$$

in which the symbols have the same significance as in Eq. (40) and α_n are the successive roots of the Bessel function $J_0(r\alpha) = 0$. One of the most important factors revealed by Shore's work is the way in which the distribution of reacted dye residues varies with the degree of reaction.

Pad–Batch Application of Reactive Dyes to Wool

Despite the many problems, the attractiveness of reactive dyes for wool dyers has stimulated considerable efforts to find ways of applying them to wool to produce optimum results. In these, the IWS pad–batch process[52] has had the most impact, offering the wool piece dyer the special advantages of cold semicontinuous processing as well as a good standard of fastness. The process involves the pad application to wool of a complex pad liquor containing an addition to dye up to 300 gm/liter urea, sodium metabisulfite, a weakly cationic surfactant, a thickening agent, and industrial alcohol. The role of the components in this complex mixture has been examined in detail by Gilchrist and Rattee,[53] while the effects of urea on dyeing has been examined by many workers.[54–56]

The complexities of the IWS pad–batch process dye liquor have been shown to be due to an attempt to achieve a balance of properties with readily available agents. When wool is padded, entrained air is not readily expelled, and the wool fibers themselves wet out extremely slowly in comparison with cotton and other materials dyed by padding

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[52] J. D. M. Gibson, D. M. Lewis, and I. Seltzer, *J. Soc. Dyers Colour.* **86**, 298 (1970).

[53] A. K. Gilchrist and I. D. Rattee, *Text. Chem. Colour.* **5**, 105 (1973).

[54] H. Niederer and P. Ulrich, *Textilveredlung* **3**, 337 (1968).

[55] R. S. Asquith and A. K. Booth, *Text. Res. J.* **40**, 410 (1970).

[56] K. R. F. Cockett, I. D. Rattee, and C. B. Stevens, *J. Soc. Dyers Colour.* **84**, 262 (1968).

[57] P. V. Danckwerts, *Trans. Faraday Soc.* **47**, 1014 (1951).

processes. As a consequence, the wool, as it emerges from the pad liquor and the nip, is virtually dry while entraining a considerable volume of solution. Normally, this would drain on batching, but by adjusting the viscosity with a thickening agent, this can be prevented. The agent itself is normally wet out with industrial alcohol and mixed into the padding liquor, and the alcohol present plays a significant role in the solvent-dependent processes that occur.

As the wool stands in its thickened impregnation liquor, it slowly wets. This process takes up to 30 minutes, and because differently damaged fibers wet out at different rates, it is necessary to control the dye uptake rate by the use of a complexing agent, which prevents dye from being adsorbed. The rate of release of dye from the complex is controlled by the use of urea, and by balancing concentrations, a satisfactory outcome is achieved. Sodium metabisulfite, meanwhile, brings about some disulfide bond fission, improving diffusion rates in the more swollen fibers. Additionally, urea acts as a swelling agent for sulfite-reduced fibers, giving a further enhancement of dye adsorption rates.

Despite the complexity of its basis, the process is simple to operate. The application of the principles underlying the process can be used to simplify the system,[58] and the use of a wetting agent that can produce wet wool in short contact times eliminates the need for some of the complicating factors.

IX. Novel Approaches to Reactive Dye Fixation

The standard approach to reactive dye fixation is to employ chemical activation. Thus, molecules are prepared that are subject to nucleophilic substitution or addition. This results in the production of dye–fiber linkages that behave in accordance with the degree of residual activation. Since not all the activation leading to the reaction can be incorporated in the leaving group or groups, stability to chemical attack varies from acceptable to poor, according to the chosen reactive system.

An alternative approach is provided by methods of fixation that produce as intermediate reactive species very highly reactive compounds that do not exhibit residual activation after fixation. One example of this is provided by the work of Karelina and co-workers,[59] who treated wool with potassium persulfate and potassium pyrosulfate in the presence of Rhodamine S to produce free radicals and subsequent

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[58] A. K. Gilchrist and I. D. Rattee, *Text. Chem. Colour.* **6**, 153 (1974).

[59] S. L. Karelina, N. P. Stepantsova, B. E. Geller, and E. P. Ivanova, *Technol. Text. Ind. USSR* (*Engl. Transl.*) No. 5, p. 75 (1971).

dye–fiber bonding. In another study, Tikhomolova[60] carried out similar dye–fiber reactions using gamma radiation to produce free radicals.

Another related approach has been used by Griffiths,[61] who has prepared a number of sulfonyl azides. These dyes will react with a variety of fibers by photochemical or thermal activation. With ultraviolet irradiation, reaction with polypropylene can be obtained as well as with other substrates. On heating, two reactions can occur with nylon. At temperatures below 120°, substitution of terminal amino groups occurs to form a sulfonamido compound, while at higher temperatures, nitrenes are formed, which react with the C—H bonds of the polymer backbone to form very stable products. Many other azide systems have been examined in this study.

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[60] M. P. Tikhomolova, N. P. Stepantsova, B. E. Geller, A. I. Shalomova, A. T. Tairova, and L. A. Kuznetsova, *Technol. Text. Ind. USSR* (*Engl. Transl.*) No. 1, p. 93 (1971).

[61] J. Griffiths, *BeP* 765,112.

Chapter II

LEATHER DYES

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I. Introduction

Leather has been important for footwear and clothing during all of recorded history and has been colored with dyes from ancient times. Although footwear continues as the major use for leather, there has been a resurgence in demand for garment leather during the past twenty years. Ever increasing leather production, tied to expanding world population, has caused a correspondingly greater demand for dyes. Presently the world market for leather dyes is estimated at $42 million annually, Europe using $20 million and the United States $12 million of this.

Dyes for garment leather have more stringent fastness requirements than those for footwear. This fact, combined with increasing governmental restrictions on the use of certain important intermediates and the overall increased demand, have justified efforts by manufacturers to find improved dyes. That they have been successful has been documented with respect to listings of Acid and Direct dyes in the "Color Index" (2nd and 3rd editions) and subsequent additions and amendments.[1,2] Dyson and Landmann show that specialty acid leather dyes (125) represent 18% of the 687 new entries in the period 1956–1972, and specialty direct dyes for leather (15) were 4.7% of the 317 new entries in the same period.[1]

A thorough search of the patent literature covering the past twenty years has shown that many dyes whose major uses are on various natural and synthetic substrates are also claimed to have utility for coloring leather. These include 1:2 metal complex dyes, reactive dyes, and cationic dyes, as well as the newer acid, direct, and miscellaneous dyes.

This chapter is intended to cover developments since 1950 in the chemistry of dyes for leather and supplements information in *CSD I* and *II*.[3] The emphasis is on the more recent developments, because of space limitations, with no intention to repeat much of the information contained in the "Color Index." During the period under consideration, a number of books[4–7] and reviews[1,2,8–16] wholly or partially concerned with dyes for leather have been published.

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[1] W. R. Dyson and A. W. Landmann, *Rev. Prog. Color. Relat. Top.* **4**, 51–59 (1973).

[2] H. E. Nursten, *J. Soc. Leather Trades' Chem.* **44**, 182–191 (1960).

[3] pp. 298, 406, 435, 437, 466, 467, 475, 476, 483, 485, 495, 505, 519, 528, 543, 544, 570, 572, 576, 578, 579, 759, 775, 781, 1209.

[4] J. S. Kirk, *in* "The Chemistry and Technology of Leather" (F. O'Flaherty, W. T. Roddy, and R. M. Lollar, eds.), Vol. III, pp. 1–15. Van Nostrand-Reinhold, Princeton, New Jersey, 1962.

[5] R. Reed, "Science for Students of Leather Technology." Pergamon, Oxford, 1966.

[6] T. C. Thorstensen, "Practical Leather Technology." Van Nostrand-Reinhold, Princeton, New Jersey, 1969.

[7] G. M. Gantz, J. R. Ellis, J. J. Duncan, J. C. Freas, R. C. Hall, M. J. Landberge, J. Moss, F. O'Neal, W. N. Pardey, and T. Vogel, *Kirk-Othmer Encycl. Chem. Technol., 2nd Ed.* **7**, 505–613 (1965).

[8] L. M. Woodley, *J. Soc. Leather Trades' Chem.* **50**, 24–32 (1966).

[9] A. R. Mossop, *J. Soc. Leather Trades' Chem.* **49**, 470–479 (1965).

[10] H. Wicki, *SVF Fachorgan Textilveredl.* **19**, 556–568 (1964).

[11] J. A. Casnocha, *Leather Manuf.* **79**, 11–19 (1962); *J. Am. Leather Chem. Assoc.* **58**, 445 (1963); *Tanner* **17**, 185–188 (1962).

[12] J. A. Casnocha, *Leather Manuf.* **73**, 24–38 (1956).

[13] C. K. Black and C. H. Geister, *J. Am. Leather. Chem. Assoc.* **48**, 682–689 (1953).

[14] R. H. Leach, *J. Am. Leather Chem. Assoc.* **48**, 605–612 (1953).

[15] J. R. Blockey and D. H. Tuck, *J. Soc. Dyers Colour.* **69**, 273–279 (1953).

[16] J. S. Kirk, *J. Am. Leather Chem. Assoc.* **51**, 526–529 (1956).

II. General Discussion

A. Leather as a Substrate for Dyes

Leather, being of heterogeneous animal origin, and tanned in any one of many ways, differs from textiles derived from vegetable fibers, animal hair, or synthetic polymers. It does not have a definite composition, even though it is derived from the protein collagen, the chemistry of which is reasonably well known.[17,18] A great variety of chemical treatments serve to change (tan) collagen into leather. Such chemical treatments, which cross-link and stabilize the collagen fibrils, vary in nature, and conditions of application. Variations in the original hide prior to tanning impose additional heterogeneity. The collagen itself, in common with other proteins, is degraded at extreme pH conditions, is sensitive to heat (denatured), and is amphoteric in character. These properties are also present in the tanned leather, modified somewhat by the tanning treatment.

The most common tanning agents are chromium salts, vegetable tannins, syntans (synthetic tannins), aldehydes, and oils, with chrome predominant. Chrome-tanned leather usually has a bluish to greenish gray color amenable to dyeing a variety of hues, and it may also be bleached white if desired. Chrome tanning is usually followed by vegetable or syntan retanning. The retanning not only modifies the physical properties of leather desirably, but also allows more level dyeing and may impart to the leather a tan to brown color if vegetable retan is used, or it may lighten the color if a syntan is used.

Wicki[10] has written an excellent review of the preparation and of the physical and chemical structure of leather in which he describes the chemical bonding of various tanning agents with collagen and the variation in properties of the resultant leather. For example, syntans which are aromatic polysulfonic acids are bonded ionically, the negative sulfonic groups pairing with positive groups in the collagen. The resultant leather is strongly negatively charged and, thus, more resistant to dyeing with anionic dyes. In this case, the leather also becomes somewhat negatively charged with respect to the original collagen, whose isoelectric point is normally at pH 5, but the change is not as drastic.

Vegetable tannins are polyphenols and glycosides containing hydroxyl groups capable of hydrogen-bonding with the amide groups and other

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[17] W. Traub and K. A. Piez, *Adv. Protein Chem.* **25**, (1971); G. N. Ramachandran, *in* "Treatise on Collagen" (G. N. Ramachandran, ed.), Vol. 1, p. 103. Academic Press, New York, 1967.

[18] M. L. Tanzer [*Science* **180**, 561 (1973)] has discussed cross-linking of collagen.

"active sites" in the amorphous regions of collagen; the bonded tannins undergo further bonding with more tannin molecules, thus filling the space in the amorphous regions of the collagen structure.

Chrome tanning is more complex in that both cations and anions are absorbed by the hide, the Cr coordinatively bonding with both free amino and carboxyl end groups in the collagen. So long as the leather containing the complexed Cr is not dried, the complexes remain very reactive and capable themselves of binding anions or cations.

Thus, it is clear that, as a result of variations in tanning procedures, the affinity of leather for subsequently applied chemicals, including dyes, may fluctuate widely. However, an understanding of the chemistry of the preparation of leather allows comprehension of the requirements for successful coloration of this unique but complex substrate. Knowledge of the past history of a particular hide is extremely desirable and usually known, for preparation, dyeing, and finishing of a hide are generally done in one tannery.

B. Dyeing of Leather

Leather is, of course, dyed to improve its appearance and make it salable in a finished form. As noted previously, some color may be imparted by the tanning agent, but usually this is supplemented with synthetic dyes and/or pigments. Leather also has inherent pigmentation and grain characteristics, which, together with factors described earlier, make attainment of uniformity of shade throughout the piece difficult, if not impossible to attain; but this makes leather difficult to duplicate synthetically, and is one factor giving it psychological appeal.

A variety of dyeing procedures are in commercial use, including drum, spray, paddle, brush, tray, and solvent dyeing, the first two being most important. Dyeing temperature is controlled within the range of 25°–60°, and the pH is set in the range 3.8–5.5. Liquor ratios are generally low; e.g., in drum dyeing, 2–8 times the weight of leather. Further information on the dyeing of leather is to be found in the references cited previously.[1,2,4–10,16]

C. Dye Properties, Classification, and Selection

Leather dyes are selected by the dyer on the bases of hue, application properties (solubility, levelness, penetration), fastness properties (light, water, perspiration, rubbing, solvents), and a tinctorial strength–cost factor. Compromises are usually required among these properties. For example, finding a dye of the proper hue is no problem, but finding one of proper hue having excellent application properties, desirable fastness properties, and low cost is indeed difficult.

Brown and black shades remain the most important leather colors representing about 85% of the total market. Brown is the traditional color, established when leather was mostly tanned with vegetable tannins, which strongly colored it in tan to brown shades.

Because dyeing is carried out at low temperatures, dyes must be soluble in the 40°–65° range. Stability to weak acids is also important because the dyes are applied at weakly acid pH (3.8–5.5).

Penetration into chrome leather is one important basis for classification of dyes. This information is helpful to the dyer, permitting him to select dyes that will produce maximum surface color coupled with adequate penetration. Since the pH of the dyebath partially controls the degree of penetration, values are determined at pH 5.0. Such values are assigned on a scale of 1 to 5 determined by visual comparison with dyes of known penetration dyed under standard conditions in the same bath at the same time. A 1 rating indicates surface dyeing, 3 is good penetration, and 5 is complete penetration. Desirability of either a 1 or 5 rating depends on the end use. In leather for footwear, only surface penetration of the dye is needed, since finish coatings that are usually pigmented are used. Dyes for garment leather, however, must penetrate uniformly and completely so that cut edges show the same color as the surface. Since lower pH causes surface dyeing, while higher pH (5.5) makes even nonpenetrating dyes penetrate, some control of penetration is possible within limits.

Outerwear requirements are also greater with regard to fastness to light, rubbing, water, and dry-cleaning solvents.

Dyes suitable for leather may be anionic or cationic in nature. These broad categories may be further subdivided. Anionic types include acid, metalized (1:1 and 1:2), mordant, direct, and developed dyes. Cationic types include the older basic and newer so-called modified basic or cationic dyes. In addition, azoic, reactive, oxidation, vat, sulfur, and miscellaneous other types have been employed. Anionic dyes, especially acid, direct, and metalized types, are by far the most important.

Nondried chrome-tanned leather (cationic in nature) has the highest affinity for anionic dyes; this affinity decreases if the leather is dried before dyeing. Direct dyes generally have the greatest affinity but do not penetrate. Lower-molecular-weight acid dyes have good affinity and penetrate best. In fact, newly tanned, nondried chrome leather is dyeable with almost all anionic dyes that are useful for natural and synthetic polyamide or cellulosic fibers.

If retanning has followed chrome tanning, as is usually the case, the cationic charge is decreased, especially if syntans are used, and basic dyes may then be used. However, generally poor fastness properties limit their use to special applications or to topping an anionic dyeing to intensify the color.

Basic dyes produce full shades on vegetable-tanned leather, combining with the tannins rather than with the leather itself. These lakes also are less fast to washing and to light than are dyeings produced with acid dyes. The acid dyes also give full bright shades on vegetable-tanned leather, while direct dyes produce only weak coloration.

Many special anionic leather dyes, largely azo, that build well on low-affinity leathers are now available. Milling acid dyes, 1:1 and 1:2 metal complexes containing such metals as Cr, Co, Ni, and Fe, and selected direct dyes are among these specialities. Also included is an intermediate type, between acid and direct, which dyes both wool and cotton but has excellent properties on leather.

Manufacturers have selected lines of dyes having compatibility with respect to properties of individual dyes within a line. These are marketed under such trade names as Airedale (YDC), Baygenal (FBy), Coranil (FH), Dermalight (S), Intrapel (CKC), Luganil (BASF), Naphthalene Leather (ICI), Polycor and Sella (CGY), and Solidermin (CFM).

In the discussion of dye chemistry that follows, the azo dyes are considered in order approximately according to the classification scheme adopted in *CSD I*, pp. 464–468, with expansion as required by the increased complexity of structure of the dyes described. Azo dye chemistry has been reviewed recently with emphasis on mono- and disazo dyes for wool, nylon, and cotton.[19] Recent practice in patent writing has been to claim the use of the new dye for as many substrates as possibly will be allowed. Thus, it is common to find nylon, wool, silk, leather, and paper claimed as substrates for the same dye. In the following discussion, therefore, only those new dye structures will be described that have been claimed to have primary or substantial use for dyeing leather. It must be understood, however, that many azo dyes with primary use on polyamides or cellulosics also are used for leather.

III. Anionic Dyes

A. MONOAZO DYES

1. *Nonmetallized Monoazo Dyes*

Of the well-known acid monoazo dyes, CI Acid Yellows 17, 23, 29, 36, 63, 65, 76; Oranges 7, 8, 10; Reds 1, 4, 7, 14, 18, 88; Violets 1, 3, 7, 12;

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[19] *CSD III*, pp. 249–301.

and Blue 92 are useful for dyeing leather. Leather[20] is said to be dyed bright yellow of excellent fastness to light, washing, solvents, and suede finishing by the dye (primuline sulfonic acid→m-$AcCH_2CONHC_6H_4$-SO_3H).[20a] Bordeaux dyes are prepared by coupling diazotized 4-nitroaniline, 2-chloroaniline, or orthanilic acid with N,N-diethylmetanilic acid.[21] A brown dye having high penetration is prepared by coupling diazotized sulfanilic acid with m-diethylaminophenol.[22]

Azo dyes imparting softness and pliability as well as brown color to the leather are obtained by coupling, e.g., diazotized sulfanilic acid with couplers prepared by condensation of brominated fatty acids with phenols, aromatic amines, or aminophenols such as m-aminophenol.[23] Tanning activity as well as color is found in dyes from diazotized napthionic acid, p-aminosalicyclic acid, or H acid coupled with phenol–formaldehyde condensates.[24] Dyeings having better fastness to perspiration are said to be produced on chrome-tanned leather if the dyes contain one or more phosphonic in place of sulfonic groups.[25]

Resorcinol is a favored intermediate for leather dye synthesis, allowing preparation of a multiplicity of configurations by virtue of its three reactive positions; two hydroxyl groups, which can chelate with metals or when free serve to confer solubility in water and hydrogen bond with the leather. It has also been converted to related multifunctional couplers by reaction with aldehydes. One example of this is reaction with aldol in the presence of formic acid. The products when coupled with diazotized anilines are light- and washfast dyes that may be applied concurrently with natural or synthetic tanning agents.[26] Variations on this theme utilize condensation products of mixtures of resorcinol and pyrocatechol with formaldehyde or of resorcinol and pyrogallol with benzaldehyde. Resorcinol, condensed with a dinitrochlorobenzenesulfonic acid, and the products coupled with a variety of diazotized mono- and diaminobenzene and naphthalene sulfonic acids, gives a series of mono- and disazo compounds that dye leather brown.[27]

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[20] The patent references cited need not necessarily be the first publications, and they do not indicate the legal patent position. Dates given parenthetically are of the original application if the country is given, or date of issue if not.

[20a] CN, *BP* 1,217,819 (France 25.1.1968).

[21] Derbenevsk Chemical Plant, *RP* 226,755 (USSR 31.5.1967).

[22] *RP* 161,685 (USSR 1.8.1962); *CA* **61**, 4521e (1964).

[23] M. I. Ganitkevich and N. A. Yaremchuk, *Izv. Vyssh. Uchebn. Zaved., Tekhnol. Legk. Promsti.* pp. 59–62 (1967); *CA* 68, 14054m (1968).

[24] *RP* 349,700 (USSR 13.7.1970); *CA* 78, 45039w (1973).

[25] FH, *BP* 868,142 (Germany 1.3.1957).

[26] FH, *DAS* 1,006,577 (18.4.1957).

[27] BASF, *DAS* 832,310 (21.2.1952).

2. *Metallized Monoazo Dyes*

Soluble chromium complexes of monoazo dyes, including the Neolan and Palatine series (1:1 complexes), have been described in *CSD I*, pp. 534–539. Neutral-dyeing metal complexes and metal complexes suitable for leather dyeing are discussed in the same chapter (pp. 540–544). Updating of the chemistry of metal-complex dyes has been accomplished by Price in *CSD III*, and more recently, Beffa and Steiner have reviewed developments in metal-containing dyes.[28] Several additional reviews on metal-complex dyes specifically related to leather dyeing have also appeared.[29–31]

The 1:1 Cr and Cu and the 1:2 Cr, Co, and Fe monoazo complexes have been and continue to be very important for the dyeing of leather. During the past twenty-five years, this area of dye chemistry has been quite thoroughly investigated. Most of the 1:2 Cr and Co complexes, sold under trade names such as Irgalan (CGY), Cibalan (CGY), Intralan (CKC), Ortolan (BASF), Amalon (AAP), Atalan (ATL), Calcofast (CCC), Isolan (FBy), Lanamid (NAC), Lanasyn (S), Nyalan (NAC), Capracyl (DuP), Dermalight (S), Remalan Fast (FH), Orcolan (ORC), and Supralan (GAF), have the potential for dyeing leather. Certain dyes of this class are presently used, such as CI Acid Yellows 114, 116, 119, 128, 129, 151; Oranges 60, 86, 87; Reds 211, 215, 251, 252, 314, 315, 316; Blues 168, 170, 171, 183, 184, 229; Green 73; Browns 19, 45; and Blacks 60, 63, 107; among many others.

Wachsmann[29] has stated that Irgalan Brown 2RL (CI Acid Brown 45) is absorbed at 60° as rapidly as a direct dye, and absorption is not decreased at 25° as occurs with direct dyes. The dyeings are fast to water and perspiration, but poor to washing, and have good fastness to light. These dyes have low degrees of penetration and dye level, making them useful for pastel shades.

The unsulfonated 1:2 Co and Cr complexes besides water solubility have considerable solubility in various organic solvents, especially alcohols, ketones, and esters, and are applicable to leather from such solutions by spraying or padding.[32]

The voluminous patent literature covering 1:2 complexes contains a small proportion of patents relating specifically to leather dyes. An even smaller number of patents relate to 1:1 complexes of monoazo

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[28] F. Beffa and E. Steiner, *Rev. Prog. Color. Relat. Top.* **4**, 60–63 (1973).

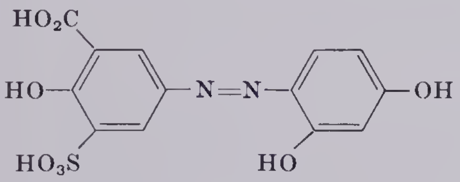
[29] H. Wachsmann, *Leder* **19**, 33–36 (1968); abstract in *J. Am. Leather Chem. Assoc.* **63**, 612 (1968).

[30] F. Grall, *Technicuir* **9**, 12–17 (1975); *CA* **83**, 12243h (1975).

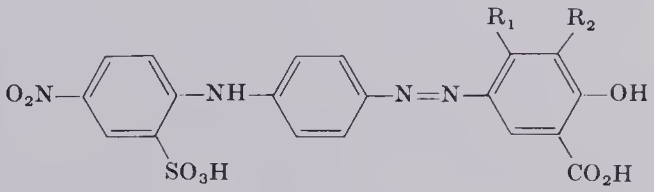
[31] G. Alexandrescu, *Ind. Usoara* **15**, 329–334 (1968); *CA* **70**, 12626s (1969).

[32] FBy, *DAS* 1,938,585 (Germany 30.7.1969); *BP* 1,267,486.

dyes. These include one covering a greenish yellow 1:1 Cr complex from 4-chloroaniline-3-sulfonic acid coupled with salicylic acid, and the brown-yellow 1:1 Cr complex of structure (I).[33] Chromium complexes of structure (II) dye leather yellowish brown.[34]



(I)



(II)

An important brown dye, CI Acid Brown 98, is covered by an expired United States patent assigned to American Cyanamid.[35] Coupling a diazotized *o*-aminonitrophenol at pH 3.6–6 with a phenylmethylpyrazolone and metallization with Fe, Cr, or other metals listed produces orange to brown dyes for leather.

The 1:2 iron complex of (III) is an olive green dye prepared by reacting diazotized 2-hydroxy-5-nitrometanilic acid with an alkyl ester of benzoylacetic acid and then with a phenylhydrazine followed by a ferric salt.[36] A similar structure in an earlier patent, curiously, is said to produce reddish orange shades on leather.[37] This is the Fe complex of the dye from diazotized 4-nitro-2-aminophenol and 1-(3-sulfophenyl)-3-methyl-5-pyrazolone.

A yellow dye, useful for dyeing leather, is formed by chroming the product of coupling diazotized (IV) with 1-phenyl-3-methyl-5-pyrazolone.[38] More complex pyrazolone coupling components are described wherein, e.g., 1-(*p*-aminophenyl)-3-methyl-5-pyrazolone is treated successively with diazotized 2-amino-6-nitrophenol-4-sulfonic acid, cyanuric chloride, aniline-2,5-disulfonic acid, dibutylamine, and copper sulfate to yield the reddish brown dye (V).[39]

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[33] FW, *FP* 1,499,060 (France 15.11.1966).

[34] FBy, *BP* 1,142,560 (Germany 8.12.1966).

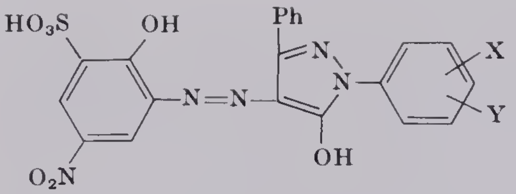
[35] CCC, *USP* 2,120,799 (1938).

[36] G, *USP* 3,423,393 (USA 17.3.1965); *BP* 1,136,715.

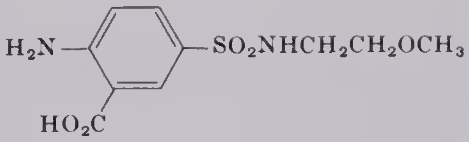
[37] BASF, *DBP* 843,275 (7.7.1952).

[38] S, *USP* 2,821,524 (1958); *SP* 322,624 (1957).

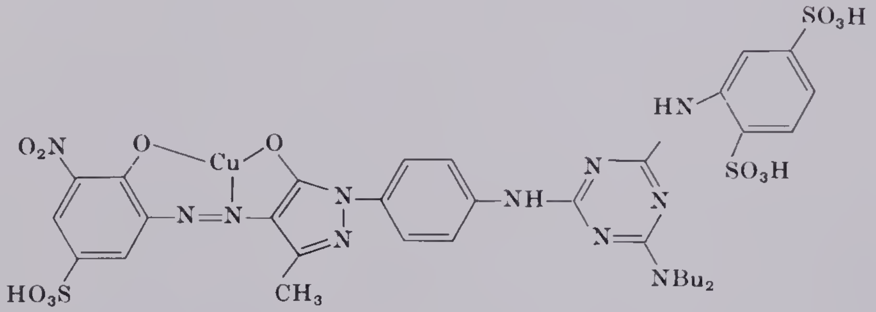
[39] CGY, *BP* 1,325,507 (Switzerland 3.9.1970); *DAS* 2,144,081; *SP* 564,582 (1975).



(III)

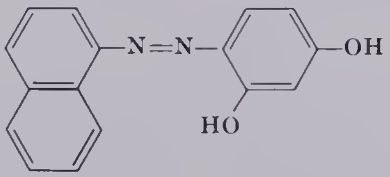


(IV)

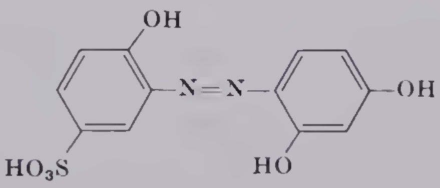


(V)

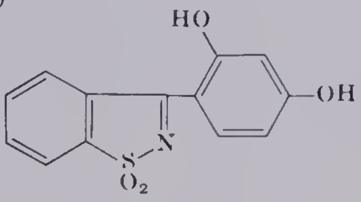
Derivatives of resorcinol have also been exploited as brown metallized dyes for leather having improved fastness to light. Atkinson and Plant have prepared Fe, Cu, and Ni complexes obtained by nitrosation and metallization of such arylazoresorcinols as (VI) and (VII).[40] Similarly, Kracker, Mohr, and Ribka describe Co, Cu, Cr, and Ni complexes, particularly Cr complexes of 4-sulfoanthranilic acid coupled with resorcinol,[41] and with 2,4-dihydroxybenzoic acid.[42] The same investigators synthesized a novel coupler (VIII) by condensation of 3-chloro-4,5-benzoisothiazole 1,1-dioxide with resorcinol in the presence of



(VI)



(VII)



(VIII)

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[40] ICI, *BP* 668,474.

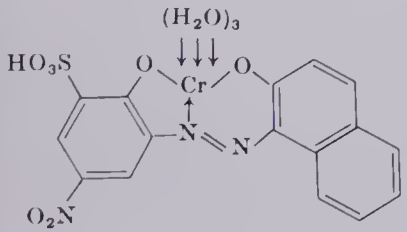
[41] FH, *DBP* 1,049,022 (1959); *BP* 875,990 (Germany 26.1.1957).

[42] FH, *DBP* 1,058,660 (1959).

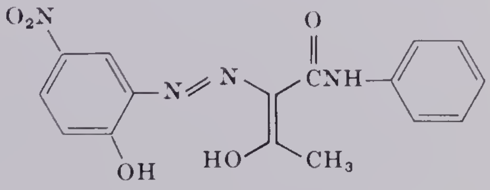
$AlCl_3$, $FeCl_3$, or H_2SO_4.[43] (VIII) was then coupled with diazotized 2-amino-6-nitrophenol-4-sulfonic acid and chromed to produce a bluish-red-brown dye for leather. The Cr complex of 6-nitro-1-diazo-2-naphthol-4-sulfonic acid → VIII was brownish bordeaux, and the dye from diazotized 2-amino-6-carboxyphenol-4-sulfonic acid was red-brown when chelated with either Co or Cr.

While unsulfonated 1:2 complexes have found extensive use on leather, sulfonic-group-containing dye complexes have not been neglected. Examples are found of symmetrical structures containing two or four sulfonic acid groups and of unsymmetrical complexes containing largely one or two sulfonic groups.

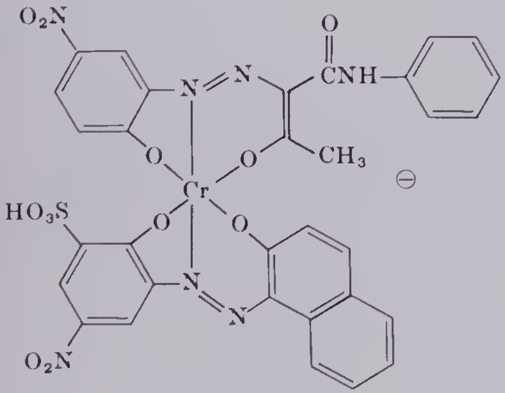
The Cr complex formed by treating the dye (picramic acid → S-acid) with ammonium chromium salicylate dyes leather green and is symmetrical, having two sulfonic groups.[44] CI Acid Black 52 belongs, at least in part, to this class and is still a very important, excellent dye for leather. It has a penetration rating of 1, is low cost, and is level dyeing. Chrome-tanned leather is dyed level, well-penetrated, neutral and reddish gray shades by the Cr and Co complexes, respectively, prepared



(IX)



(X)



(XI)

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[43] FH, *DBP* 1,002,488 (1957).

[44] FW, *EGP* 25,052 (1963).

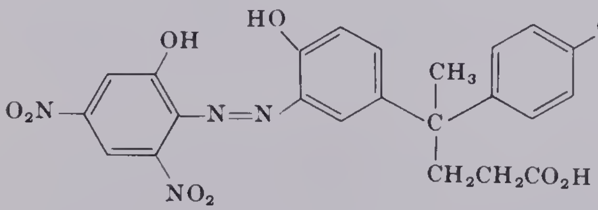
from the dye (6-nitro-1-diazo-2-naphthol-4-sulfonic acid → γ-acid).[45] This complex contains four SO_3H groups.

Ciba chemists have developed unsymmetrical Cr dye complexes containing only one sulfonic group[46,47] and processes for their application.[48] These are prepared by combining an initial 1:1 Cr complex of a monoazo dye containing an SO_3H group such as (IX) with an unsulfonated monoazo dye such as (X) to produce, in this case, a yellowish brown dye having primarily the structure (XI).

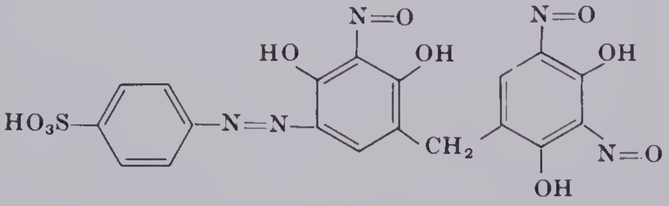
Finally, unsymmetrical Cr complexes containing a sulfonic group in each of the monoazo precursors are disclosed.[49] Thus, a gray leather dye is formed by heating the 1:1 Cr complex (IX) at pH 5.5 with the monoazo compound (4-nitro-2-aminophenol → N-tosyl-γ-acid).

One of the components of such complexes may be disazo in which one of the azo bonds has no adjacent metallizable groups. Sandoz has claimed 1:2 Cr complexes that are olive dyes for leather and are formed from mixtures of 3′-amino-4′-hydroxy-1,1′-azobenzene-3-sulfonamide → 1-(2-ethoxyethoxycarbonylamino-7-hydroxynaphthalene and 2-amino-1-hydroxy-4-nitro-6-acetylaminobenzene → the same coupler. These dyes are very soluble in polar organic solvents.[50]

Recently, a number of investigators have used polyfunctional phenolic couplers. Wicki has claimed a dark brown Co complex derived from the compound (XII),[51] while Sailer and Frank have patented dyes utilizing polyhydroxy-substituted diphenylmethane, benzhydrol, or dibenzylamine and their oxidized, nitrosated, metallized, and/or amine



(XII)



(XIII)

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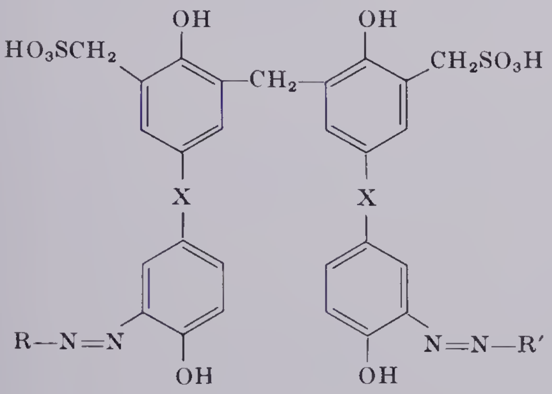
[45] J. Jarkovsky, Z. J. Allan, and V. Heller, *CzechP* 106,787 (1963).
[46] CIBA, *BP* 1,001,840 (1965).
[47] CGY, *BP* 1,248,484 (Switzerland 14.5.1968); *DAS* 1,922,900 (1969).
[48] CIBA, *BP* 1,006,894 (1965).
[49] Gy, *BP* 1,139,149 (Switzerland 22.11.1965); *FP* 1,501,380 (1967).
[50] S, *BP* 1,143,643 (Switzerland 23.7.1965).
[51] S, *SP* 492,761 (1970).

salt derivatives.[52] For example, the nitrosoazo dye (XIII) was prepared by coupling 2,2′,4,4′-tetrahydroxydiphenylmethane with diazotized sulfanilic acid and nitrosating at 10°. Reaction of the nitrosoazo dye with $FeCl_3$ at pH 5.5 gave the iron complex that dyed leather brown-yellow shades changing to green.

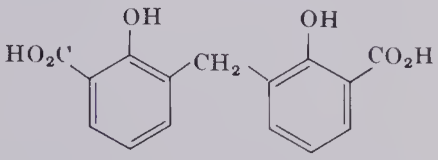
B. Disazo Dyes

1. *Disazo Dyes* (A → Z ← A)

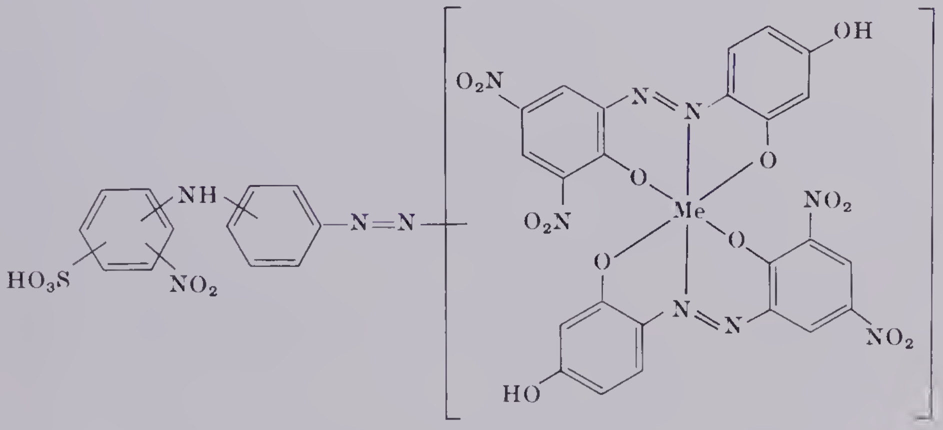
As would be expected, the use of polyfunctional phenolic couplers described above has been extended to dis- and polyazo dyes. Sailer and Frank claim polyazo dyes similar to (XIII) wherein two (or more) equivalents of diazotized sulfanilic acid are coupled prior to nitrosation, oxidation, or metallization.[53] They also use dimers prepared by



(XIV)



(XV)



(XVI)

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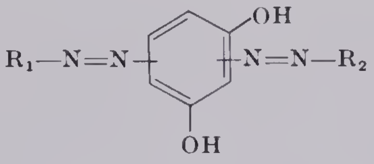
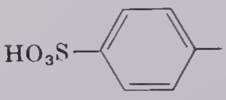
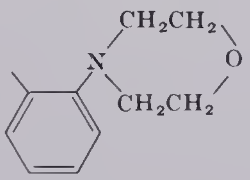
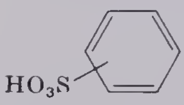
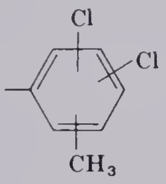
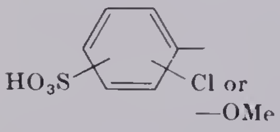
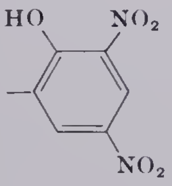
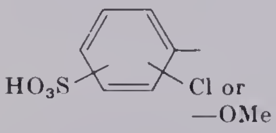
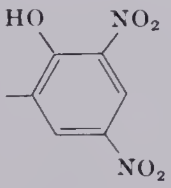
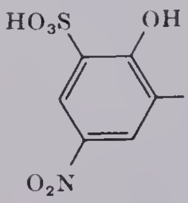
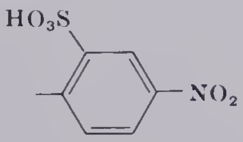
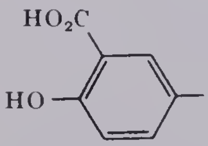
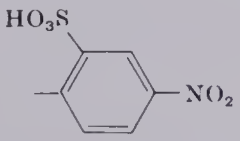
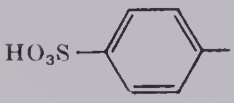
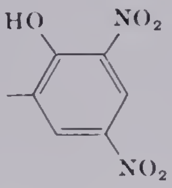
[52] CN, *DAS* 2,149,513 (1972); *BP* 1,375,369 (France 5.10.1970).

[53] CN, *BP* 1,383,437 (France 26.1.1971).

TABLE I

DISAZO COUPLINGS WITH RESORCINOL



R_1	R_2	Metal	Hue on leather	Reference
		—	Reddish brown	56*a*
		—	Yellow-brown to Reddish brown	57
		Cr	Dark brown	58–60
		Fe	Yellow-brown	61,62
		Fe Cu	Olive-brown Brown	63 63
		Cr	Yellowish brown	64
		Cr	Dark brown	65

sulfomethylation of condensation products of bisphenols such as 4,4′-dihydroxydiphenylsulfone or 4,4′-dihydroxydiphenylpropane with formaldehyde.[54] Structures such as (XIV), in which X is $—SO_2—$ or $—C(CH_3)_2—$ and R and R′ are the same or different substituted phenyl, naphthyl, diphenyl, or phenylazophenyl radicals, when metallized with Fe, Cu, Cr, Co, or Ni, are said to dye leather yellowish beige to blue shades that are fast to washing, solvents, and light.

Wicki has also extended his work to disazo couplings with polyfunctional phenols, particularly of diazonium salts from metanilic acid, picramic acid, and/or 4-amino-4′-nitrodiphenylamine-2′-sulfonic acid with (XV), to give yellow-brown dyes.[54a] He also claims improved exhaustion on leathers of low affinity for the 1:2 metal complexes (XVI) based on resorcinol, picramic acid, and, preferably, aminonitrodiphenylaminesulfonic acid.[55]

Bauman has claimed a series of disazo and polyazo resorcinol dyes that are made by dimerizing with aldehydes in acid medium.[56] They are said to dye chromed calfskin much more strongly than before dimerization. For example, metanilic acid → resorcinol is dissolved in dilute HCl and treated with 40% CH_2O to give a yellowish brown dye. Other couplers listed give reddish browns. Some of the dyes are metallized with Cu, Fe, or Co and may also be oxidized with H_2O_2.

A number of patents have been issued claiming disazo couplings with resorcinol, some of which are also metallized. These are listed in Table I and, of course, are essentially variants of well-known resorcinol browns such as CI Acid Browns 14 and 24.[56a–65]

The dye (2-amino-5-nitrophenol-4-sulfonic acid → di-J-acid), treated with copper sulfate, dyed leather fast violet shades.[66] Similarly, the coppered dye (1-amino-2-naphthol-4-sulfonic acid → di-J-acid) gave fast navy blue shades on leather.

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[54] CN, *USP* 3,891,617; *BP* 1,360,368 (France 26.1.1972).

[54a] S, *BP* 1,257,581 (Switzerland 19.2.1969); *DAS* 2,006,170 (1970).

[55] S, *USP* 3,787,387 (Switzerland 7.8.1969); *BP* 1,313,382; *DAS* 2,038,473 (1971).

[56] BASF, *BP* 1,053,928 (Germany 13.11.1962); *FP* 1,374,163 (1964).

[56a] ICI, *BP* 687,300.

[57] FH, *DBP* 1,117,239 (1961).

[58] FW, *BP* 932,024 (1963).

[59] FW, *FP* 1,308,768 (1962).

[60] FW, *EGP* 33,019 (1965).

[61] FW, *FP* 1,384,423 (1965).

[62] FW, *BP* 1,051,219 (1964); *EGP* 44,754 (1966).

[63] BASF, *BP* 1,073,839 (Germany 12.6.1965) (1967).

[64] S, *DAS* 2,040,505 (1971).

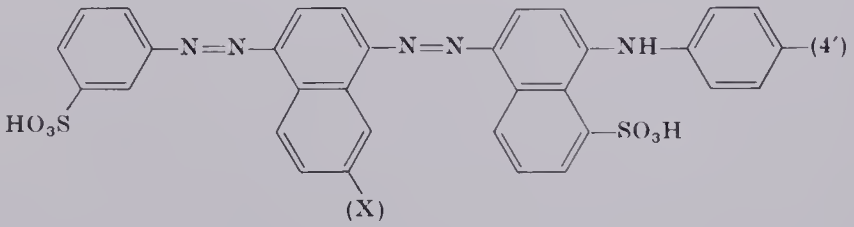
[65] BASF, *DAS* 1,935,005 (1971).

[66] BASF, *DAS* 2,311,396 (1974).

2. *Disazo Dyes* (A → M → E)

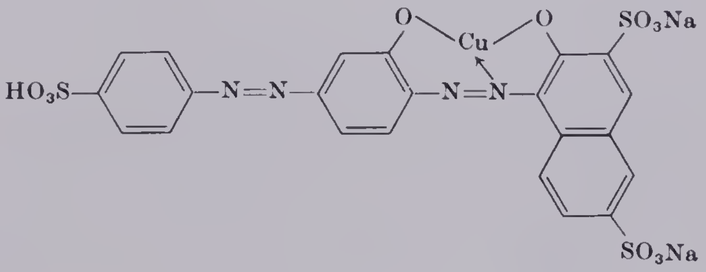
Dyes having bright red hue are included in this class. Among the older examples are CI Acid Reds, 66, 73, 115, 151 and CI Direct Reds 16 and 81. Armbrecht and Sommer have recently disclosed that the dye (sulfanilic acid → *m*-toluidine → J-acid) imparts fast claret shades to box calf- and sheepskin.[67]

Navy blue dyes of this class continue to have some importance, e.g., CI Acid Blue 113 and Direct Blue 67. Nursten has compared the three milling acid navy dyes of similar structure, CI Acid Blues 113, 118, and 120.[2] He states that adding a 4′-methyl group to *N*-phenyl peri acid, thus changing Blue 113 (XVII) to 120, has little effect on penetration; however, moving the sulfonic group from the terminal phenyl to the X position on the naphthalene nucleus and adding the methyl group to make Blue 118 drastically reduces solubility, yet increases penetration slightly. Dyes such as these, however, have generally poor washfastness on chrome leather.



(XVII)

Pfitzner and Baumann have claimed violet to blue dyes having the structure (XVIII) and similar complexes by oxidative coppering of red disazo dyes produced from (4-aminoazobenzene → R-salt) and related dyes.[68]



(XVIII)

3. *Disazo Dyes* (E ← D → E)

Dyes of this class vary in hue from yellow through blue. There has been awakened interest in research directed to substitutes for important

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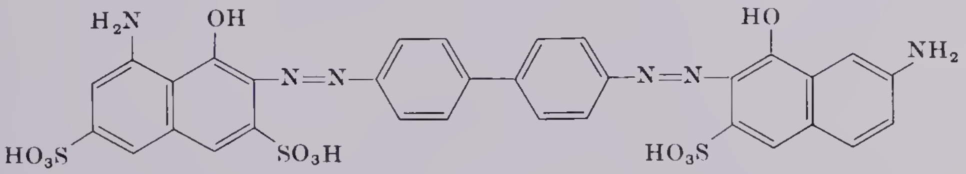
[67] FH, *BP* 1,349,098 (Germany 30.11.1970); *DAS* 2,058,816 (1972).

[68] BASF, *DBP* 930,770 (1955).

dyes of this class derived from benzidine, a known carcinogen. Manufacture of this intermediate has been under strict governmental regulations in recent years, resulting in withdrawal of most firms from production and sale of leather dyes requiring its use. Because many popular leather dyes, especially low-cost blacks, are no longer available, or are in short supply, a search has been in progress for suitable alternatives.

One important base for blacks has been CI Direct Blue 2 (XIX), which develops on the fiber by diazotization and coupling with *m*-toluylenediamine and then has good fastness properties. Although analogous dyes using tolidine or dianisidine in place of benzidine have been placed on the market, they have not succeeded in filling the gap. More complex structures, to be discussed later, may be adequate replacements.



(XIX)

Other substitute colors, however, have been developed by use of 4,4′-diaminobenzanilide. Successive coupling with salicylic acid and then naphthionic acid gives a light- and washfast orange dye for leather[69]; coupling with a pyrazolone or naphthalene derivative followed by a phenol and then condensing with a benzenesulfonyl chloride yields yellow to violet dyes having good fastness to light and washing.[70] Diaminobenzene-sulfanilides are similarly useful bases.[71]

Diamines of the benzene series also have been used.[72] Tetrazotized 2,6-diaminochlorobenzene-4-sulfonic acid, coupled first with γ-acid under strongly acid conditions, and then with a second component such as 2-naphthol, gives a bluish red leather dye. Similarly, tetrazotized 2,4-diaminochlorobenzene-6-sulfonic acid coupled with two equivalents of R-salt gives a bordeaux disazo dye.[73]

The disazo dye obtained by coupling tetrazotized 4,4′-diamino-2,2′-dimethyldiphenylmethane with one equivalent each of R-salt and Schaeffer's salt, unlike the corresponding symmetrical dyes, has very good solubility in water and dyes leather a brilliant brick red, full-

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[69] CN, *DAS* 2,362,994 (1974).

[70] CN, *BeP* 809,883 (France 18.1.73) (1974).

[71] CN, *BeP* 823,537 (France 19.12.73) (1974).

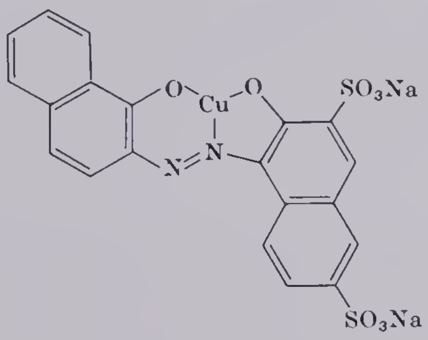
[72] BASF, *BP* 697,709.

[73] BASF, *BeP* 797,446 (Germany 29.3.72) (1973); *DAS* 2,215,238 (1973).

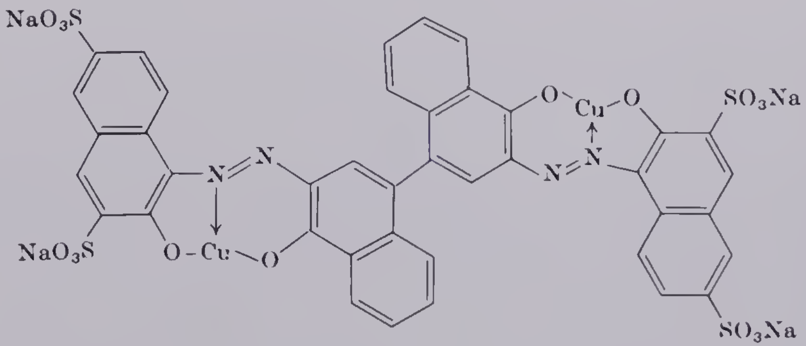
surface color.[74] Other diamines have been used, including 4,4′-dichloro-2,2′-diaminodiphenyl sulfide, sulfoxide, sulfone, 4,4′-diaminodiphenyl sulfone,[75] and 4,4′-diaminodiphenylmethane 3,3′-dicarboxylic acid.[76]

Blue direct dyes for cellulose and leather in which *o*-dianisidine is the diazonium component have been described.[77–79]

A unique method for dimerizing coppered monoazo naphthalene derivatives in aqueous solution with H_2O_2 at pH 5.5 and 60° is claimed by BASF.[80] Thus, (XX) is converted to (XXI), a bluish violet on chrome leather.



(XX)



(XXI)

A red disazo dye is obtained by phosgenation of the monoazo chrome complex derived by coupling 6-nitro-1-diazo-2-naphthol-4-sulfonic acid with 1-(4-aminophenyl)-3-methyl-5-pyrazolone and metallizing with ammonium chromium salicylate.[81]

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[74] BASF, *USP* 2,791,580; *BP* 751,996.

[75] CIBA, *SP* 309,566 (1955); 311,495 (1956); 311,497; 311,498; 311,499.

[76] BASF, *BP* 753,771 (1956).

[77] CFM, *DBP* 1,081,990 (1960).

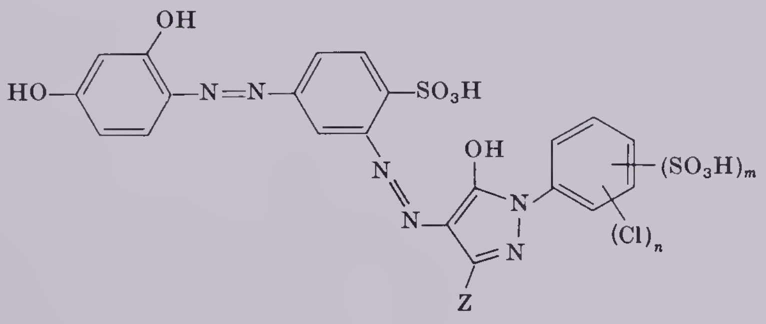
[78] FBy, *BP* 1,368,563 (Germany 5.11.1971).

[79] FBy, *BP* 1,342,858 (Germany 14.8.1971); *DAS* 2,140,864 (1973).

[80] BASF, *BP* 1,327,965 (Germany 14.1.1970).

[81] FW, *EGP* 22,183 (1961).

A novel series of yellow to brown disazo dyes has been prepared by oxidation of dyes having the generic structure (XXII).[82,83] The parent disazo dyes are prepared by coupling diazotized 4-acetamino-2-aminobenzenesulfonic acid with a pyrazolone, deacetylation, diazotization, and coupling with resorcinol. Analogous structures were made, without the sulfonic acid group on the center benzene ring, by coupling *m*- or *p*-nitroaniline with a pyrazolone, reducing the nitro group, diazotizing, and coupling with resorcinol[84,85] In (XXII), use of acetoacetanilide, G-salt, salicylic acid, or the Cu complex of (2-amino-phenol-4-sulfonic acid → resorcinol) without oxidation gives additional yellow, orange, and reddish brown leather dyes.[86,87]



(XXII)

C. TRISAZO DYES

1. *Trisazo Dyes* $\left(\begin{matrix} A^1 \rightarrow T \leftarrow A^2 \\ \uparrow \\ A^3 \end{matrix}\right)$

Dyes for leather having this generic structure are all browns based on resorcinol or polyhydric phenol couplers. Soviet investigators have presumably overcome the difficulty in achieving high yields of trisazo dye by carrying out the couplings of diazotized naphthionic acid (three equivalents) with resorcinol at 35°–60°.[88] Intermediates that are favorite components for use with resorcinol are H-acid, aminonitrodiphenylaminesulfonic acids, *p*-nitroaniline, naphthionic acid, Cleve's acids, and sulfanilic acid. H-acid is frequently diazotized and coupled

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[82] CN, *USP*, 3,840,514 (1972).

[83] CN, *DAS* 1,927,211 (France 30.5.1968) (1970).

[84] Fran, *BP* 1,267,937 (France 30.5.1968); *DAS* 1,927,212 (1969).

[85] CN, *BP* 1,220,304 (France 30.5.1968); *DAS* 1,927,596 (1969).

[86] CN, *FP* Addn. 95,352 (1970) (Addn. to *FP* 1,480,372).

[87] CN, *BP* 1,180,781 (France 31.3.1966); *FP* 1,480,372 (1967).

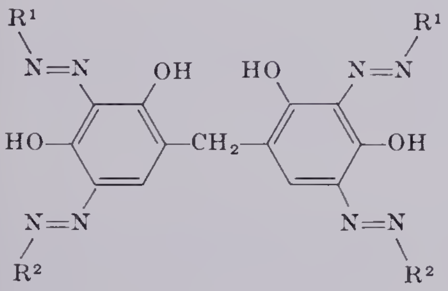
[88] L. B. Gurvich and I. N. Alatyrtseva, *RP* 157,959 (1963).

TABLE 11

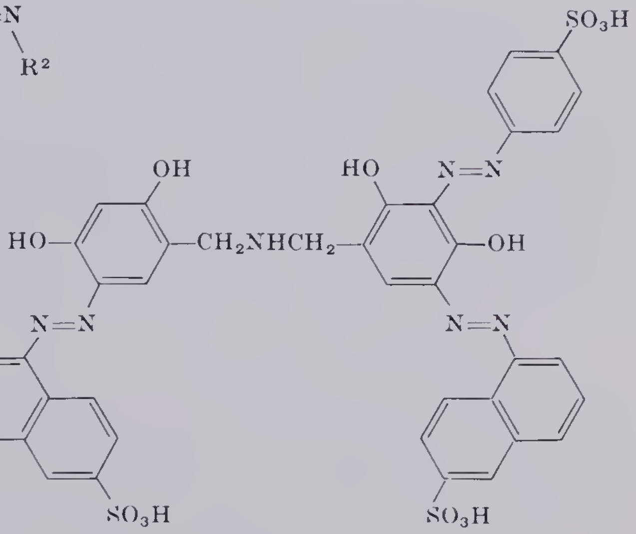
Trisazo Couplings with Resorcinol

First diazo component	*Second diazo component*	*Third diazo component*	*Metal*	*Color*	*Reference*
H-acid	4-Amino-2′,4′-dinitro-6-carboxydiphenylamine	4-Amino-2′,4′-dinitro-6′-carboxydiphenylamine	—	Yellow-brown	89
H-acid	4-Amino-4′-nitro-2′-sulfamidodiphenylamine	*p*-Nitroaniline	—	Olive	89
H-acid	Naphthionic acid	4-Amino-2′,6′-dinitrodiphenylamine	—	Dark brown	89
H-acid	4-Amino-4′-nitro-2′-sulfodiphenylamine	*p*-Nitroaniline	—	Dark brown	90
1-Amino-6-nitro-2-naphthol-4-sulfonic acid	4-Amino-2-sulfodiphenylamine	*p*-Nitroaniline	Cu, Fe, Cr, Co, Ni	Dark brown	91
Picramic acid	4-Amino-4′-nitro-2′-sulfodiphenylamine	*p*-Nitroaniline	Fe	Dark yellow-brown	92
Picramic acid	4-Amino-2-sulfodiphenylamine	*p*-Nitroaniline	Fe	Dark brown	93
Dehydrothiotoluidinesulfonic acid	H-acid	*p*-Nitroaniline	—	Yellow-brown	94
2-Amino-6-nitrophenol-4-sulfonic acid	Picramic acid	4-Amino-4′-nitro-2′-sulfodiphenylamine	Fe	Yellow-brown	95
H-acid	4-Aminodiphenylamine	*p*-Nitroaniline		Red-brown	96

first in the 4 position, followed by more energetic diazonium salts. It is likely that at least a portion of the third diazo component couples ortho to the —OH of the H-acid. Some combinations that have been patented are listed in Table II.[89–96]



(XXIII)



(XXIV)

Polyazoresorcinol dyes (XXIII) can be prepared by either coupling first and reacting the monoazo dye with formaldehyde or by coupling with a resorcinol–formaldehyde condensate.[97] For example, sulfanilic acid was diazotized and coupled with resorcinol, the product treated with 40% CH_2O in acid solution, and then coupled with diazotized 2-chloro-4-nitroaniline; the dye gave yellowish brown shades on leather.

Polyhydroxy compounds, some of which have been described above as coupling components of mono- and disazo dyes, are also employed

[89] S, *BP* 1,037,012 (Switzerland 28.2.1962); *FP* 1.348.925 (1964).

[90] S, *BP* 1,306,836 (Switzerland 9.7.1969); *DAS* 2,033.602 (1971).

[91] S, *BeP* 827.700 (Switzerland 10.4.1974) (1975); *DAS* 2,514.008 (1975).

[92] S, *BP* 1.306,527 (Switzerland 23.5.1969); *DAS* 2,024,047 (1970).

[93] S, *BP* 1,099.641 (Switzerland 22.4.1964); *BeP* 661,888 (1965).

[94] S. *BP* 1,023.376 (Switzerland 16.10.1961); *USP* 3.179.650 (1965).

[95] FBy, *BP* 1,365,798 (Germany 16.12.1971); *DAS* 2,162,419 (1971).

[96] FH, *BP* 779,486.

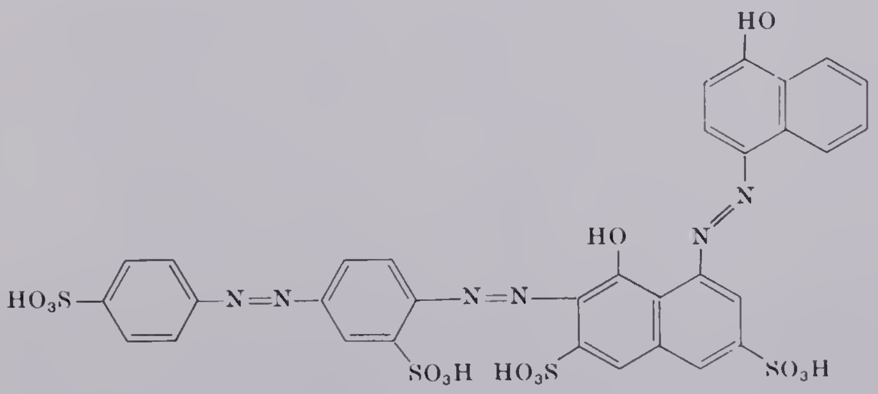
[97] S, *SP* 469,064 (Switzerland 15.10.1965) (1969); *FP* 1,503,833 (1967).

in trisazo structures. 3,3′-Dihydroxydiphenylamine coupled successively with diazotized H-acid, sulfanilic acid, and 2-chloro-4-nitroaniline to give a dark red-brown dye.[98] A yellowish brown is formed by coupling diazotized 4-amino-4′-nitrodiphenylamine-2′-sulfonic acid and two equivalents of aniline with the same coupler.[99]

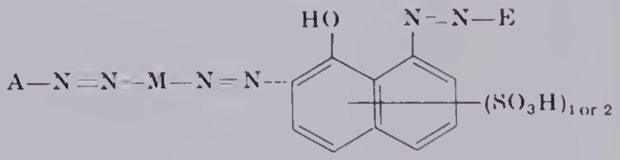
The dye of structure (XXIV) is claimed in recent patents to dye leather of various tannages in brown shades.[100] Dyes formed by use of other diazonium salts are also claimed generically.

2. *Trisazo Dyes* (A → M¹ → M² → E)

Compounds resulting from coupling diazotized aminoazobenzenes with 1-amino-8-naphthol-3,6-disulfonic acid in alkaline medium, diazotizing the product, and coupling with naphthols dye leather and furs fast green or black shades.[101] A typical structure is the green dye (XXV). Similar dyes claimed for leather (and cotton) are of the generic structure (XXVI), wherein A is a phenyl or naphthyl derivative, M is a naphthylene, and E is an acetoacetarylide.[102]



(XXV)



(XXVI)

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[98] FH, *BP* 779,487.

[99] FH, *BP* 868,856 (Germany 28.11.1956); *USP* 2,897,188 (1959).

[100] CN, *USP* 3,915,952 (France 26.1.1971); *DAS* 2,203,614 (1972).

[101] FH, *DAS* 2,362,881 (1975).

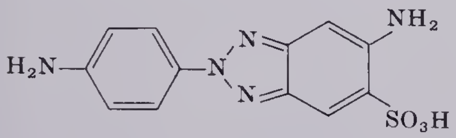
[102] FBy, *BeP* 797,322 (Germany 28.3.1972) (1973).

3. *Trisazo Dyes* (E′ ← D → M → E^2)

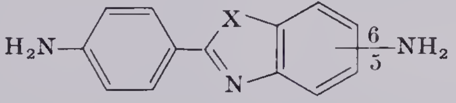
Dyes of this class and subsequent tris- and polyazo classes have potential as replacements for benzidine-based products. Successive coupling of tetrazotized 4,4′-diaminobenzanilide with salicylic acid and Cleve's 1,6 (or 1,7) acid, followed by diazotization and coupling with γ-acid gives a khaki-green dye for leather.[103]

4,4′-Diaminobenzenesulfanilide has been used for the preparation of yellow, blue, green, brown, and black dyes that have excellent penetration and fastness to light, washing, dry cleaning, acids, perspiration, and rubbing.[104] The tetrazotized diamine is coupled first with salicylic acid or a pyrazolone, then with Cleve's acid; the aminodisazo compound is diazotized and coupled with phenol or a pyrazolone to give, e.g., golden yellow dyes.

Heterocyclic diamines have also been claimed, such as (XXVII)[105] and (XXVIII),[106] as central components of trisazo dyes.



(XXVII)



X = —NR—, —S—, —O—
R = —H, —1—4C alkyl,
phenyl or benzyl, when X = NR.

(XXVIII)

4. *Trisazo Dyes* (A → Z ← D → E)

One of the most important black dyes for leather is CI Direct Black 38 (XXIX), commonly known as Direct Black E. It is cheap, applicable to chrome- and chrome–vegetable-tanned leathers, but has insufficient penetration on suedes, is not exceptionally fast to wet treatments, and turns browner in the presence of acids. Over the years, many attempts have been made to improve these properties by making structural variations. A number of these are shown in Table III[107–124] together with some related blue and green dyes.

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[103] CN, *DAS* 2,362,996 (1974).

[104] CN, *BeP* 824,623 (France 22.1.1974) (1975); *DAS* 2,501,827 (1975); *BeP* 824,624 (1975); *DAS* 2,500,426 (1975).

[105] CGY, *DAS* 2,329,126 (Switzerland 9.6.1972) (1973).

[106] CFM, *BeP* 829,209 (Germany 20.5.1974) (1975).

[107] CFM, *BP* 774,612.

[108] Fran, *FP* 1,011,992 (1952).

[109] Gy, *BP* 1,098,126 (Switzerland 5.3.1965).

[110] YDC, *BP* 854,957 (1958).

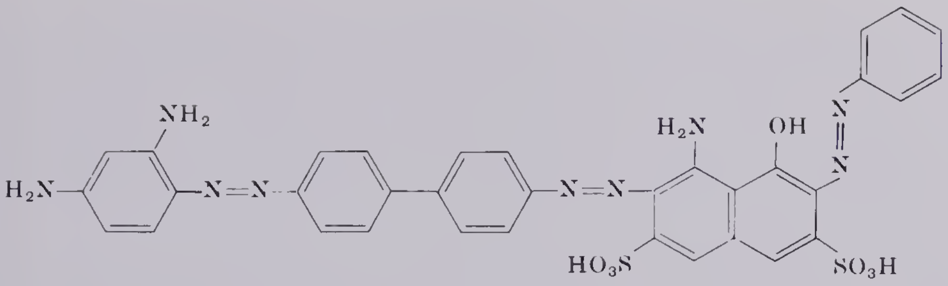
[111] CFM, *DBP* 1,019,417 (1957).

TABLE III

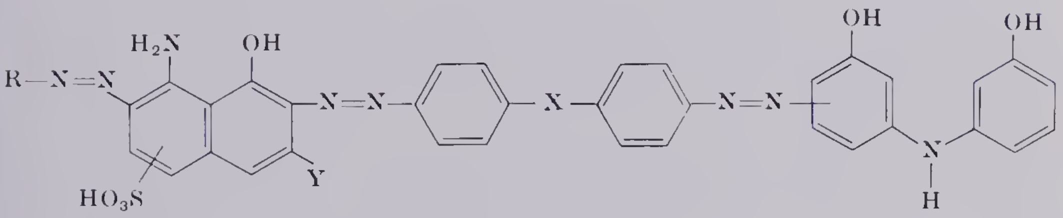
Benzidine Dyes Related Structurally to CI Direct Black 38

$$\text{E} \xleftarrow{(3)} \text{Benzidine} \xrightarrow[\text{acid}]{(1)} \text{H-acid} \xleftarrow[\text{alk.}]{(2)} \text{A}$$

Diazo component A	*Coupler E*	*Color on leather*	*Reference*
Aniline	2,8-Dihydroxy-napthalene-6-sulfonic acid	Reddish blue	107
Sulfanilic acid	1-Amino-8-naphthol-4-sulfonic acid	Blue	108
Aniline-2,5-disulfonic acid	Resorcinol + *m*-aminophenol	Black	109
Aniline	2,4-Diaminotoluene-5-sulfonic acid	Black	110
4-Methoxyaniline-3-sulfonic acid	*m*-Aminophenol	Bluish black	111
2-Aminotoluene-5-sulfonic acid	*m*-Aminophenol	Bluish black	112
p-Aminobenzoic acid	*m*-Phenylenediamine	Black	113
Aniline	*o*-Phenylenediamine	Bluish black	114
Aniline	*m*-Aminophenol	Black	115
Sulfanilic acid	*m*-Phenylenediamine-4-sulfonic acid	Greenish black	116
Aniline	*m*-Aminophenol	Black	117
Metanilamide	*m*-Aminophenol	Reddish black	118
2-Methoxyaniline-5-sulfonic acid	Acetoacetanilide-4-sulfonic acid	Yellowish green	119
Sulfanilic acid	R-acid	Reddish navy blue	120
Aniline	2′-Hydroxyphenylglycine	Black	121
Aniline	*m*-Phenylenediamine	Black	122
Metanilic acid	*m*-Aminophenol	Black	123
Sulfanilic acid	3-*o*-Toluidinophenol	Bluish black	124



CI Direct Black 38
(XXIX)



(XXX)

R = Ar (benzene or naphthalene series).
X = direct link. —CH=CH—, —NHCONH—, —CO—, —O—, —S—, —NH—, —CONH—.
Y = —H, —SO_3H

FH have patented closely related structures (XXX) in which the pH and order of the first two couplings is reversed and in which diamines other than benzidine are used.[125,126] These dyes are violet, blue, green, or black, depending on the particular components chosen.

More recently, recognition of health hazards associated with the use of benzidine has revived interest in finding blacks to replace the

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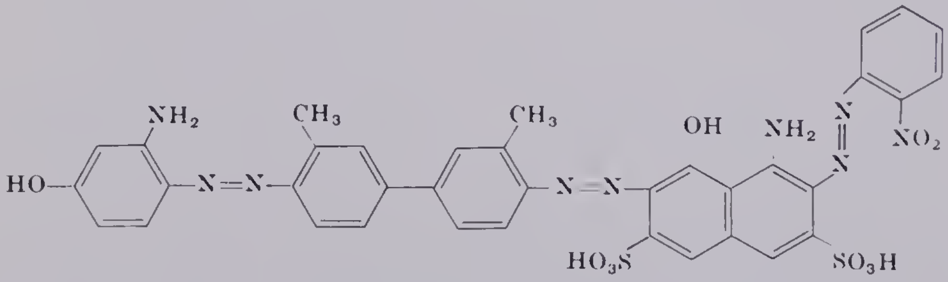
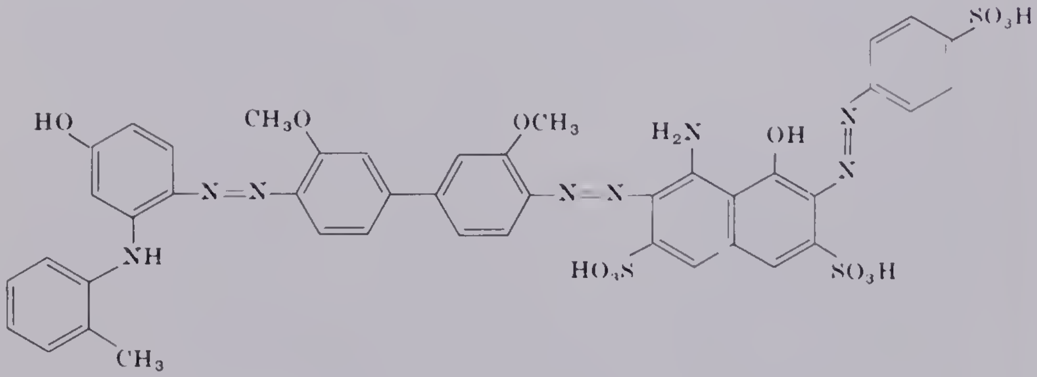
[112] CFM, *BP* 798,545 (1958).
[113] CFM, *BP* 796,790 (1958).
[114] CFM, *BP* 773,913 (1957).
[115] CFM, *BP* 765,087.
[116] CIBA, *BP* 704,043.
[117] CFM, *DBP* 1,031,273 (1958).
[118] CFM, *BP* 820,199 (1959).
[119] FH, *BP* 858,556 (Germany 21.12.1956); *DBP* 1,044,318 (1958).
[120] CIBA, *BP* 706,157.
[121] CFM, *FP* 1,428,309 (1966).
[122] T. Tanaka (Nippon Chemical Works Co. Ltd.), *JP* 74,117,780 (1974).
[123] G. Alexandrescu, *Ind. Usoara* **14**, 394–396 (1967); *CA* **68**, 14112d (1968).
[124] FBy, *BP* 1,064,924 (Germany 16.3.1965) (1967).
[125] FH, *USP*. 2,871,230; *BP* 795,232.
[126] ICI, *BP* 685,078.

economical Direct Black 38, and a large number of structural variations using other diamines in place of benzidine have been patented. Among the diamines used are phenylenediamines, *o*-tolidine, *o*-dianisidine, benzidine-2,2′-disulfonic acid, 4,4′-diaminostilbene-2,2′-disulfonic acid, 4,4′-diaminodiphenylaminesulfonic acid, 4,4′-diaminodiphenyl sulfides, 4,4′-diaminobenzanilide, and XXVIII.

The phenylenediamine central structure is generated by use of 4-nitroaniline: diazotization, coupling at low pH with H-acid, coupling of diazotized aniline, sulfanilic acid, or other amine of the benzene or naphthalene series at alkaline pH, reduction with Na_2S, diazotization, and coupling with *m*-aminophenol,[126,127] Schaeffer, R- or G- acid.[128] An alternative method for generating the phenylenediamine structures is use of monoacylated phenylenediamines or their sulfonic acids, in which case an hydrolysis is used after the second coupling instead of the reduction.[129,130]



(XXXI)



(XXXII)

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[127] S, *BeP* 805,235 (Switzerland 26.9.1972) (1973); *DAS* 2,347,551 (1974).

[128] FH, *DAS* 2,305,616 (1973).

[129] S, *BeP* 830,284 (1975).

[130] FH, *BeP* 810,677 (1974).

Modifications of the CI Direct Black 38 structure have been patented, using *o*-tolidine in place of benzidine and other minor substitutions[131]; the greenish black dye (XXXI) is claimed.[132] *o*-Dianisidine in a similar combination is used to make a trisazo black dye for leather (XXXII).[133] Analogous structures have been disclosed in which a mixture of dyes is prepared according to the scheme[134]:

$$m\text{-Phenylenediamine} \xleftarrow{(3)} \text{dianisidine} \xrightarrow{(1)} \text{H-acid} \xleftarrow{(2)} \text{aniline}$$

Green trisazo dyes containing dianisidine are also claimed.[135]

Black dyes for chromed velour split leather are prepared by coupling tetrazotized benzidine-2,2′-disulfonic acid with H-acid, adding *m*-phenylenediamine, and coupling the disazo dye with diazotized aniline.[136] Benzidine-2,2′-disulfonic acid has also been used to make a dark green leather dye by coupling first with H-acid at low pH, coupling diazotized 4-nitroaniline with the azo–diazonium compound, and finally coupling with *m*-aminophenol.[137] Still another green dye is claimed wherein *p*-nitroaniline is coupled first with H-acid and then the azo–diazonium

TABLE IV

SOME NONBENZIDINE BLACK TRISAZO DYES

$$\text{A} \xrightarrow[\text{(alk.)}]{(2)} \text{H-acid} \xleftarrow[\text{(acid)}]{(1)} \text{D} \xrightarrow{(3)} \text{E}$$

Diazo component A	*D*	*Coupler E*	*Color*	*Ref.*
Aniline	XXXIII	*m*-Phenylenediamine (then tosylation)	Black	141
Aniline	XXXIII	Resorcinol	Green-black	142
o-Anisidine	XXXIV	*m*-Phenylenediamine	Black	143
Aniline	XXXV	*m*-Phenylenediamine	Black	144
Aniline	XXXVI	*m*-Phenylenediamine	Black	145
Sulfanilic acid	XXXVII	*m*-Aminophenol	Black	146
Naphthionic acid	XXXVII	SS-acid	Blue	147
o-Anisidine	XXXVII	SS-acid	Blue	148
Sulfanilic acid	XXXVII	3′-Hydroxyphenylglycine	Black	149
Aniline	XXXVII	H-acid + *m*-aminophenol	Reddish black	150
Aniline	XXXVII	*m*-Phenylenediamine	Reddish black	151, 152

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[131] NSK, *JP* 73,43,726 (1973).

[132] NSK, *JP* 73,43,727 (1973).

[133] FBy, *DAS* 2,208,973 (1973); *BeP* 783,019 (1972).

[134] Japan Chemical Works Co., Ltd., *JP* 74,113,825 (1974).

[135] FBy, *BP* 1,349,611 (Germany 8.6.1971); *BeP* 784,510 (1972).

[136] FBy, *DAS* 2,159,380 (1973); *BeP* 791,994 (1972).

[137] S, *BeP* 651,354 (1964).

TABLE V

Some Nonbenzidine Trisazo Dyes

$$\text{A} \xrightarrow[\text{acid}]{(1)} \text{H-acid} \xleftarrow[\text{alk.}]{(2)} \text{D} \xrightarrow{(3)} \text{E}$$

A	*D*	*E*	*Color*	*Ref.*
o-Nitroaniline	XXXIII	3-Hydroxy-2′-methyldiphenylamine	Greenish black	153
2,4-Dichloroaniline	XXXIII	3-Hydroxydiphenylamine	Black	154
p-Nitroaniline	XXXV	Resorcinol	Green	155
p-Nitroaniline	XXXVII	Phenol	Green	156
p-Nitroaniline	XXXVIII	*m*-Phenylenediamine	Black	157

compound from benzidine-2,2′-disulfonic acid → 1-phenyl-3-methyl-5-pyrazolone is added and allowed to couple at alkaline pH.[138]

Bluish black dyes with a stilbene-2,2′-disulfonic acid central component are made by coupling diazotized 4-amino-4′-nitrostilbene-2,2′-disulfonic acid at low pH with H-acid, coupling diazotized aniline at alkaline pH, reducing the nitro group, diazotizing, and coupling with *m*-cresol.[139] Similar structures are prepared, said to be green, in which the terminal OH group is etherified or esterified.[140]

In Tables IV[141–152] and V[153–157] are listed dyes of similar structures prepared from 4,4′-diaminodiphenylamine-2-sulfonic acid

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[138] S, *BP* 1,069,327 (Switzerland 5.9.1963); *BeP* 651,355 (1964).

[139] KYK, *JP* 74,57,029 (1974).

[140] FBy, *BeP* 822,982 (1974).

[141] CGY, *DAS* 2,336,393 (1974).

[142] CFM, *BP* 761,800.

[143] BASF, *BeP* 784,523 (1972).

[144] S, *DAS* 2,261,399 (1973).

[145] S, *DAS* 2,261,398 (1973).

[146] S, *DAS* 2,306,769 (1973); *BeP* 795,378 (1973).

[147] CN, *DAS* 2,400,515 (1974); *BeP* 809,884 (1974).

[148] CN, *DAS* 2,401,594 (1974); *BeP* 809,885 (1974).

[149] Acna, *USP* 3,928,313; *BeP* 825,162 (1975).

[150] Acna, *DAS* 2,414,303 (1974); *BeP* 812,900 (1974).

[151] Acna, *DAS* 2,255,652 (1973).

[152] FBy, *BP* 1,327,915 (Germany 6.3.1971).

[153] FBy, *DAS* 2,215,952 (1973); *BeP* 797,576 (1973).

[154] BASF, *DAS* 2,254,835 (1974); *BeP* 807,102 (1973).

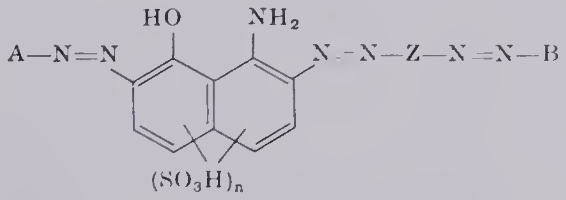
[155] BASF, *BP* 870,698 (Germany 19.12.1958); *DBP* 1,107,357 (1958); *BP* 785,101 (1957).

[156] FBy, *BP* 1,327,914 (Germany 6.3.1971).

[157] BASF, *DAS* 2,416,670 (1975); *BeP* 827,564 (1975).

(XXXIII), 4,4′-diaminodiphenyl sulfide (XXXIV), 2,4′-diaminodiphenyl sulfide (XXXV), 4,4′-diamino-2-carboxydiphenyl sulfide (XXXVI), 4,4′-diaminobenzanilide (XXXVII), and 3′,4-diamino-*N*′-methyl benzenesulfanilide (XXXVIII).

Blue, green, and black shades are conferred to leather by structures (XXXIX) of this class in which Z is generated from (XXVIII), AN_2 is a diazo component, and B is a coupling component.[158] Brown trisazo



(XXXIX)

dyes of the structure (A → Z ← D → E) are also frequently found in the patent literature in which Z is resorcinol, *m*-phenylenediamine, *m*-aminophenol, or derivatives of these couplers. Examples of this class are CI Direct Browns 1A, 6, and 95, all of which are based on benzidine. As stated earlier, replacement of this intermediate in blacks by other diamines has been proposed. Typical combinations from Cassella and ACNA are listed in Table VI.[159–169]

Earlier patents issued to Sandoz claim brown leather dyes of the same generic structure, but based on the stilbene-2,2′-disulfonic nucleus in place of diphenyl. For example, diazotized 4-amino-4′-(4″-hydroxyphenylazo)stilbene-2,2′-disulfonic acid coupled with the Cu complex of 2-aminophenol-4-sulfonic acid → resorcinol gave a reddish brown dye for chromed suede.[170] Other patents claim variations of this structure[171] and synthesis by reversed order of coupling.[172]

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[158] CFM, *BeP* 829,210 (1975).

[159] CFM, *DBP* 1,021,106 (1957).

[160] CFM, *DBP* 1,018,173 (1957).

[161] CFM, *DBP* 1,019,026 (1957).

[162] CFM, *DBP* 1,019,027 (1957).

[163] CFM, *DBP* 1,019,779 (1957).

[164] CFM, *DBP* 1,021,969 (1958).

[165] CFM, *DBP* 1,056,759 (1959).

[166] CFM, *DBP* 1,079,248 (1960).

[167] CFM, *DBP* 1,090,799 (1960).

[168] Acna, *DAS*, 2,503,654 (1974); *BeP* 825,021 (1975).

[169] Acna, *DAS* 2,505,188 (1975); *BeP* 825,409 (1975).

[170] S, *SP* 312,189 (1956).

[171] S, *SP* 313,103–313,118 (1956).

[172] S, *SP* 312,964 (1956).

TABLE VI

SOME NONBENZIDINE BROWN TRISAZO DYES

$$A \longrightarrow Z \longleftarrow D \longrightarrow E$$

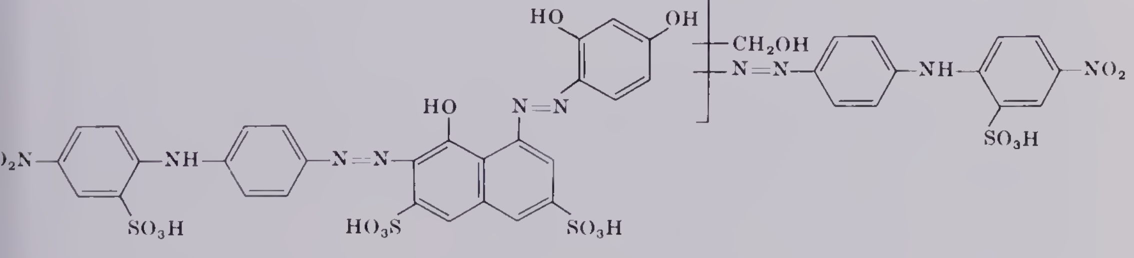
A	*Z*	*D*	*E*	*Color*	*Ref.*
Sulfanilic acid	Resorcinol	XXXIII	*m*-Phenylenediamine	Violet-brown	159
p-Nitroaniline	Resorcinol-4-sulfonic acid	XXXIII	*m*-Aminophenol	Brown	160
Sulfanilic acid	*m*-Phenylenediamine-4-sulfonic acid	XXXIII	Resorcinol	Red-brown	161
Aniline-2,5-disulfonic acid	*m*-Aminophenol	XXXIII	Resorcinol	Brown	162
Sulfanilic acid	7-Hydroxy-1-naphthylamine	4,4′-Diamino-diphenylamine-2′,3-disulfonic acid	Resorcinol	Violet-brown	163
Aniline-2,5-disulfonic acid	1,3-Diamino-4-chlorobenzene	XXXIII	1,3-Diamino-4-chlorobenzene	Brown	164
Sulfanilic acid	Resorcinol	XXXIII	Resorcinol	Red-brown	165
Sulfanilic acid	2,3-Dihydroxynaphthalene-6-sulfonic acid	XXXIII	Resorcinol	Olive-brown	166
Aniline	H-acid and resorcinol	XXXIII	Salicylic acid	Brown	167
2-Aminophenol-4-sulfonic acid	Resorcinol + Cu	XXXVII	*m*-Aminophenol	Brownish yellow	168
2-Aminophenol-4-sulfonic acid	Resorcinol + Cu	XXXVII	Salicylic acid	Reddish brown	169

5. *Trisazo Dyes* (A → M → Z ← A)

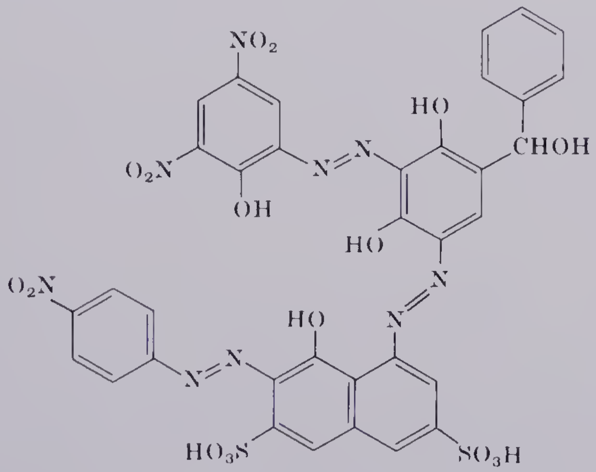
The final class of trisazo dyes for leather are brown or olive in which the Z component is a polyfunctional phenolic compound. An olive dye is[173]

1-Naphthylamine-5-sulfonic acid $\longrightarrow$ 1-naphthylamine-7-sulfonic acid $\xrightarrow{\text{(alk.)}}$
H-acid $\longrightarrow$ resorcinol $\longleftarrow$ *p*-nitroaniline

In the dark brown dye (XL), the bifunctional coupler is prepared by treating resorcinol with 38% aqueous formaldehyde in aqueous NaOH at 0°–5°.[174]



(XL)



(XLI)

A deep brown dye is prepared according to the scheme[175]:

p-Nitroaniline $\xrightarrow{(3)}$ 2-amino-3-naphthol-6-sulfonic acid $\xrightarrow{(1)}$ 3,3′-dihydroxydiphenylamine
$\xleftarrow{(2)}$ 4-aminodiphenylamine-2-sulfonic acid

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[173] FBy, *USP* 3,862,118; *BP* 1,341,646 (Germany 5.8.1971).
[174] S, *USP* 3,751,407; *BP* 1,310,825 (Switzerland 13.5.1969).
[175] FH, *BP* 815,737 (1959).

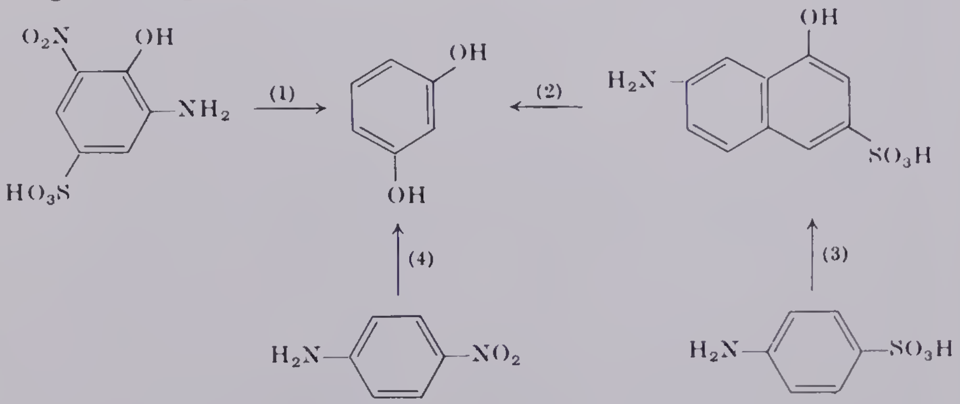
Analogously, in a recent patent, 2,4-dihydroxybenzhydrol is used as the bifunctional coupler to form brown dyes having very bright shades fast to light and wet rubbing. Specific claims include structure (XLI).[176]

D. Tetrakisazo Dyes

1. *Tetrakisazo Dyes*

$$\left(\begin{tikzcd} A^1 \arrow[r] & M \arrow[r] & Z & A^2 \arrow[l] \\ & & A^3 \arrow[u] & \end{tikzcd}\right)$$

Brown dyes containing the monoazo compound (H-acid → resorcinol) constitute this class. By coupling to this nucleus successively one equivalent of diazotized picramic acid in weakly alkaline medium, followed by two equivalents of diazotized *p*-nitroaniline and then converting the brown product to the yellower Fe complex, the fastness to wet treatments has improved.[177] Earlier, Francolor had used three equivalents of diazotized primuline sulfonic acid coupled with the same monoazo intermediate to produce dark browns, which were also metallized with Cu, Cr, or other metals.[178] They also claim the dye having the coupling sequence in Scheme 1.



Scheme 1

A yellowish-brown dye results from diazotization of the monoazo intermediate sulfanilic acid → 1-(3′-aminophenyl)-3-methyl-5-pyrazolone, coupling with (H-acid → resorcinol) and finally adding diazotized aniline.[179] Another representative of this type is the greenish brown dye formed by coupling (H-acid → resorcinol) first with diazotized *p*-anisidine, then with 4-aminoazobenzene-4′-sulfonic acid.[180]

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[176] CN, *USP* 3,943,122 (1976); *DAS* 2,201,512 (1972); *BP* 1,379,971 (France 14.1. 1971).

[177] FBy, *DBP* 951,949 (1956); *BP* 764,051.

[178] Fran, *FP* 1,012,664 (1952).

[179] FH, *BP* 1,238,780 (Germany 17.4.1968); *FP* 2,006,380 (1969).

[180] M. Vesely, V. Kmonicek, F. Vondrak, and J. Kunt, *CzechP* 123,388 (1967).

2. *Tetrakisazo Dyes*

$$\left(\begin{tikzcd} \mathrm{E} & \mathrm{D} \arrow[l, "(3)"'] \arrow[r, "(4)"] & \mathrm{Z} & \mathrm{A}^1 \arrow[l, "(1)"'] \\ & & \mathrm{A}^2 \arrow[u, "(2)"'] & \end{tikzcd}\right)$$

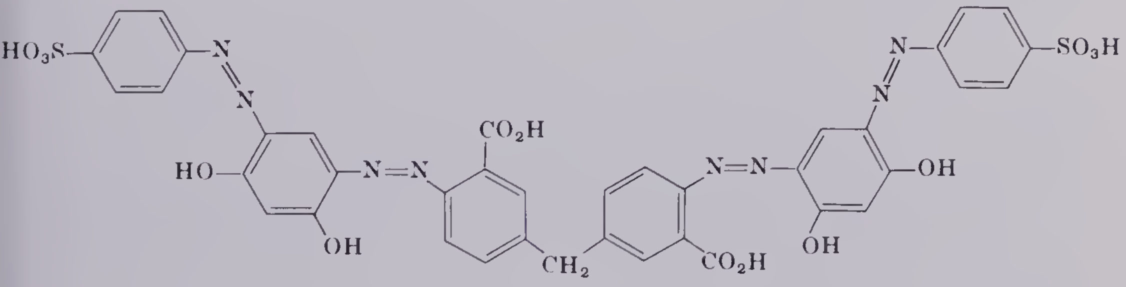
Dark brown dyes of good solubility in acid baths having good covering power on chrome-tanned leather are made by coupling, e.g., diazotized 2-naphthylamine-6,8-disulfonic acid with the monoazo intermediate H-acid → resorcinol and then adding the diazonium salt prepared by monocoupling tetrazotized benzidine with salicylic acid.[181]

3. *Tetrakisazo Dyes* ($A^1 \rightarrow Z^1 \leftarrow D \rightarrow Z^2 \leftarrow A^2$)

Brown and black dyes of this structure have been claimed. The symmetrical reddish brown product (XLII) gave a Co complex that dyed leather yellowish brown; the Cu complex was medium brown, and the Cr complex reddish brown.[182] Black dyes result from the coupling sequence[183]:

$$\begin{tikzcd} \text{Sulfanilic acid} \arrow[r, "(2)", "\text{alk.}"'] & \text{H-acid} & \text{benzidine} \arrow[l, "(1)"', "\text{acid}"] \arrow[r, "(3)"] & {} \\ & \text{3,3}'\text{-dihydroxydiphenylamine} & \text{sulfanilic acid} \arrow[l, "(4)"'] & \end{tikzcd}$$

Other diamines such as (XXXIV) and (XXXVII) are also included in the generic claims, as well as 4,4′-diaminostilbene.



(XLII)

4. *Tetrakisazo Dyes* ($A \rightarrow Z \leftarrow D \rightarrow M \rightarrow E$)

The dyes (XLIII) and related structures, which are brown on chrome suede leather, are prepared by condensation of 4,4′-dinitrostilbene-2,2′-disulfonic acid with 4-aminoazobenzene-4′-sulfonic acid, reduction

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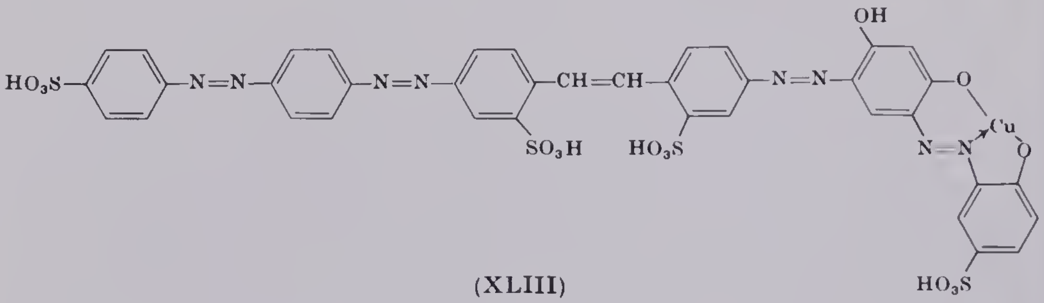
[181] Gy, *BP* 752,801 (1956); *DBP* 950,227 (1956).

[182] BASF, *BP* 785,084 (1957).

[183] FH, *BP* 763,064 (1956).

with Na_2S, diazotization, and coupling with the copper complex of (2-aminophenol-4-sulfonic acid → resorcinol).[184]



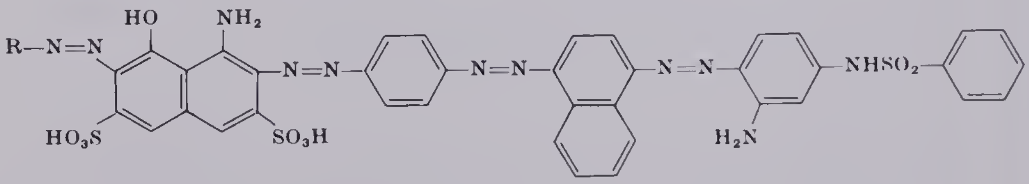
(XLIII)

Black dyes of this class which are possible substitutes for benzidine-based CI Direct Black 38 have been disclosed. Successive reaction according to the scheme:

$$\text{Aniline} \xrightarrow[\text{alk.}]{(2)} \text{H-acid} \xleftarrow[\text{acid}]{(1)} p\text{-nitroaniline} \overset{(3)}{\text{(reduction)}} \xrightarrow{(4)}$$

$$\text{mixed Cleves 1,6/1,7 acids} \xrightarrow{(5)} \text{resorcinol}$$

gave fast black shades on leather.[185] Several structures quite similar to these e.g., Coriamine Black BR, are revealed by Polish workers. The color of these dyes (XLIV) ranges from bluish black when R is m-HO_3S—C_6H_4— to greenish black when R is 4,1-HO_3S—$C_{10}H_6$—.[186]



(XLIV)

5. *Tetrakisazo Dyes* ($E^1 \leftarrow M^1 \leftarrow D \rightarrow M^2 \rightarrow E^2$)

Dyes of this class are variations of the important CI Direct Black 22, which has the constitution:

$$\text{4,4}'\text{-Diaminodiphenylamine-2-sulfonic acid} \overset{\text{alk.}}{\rightrightarrows} \gamma\text{-acid (2 moles)} \rightrightarrows$$

$$\text{1,3-phenylenediamine (2 moles)}$$

One recent East German patent appears to cover CI Direct Black 22 itself, and some substitution products [mainly of the phenylenediamine,

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[184] S, *USP* 2,749,333 (1956); *BP* 773,790; *SP* 335,783 (1959).

[185] M. J. Smith (Williams Hounslow Ltd.), *DAS* 2,417,943 (1974).

[186] E. Kubicki and W. Szymanski, *Biul. Inf., Barwniki Srodki Pomocnicze* **19**, 5–14 (1975); *CA* **83**, 195200j (1975).

e.g., 1,3-phenylenediamine-4-sulfonic and 3-(2-hydroxyethylamino)-aniline] are included.[187] 2R-acid in place of γ-acid in the CI Direct Black 22 structure[188] and use of 1,3-phenylenediamine-2-sulfonic acid have been claimed. Black dyes are obtained by coupling tetrazotized *o*-tolidine at alkaline pH first with H-acid, then with γ-acid, tetrazotizing and coupling with two equivalents of *m*-aminophenol.[189]

6. *Tetrakisazo Dyes* ($E^1 \leftarrow D^1 \rightarrow Z \leftarrow D^2 \rightarrow E^2$)

Black dyes of this class have been patented recently by two companies. An acid-resistant dye is prepared by diazotization of *p*-nitroaniline, coupling with H-acid at low pH, coupling at alkaline pH with diazotized 4-amino-4′-nitro-2′-sulfodiphenylamine, reduction with Na_2S, tetrazotization, and coupling with *m*-phenylenediamine.[190] Similar black dyes are prepared by diazotizing and coupling sequentially two equivalents of a 4-aminoacetanilide at acid and then alkaline pH, hydrolyzing the acetyl groups, tetrazotizing, and coupling with a suitable end component.[191]

7. *Tetrakisazo Dyes* ($E \leftarrow D \rightarrow Z \leftarrow M \leftarrow A$)

Brown dyes and their Cu complexes, which penetrate well, have been disclosed. An example is[192]

$$\text{Salicylic acid} \xleftarrow{(1)} \text{4,4'-diaminodiphenylamine-2-sulfonic acid} \xrightarrow{(3)}$$

$$\text{resorcinol} \xleftarrow{(2)} \text{H-acid} \xleftarrow{(4)} \text{aniline}$$

E. PENTAKISAZO AND HEXAKISAZO DYES

Both symmetrical and unsymmetrical reddish blue to black dyes have been prepared by coupling tetrazotized 4,4′-diaminoazobenzene with an amino- or hydroxyaminonaphthalenesulfonic acid, diazotizing and coupling with *m*-aminophenol or NW-acid. An example is[193]:

$$m\text{-Aminophenol} \xleftarrow{(2)} \text{H-acid} \xleftarrow{(1)} \text{4,4'-diaminoazobenzene} \xrightarrow{(1)}$$

$$\text{H-acid} \xrightarrow{(2)} m\text{-aminophenol}$$

The product is said to be more soluble and to penetrate better than the corresponding dye derived from benzidine.

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[187] FW, *EGP* 110,508 (1974).

[188] FBy, *DAS* 2,140,866 (1973); 2,140,867 (1973); *BP* 1,379,133 (Germany 14.8.1971).

[189] CFM, *DAS* 2,408,907 (1975).

[190] S, *BeP* 817,381 (1974); *DAS* 2,431,873 (1975).

[191] FBy, *BeP* 804,764 (1972).

[192] CFM, *BP* 819,840.

[193] CN, *BeP* 804,832 (1973); *DAS* 2,346,462 (1974).

Brown hexakisazo dyes are disclosed that are prepared according to the scheme:

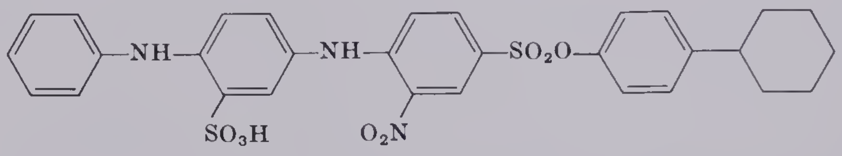
$$\text{Picramic acid} \xrightarrow{(2)} \text{resorcinol} \xleftarrow{(1)} \text{H-acid} \xleftarrow{(3)}$$

$$\text{4,4}'\text{-diaminodiphenyl sulfide} \xrightarrow{(3)} \text{H-acid} \xrightarrow{(1)} \text{resorcinol} \xleftarrow{(2)} \text{picramic acid}$$

4,4′-Diaminodiphenylsulfone and benzidine are also listed as center components.[194]

F. Nonazo Anionic Dyes

Acid nitro dyes, of primary interest on wool, silk, and nylon, are also useful in leather dyeing. Acid Leather Brown EGB (CI 10415) has considerable importance.[195] It is prepared by condensing 1 mole of toluquinone with 2 moles of 4-amino-2-methyl-4′-nitrodiphenylamine-2′-sulfonic acid in the presence of sodium carbonate and manganese dioxide.[196] In a recent and improved process, the condensation is effected at pH 3–6, which produces dyes having olive to olive-brown hues on leather, whereas the original dye gives yellowish to medium browns.[197] Sandoz have claimed dyes such as (XLV) for leather and polyamide fibers.[198]



(XLV)

Anthraquinone acid dyes of importance for production of bright blue shades on leather include CI Acid Blues 25, 45, 62, 78, 80, and 129. Newer dyes of this type, of primary use on nylon and wool, have also been claimed to be useful for dyeing leather.[199,200] Triphenylmethane dyes and Xanthene dyes, such as CI Acid Red 52, Violets 9, 49, Blues 7, 9, 83, 90, and 147, are also used for very bright blue shades.

Bright turquoise and green shades are produced by sulfonated phthalocyanines. For example, the reaction product of tris(chloromethyl)copper phthalocyanine with the potassium salt of glycine dyes chrome leather from a neutral bath.[201] Dyes for leather are also

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[194] BASF, *DBP* 955,802 (1957).

[195] *DRP* 414,390; *CI* 10415.

[196] *BIOS* **1548**, 70.

[197] FH, *DAS* 2,305,048 (1974); *BeP* 810,567 (1974).

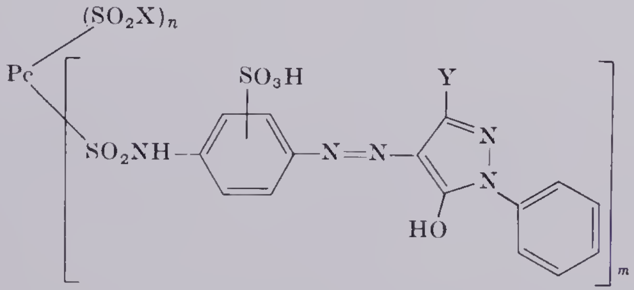
[198] S, *BP* 1,347,897 (Switzerland 4.5.1970).

[199] S, *SP* 360,746 (1962).

[200] S, *BP* 1,161,941 (Switzerland 2.2.1966).

[201] BASF, *DBP* 843,725 (1952).

produced by treating sulfonamides of phthalocyanines with a 1,2-alkyleneimine or a 2-haloethylamine.[202] Green to blue azo phthalocyanine leather dyes of the structure (XLVI) have also been reported.[203] Copper phthalocyanine tetrasulfonyl chloride condensed with 1,3-diaminobenzene-4-sulfonic acid is diazotized and coupled with, e.g., 2′,5′-dichloro-4′-sulfo-1-phenyl-3-methyl-5-pyrazolone, to yield a yellowish-green dye.



Pc = copper phthalocyanine
X = —OH, or —NH-alkylene—OH
Y = —CH$_3$ or —CO$_2$H
Z may be substituted by halogen, alkyl or —SO$_3$H

$m = 1\text{–}4 \qquad n = 0\text{–}3 \qquad m + n = 4$

(XLVI)

IV. Cationic Dyes

While about forty references have been found describing new cationic dyes for leather, nearly all of them claim use on many other substrates, primarily on acrylic fibers. Since the chemistry of basic and cationic dyes for synthetic fibers has been reviewed in *CSD IV*, no attempt will be made here to cover this extensive literature. Many of the known cationic dyes that are useful for synthetic fibers may also be used on leather. Indeed, older basic dyes such as CI Basic Yellow 2; Oranges 1 and 2; Reds 1, 2, and 10; Violets 1, 3, and 10; Blue 9; Green 4; and Browns 1, and 4 continue to be important. Casnocha has reviewed basic dyes and their application in leather coloring.[204]

A process for dyeing chrome leather with basic dyes in the presence of a lauryl sulfate salt and a nickel salt claims improved lightfastness caused by inclusion of Ni.[205]

Azo cationic dyes specifically for surface dyeing of leather without penetration are made from diazotized aromatic amines coupled with

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[202] BASF, *BP* 1,010,236 (1965).

[203] CN, *BP* 1,220,143 (France 17.5.1967).

[204] J. A. Casnocha, *Leather Manuf.* **72**, 21 (1955); *CA* **49**, 7859a (1955).

[205] HCC, *JP* 74,117,601 (1974).

hydroxybenzopyrylium salts having reactive methyl groups on the heterocyclic rings.[206,207] The dyes have a slight tanning effect because of their phenolic OH groups and produce bright hues. An example is the bright red azo dye from diazotized aniline coupled with 2,4-dimethyl-7-hydroxybenzopyrylium chloride. The reactive 2-methyl group in the latter intermediate can also be condensed with aldehydes, nitroso compounds, or formic acid derivatives to produce leather dyes.

V. Reactive Dyes

Although reactive dyes have the potential to provide best fastness to wet treatments of finished leather and bright shades, that potential has not yet been realized commercially, at least in the United States. Over a hundred references describe products or processes for dyeing leather with reactive dyes. Two-thirds of these are patents in which leather is included as one of at least several substrates to which the dyes are applicable. These will not be detailed, because reactive dyes in general have been adequately reviewed in *CSD VI* and elsewhere.

Reactive dye types applicable to leather are fewer than for synthetic fibers. The natural properties of the leather must be preserved; therefore maximum temperature is 65° and excess alkalinity must be avoided. Generally, dichlorotriazinyl (ICI Procion M), sulfatoethylsulfonyl (Hoechst Remazol), and trichloropyrimidyl (Geigy Reactone, Sandoz Drimaren) groups have been investigated most for leather. Leather dyeing with reactive dyes has been reviewed, but usually from a limited viewpoint.[208–217]

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[206] FBy, *DBP* 1,002,286 (1957).

[207] FBy, *DBP* 959,668 (1957).

[208] G. C. Travers, *Dyer, Text. Printer, Bleacher Finish.* **129**, 529–532 (1963).

[209] W. Pauckner, *Rev. Tech. Ind. Cuir* **67**, 116–118, 120–121 (1975); *CA* **83**, 99240b (1975).

[210] I. N. Alatyrtseva, R. I. Krimker, and G. L. Metzik, *Kozh.-Obuvn. Promst.* **3**, 26–28 (1961); *CA* **57**, 10003h (1962).

[211] M. L. Fein, S. J. Viola, and E. M. Filachione, *J. Am. Leather Chem. Assoc.* **65**, 584–592 (1970).

[212] R. H. Ricketts, *Bull. Assoc. Fr. Ing., Chim. Tech. Ind. Cuir Doc. Inf. Cent. Tech. Cuir* **26**, 240–254 (1964); *CA* **62**, 9368a (1965).

[213] T. C. Mullen, *J. Soc. Leather Trades' Chem.* **46**, 162–175 (1962); *SVF Fachorgan Textilveredl.* **19**, 569–576 (1964).

[214] H. Zahn and G. Reinert, *Leder* **19**, 1–8 (1968); *J. Am. Leather Chem. Assoc.* **63**, 495 (1968) (abstr.).

[215] K. Rosenbusch and G. Siebott, *Leder* **19**, 294–296 (1968); *J. Am. Leather Chem. Assoc.* **64**, 369 (1969) (abstr.); R. Seyd, *J. Soc. Leather Trades' Chem.* **54**, 405–408 (1970).

[216] V. Luca, *Ind. Usoara* **16**, 79–85 (1969).

[217] I. Botev, *Kozhi Obuvki* **5**, 4–7 (1964); *CA* **62**, 2868h (1965).

Travers states that sheepskins may be dyed with Procion dyes in the drum machine at pH 7–8.5 and 20°–50°, reserving the wool a pure white.[208] Leathers with various tannages give equally fast dyeings with vinylsulfone, dichlorotriazine, and trichloropyrimidine dyes, and the dyeings are faster to wet treatments than those from metal complexes.[209]

Mullen has discussed the application of Procion dyes to leather.[213] The bath pH is the most important factor in fixation, a pH between 7 and 8.5 being required for optimum results. These dyes have been of principal interest for glove leather and clothing suedes, where levelness of dyeing and wetfastness are required. They have only limited build, and for this reason a "sandwich" dyeing process has been developed.[218] This is a double application of dye with an intermediate treatment with a fixing agent. Monochlorotriazinyl dyes are not yet applicable to leather.[218]

Reactive dyes attach to the ϵ-amino group of lysine and hydroxylysine of the collagen.[214] When more than one reactive group is present, a tanning effect is apparent.

Sulfatoethylsulfonyl dyes are said to have no affinity for collagen, but when converted to vinyl sulfonyl by alkali, they form covalent links with lysine, hydroxylysine, arginine, tyrosine, or hydroxyproline.[215] These dyes have good fastness to light, alkali, solvents, water, and perspiration, and are recommended for chamois leather.[215] Dyeing of Remazols is carried out at pH 10 and 20°–40° for 30–60 minutes. The wetfastness is further improved by drying the dyed leather at the maximum possible temperature, about 60°. Remazol dyes have been reacted with synthetic tannins to produce colored tanning agents.[219]

Brown reactive dyes specifically for leather are metal complex azo dyes incorporating the dichlorotriazinyl nucleus. Copper complexes of disazo compounds are said to be particularly useful for dyeing leather lightfast reddish brown shades from a cold alkaline dyebath, with good reserve of wool.[220] Thus, 5-acetylaminoanthranilic acid is diazotized and coupled with the Cu complex of 2,2′,4-trihydroxyazobenzene-3′,5′-disulfonic acid in presence of sodium carbonate and pyridine. After hydrolysis with aqueous NaOH, the product is condensed with cyanuric chloride at pH 6.5.

Disazo 1:2 chromium complexes also give fast browns on leather.[221]

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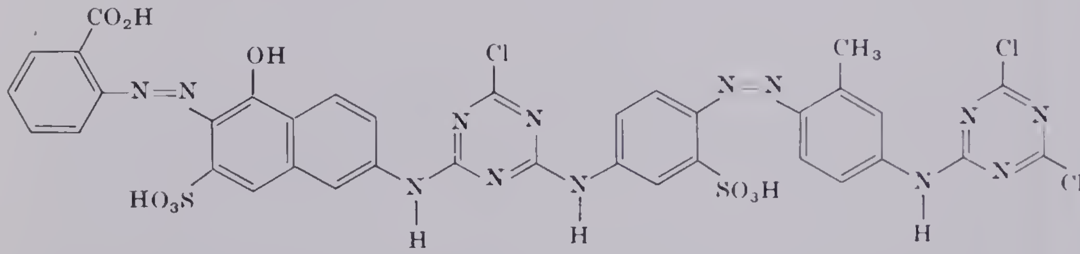
[218] ICI, "Technical Information Bulletin, Dyehouse No. 916."

[219] BASF, *BeP* 647,778 (1964).

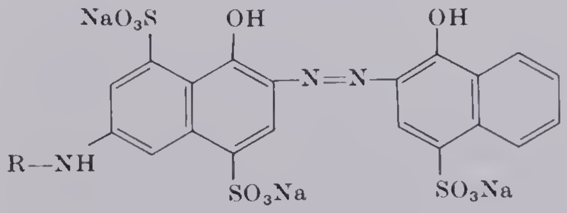
[220] ICI, *BP* 973,228 (1962).

[221] ICI, *BeP* 642,676 (1964).

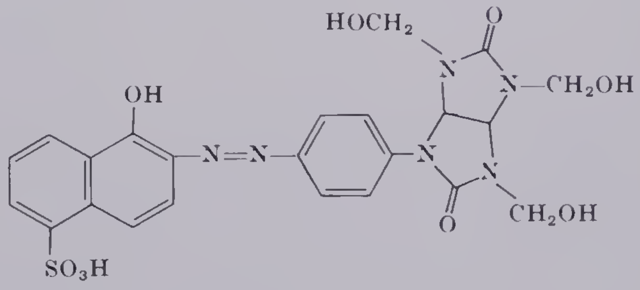
A typical structure is the 1:2 Cr complex of (XLVII). The unsymmetrical 1:2 Cr complex prepared by heating an aqueous solution of the 1:1 Cr complex of [2-amino-4-nitrophenol-6-sulfonic acid → 1-(4′-sulfophenyl)-3-methyl-5-pyrazolone] with (anthranilic acid → J-acid) and reacting the resultant 1:2 complex with cyanuric chloride also gives a brown dye having good penetration and excellent fastness to washing and light, with excellent wool reserve.[222]



(XLVII)



(XLVIII)



(XLIX)

The blue-black (1:2 Cr) complex of (XLVIII), in which R represents trichloropyrimidyl, is fast on chrome-tanned calfskin.[223] Copper (1:1) complexes of similar structures give dark blue dyeings. Other reactive groups, such as α,β-dibromopropionylamino-,[224] haloacylaminome-

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[222] ICI, *BP* 1,110,364 (1966).

[223] S, *SP* 466,214 (1969).

[224] CGY, *DAS* 2,058,075 (1971).

thyl,[225] haloacylamino- or acryloylamino-,[226] and hydrazinium-[227,228] groups are found on dyes claimed to color leather.

Simultaneous dyeing and tanning of leather is accomplished by using dyes of any chemical class containing at least one vinyl or isopropenyl group activated by a carbonyl group, with acrylic acid, methacrylic acid, and/or vinyl sulfonic acid and copolymerizing.[229] Simultaneous dyeing and finishing is also claimed by treatment of leather with an aqueous solution or dispersion containing a polymer, one or more dyes, and a cross-linking agent, carrying reactive *N*-methylolamide groups or their alkyl ethers, and heating at 20°–120° in the presence of an acid or alkaline catalyst.[230] A typical red dye is (XLIX), which is said to give uniformly red leather and to have outstanding mechanical and chemical fastness properties.

VI. Azoic Dyes

Coloring of leather by diazotizing and developing was in commercial production as early as 1910.[14] An important use of this method is for black suedes, where full shades with maximum fastness to crocking can be obtained based on certain dyes that are applied to the leather, diazotized, and coupled with 2-naphthol or *m*-toluylenediamine.[7]

A method was given in 1954 in which mixtures of a coupling component, such as 3-hydroxy-2-naphthoic-*m*-carboxyanilide, and the antidiazotate from 2-amino-5-chlorotoluene were applied together, and red, well-penetrated color was developed by treatment with dilute acetic acid.[231] Subsequently, methods were patented for applying the azoic coupling component first at an initial pH of 7–9 and final pH of 3–7 and then treating with a diazotized amine free of solubilizing groups.[232] Stronger, more uniform dyeings were obtained if the coupler was applied in the presence of a formaldehyde-yielding substance.[233] In a later development, levelness and penetration were improved by applying the azoic coupler in the presence of an α-sulfo-substituted long-chain fatty acid.[234]

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[225] S, *BP* 1,010,184 (1965).

[226] S, *BP* 1,010,232 (1965).

[227] S, *BP* 1,009,432 (1965).

[228] CIBA, *CP* 723,061 (1965).

[229] BASF, *BP* 1,186,278 (Germany 22.7.1966).

[230] BASF, *BP* 1,063,219 (Germany 16.10.1964); *FP* 1,454,622 (1966).

[231] FH, *BP* 707,884.

[232] G, *USP* 2,913,301 (1959).

[233] G, *USP* 2,913,302 (1959).

[234] G, *USP* 3,409,384 (1965).

Rodinov reported dyeing sheepskins dark blue to black by treatment with H-acid at 38°–40° and pH 2.0–2.7, development with diazotized 4-amino-4′-methoxydiphenylamine, and finally treatment with acidic potassium bichromate.[235]

The above processes generally require the use of wet, pure Cr-tanned, unfinished leather. Thomas, in 1966, discussed a process for dyeing dry, retanned glove leathers. His method comprises rewetting with a nonionic wetting agent, acidifying to pH 4–4.5, treating with a cationic mordant, and degreasing prior to dyeing by hand brushing of the dye, diazotization, and development.[236]

Recently, 4,4′-diaminoazobenzene has been used as the diazo component, directly diazotizable on leather, coupling with any of various aminonaphthol sulfonic acids in a one-stage process presenting no health hazard.[237] New couplers of the pyridone series are claimed as useful for dyeing or printing of leather by development on the leather.[238]

An improved process for azoic dyeing of leather without changing the surface or physical properties comprises incorporating into the leather a diazonium component and a coupling component in a nonaqueous solvent and adding other materials required for coupling in a solvent or as a vapor.[239] The coupling component may be a phenolic tanning agent or the usual naphthol. Patterns can be applied to the surface by using a light-sensitive diazonium component and photoimaging the surface before coupling. A diazonium borofluoride is usually used, and development is brought about with ammonia fumes.

It is claimed that azoic dyes are produced on leather by first treating with 1,5- or 2,7-dihydroxynaphthalene, oxidizing with H_2O_2 to form 1,5-dihydroxy-3,4-naphthoquinone or 2,7-dihydroxy-1,4-naphthoquinone and using these as couplers.[240] This is improbable, because the oxidation step will give indefinite products, and diazonium salts will mainly undergo decomposition by interaction with quinones.

VII. Miscellaneous Dyes

As stated earlier, vat dyes have found little use for dyeing leather because the conditions for vatting include high alkalinity. However,

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[235] A. M. Rodionov, *Kozh.-Obuvn. Promst.* 7, 18–20 (1959); *CA* 54, 6133 (1960).

[236] B. Thomas, *Bull. Assoc. Fr. Ing., Chim. Tech. Ind. Cuir Doc. Inf. Cent. Tech. Cuir* 28, 271–275 (1966); *J. Am. Leather Chem. Assoc.* 62, 460 (1967) (abst.).

[237] Acna, *BeP* 807,152 (1973).

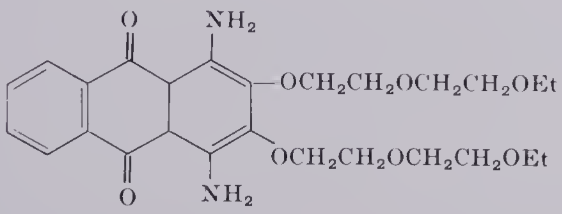
[238] CGY, *SP* 563,495 (1975); *BeP* 801,374 (1973).

[239] DuP, *USP* 3,933,423 (1976).

[240] A. I. Levchenko, *RP* 126,472 (1960); *CA* 54, 16891b (1960).

level dyeings of improved fastness to light and washing can be obtained by spraying with an aqueous solution of a sulfuric acid ester of a leuco vat dye and then treating it with an acid solution.[241] Excellent yellow dyeings are reported from spraying one side of leather with, e.g., Algosol Golden Yellow IGK (CI Solubilized Vat Yellow 4) in aqueous solution with $NaNO_2$, partly drying, brushing with 2% HCl, and finally spraying with 2% ammonia. Solubilized vat dyes are also applicable by treating the dyed leather with H_2SO_4 and $K_2Cr_2O_7$ and removing the chrome color with HCO_2H and $NaHSO_3$, or by dyeing with tartaric acid and aluminum chloride in the bath and irradiating with a strong arc lamp.[242]

An example of nonionic anthraquinone dyes[243] for dyeing pelts and hair, in which the anthraquinone nucleus is connected by one or more hetero atoms such as O or S to a polyoxyethylene chain, is the bluish red dye (L).



(L)

Leather tanned with cationic tanning agents contains free aromatic amino groups in large amount. Such leather, treated with nitrite solutions and acid, and subsequently coupled with phenol, active methylene compounds, or aromatic amines, is colored any of a variety of hues dependent on the coupler.[244]

Oxidation dyes, such as commonly used for fur dyeing, are also applicable to leather. Dyeing with amines, diamines, phenols, or naphthols and then oxidizing imparts brown to black hues to leather.[245] Oxidation of formaldehyde–resorcinol resin by potassium bromate has been found to improve its tanning properties for sheepskin suede and to result in dyed leather tissue resistant to water and to nonpolar solvents.[246]

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[241] G, *USP* 2,872,277 (1959).

[242] *Leder* **6**, 5–9 (1955); *CA* **49**, 8624 (1955).

[243] Therachemie, *DBP* 1,207,916 (1965).

[244] FBy, *DBP* 1,007,731 (1957).

[245] A. I. Levchenko, *Izv. Vyssh. Uchebn. Zaved., Tekhnol. Legk. Promsti.* **4**, 29–33 (1959); *CA* **54**, 7197f (1960).

[246] Y. A. Romanov, A. N. Nikolaev, V. I. Smirnov, and I. P. Strakov, *Kozh.-Obuvn. Promst.* **14**, 5–9 (1973); *CA* **79**, 67841z (1973).

Organic pigments are used extensively for finishing leather, and their requirements include fastness to light, weather, chemicals, and heat. Those selected from the disazo-substituted benzidine class, Naphthol AS class, manganese lakes, and phthalocyanines are satisfactory for aqueous finishing.[247]

Transfer printing, wherein the leather surface is brought into contact with a temporary carrier of paper, aluminum, or regenerated cellulose carrying a transferable film of vinyl resin and one or more pigments, and an underlying layer of ethylcellulose, has been patented.[248]

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[247] K. Merkle, *Leder* **16**, 105–11 (1965); *CA* **63**, 10170f (1965).

[248] CGY, *USP* 3,794,544 (Switzerland 18.2.1970).

Chapter III

SOLVENT DYES

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I. General Discussion

A. INTRODUCTION

Drawn from a large number of chemical groups, the disperse dyes, solvent dyes, and pigments have in common the property of being water insoluble. Chemically there are few differences between the disperse dyes and some of the solvent dyes. For instance, the well known CI Disperse Yellow 3 is also known as CI Solvent Yellow 77. Also, CI Disperse Blue 7 is the same as CI Solvent Blue 69.

The difference between disperse dyes and solvent dyes is mainly in their use. Disperse dyes are usually used in dispersed form in aqueous medium for synthetic fibers. Dyeing usually requires an organic solvent as carrier or the use of high temperature to achieve the final

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coloration of the fibers. Whether the carrier's function is solely as a solvent for dyes, however, is debatable. The solvent dyes, on the other hand, are used to color materials through their ability to dissolve in an organic solvent or substance. Recently developed solvent dyeing processes (see Chapter IV), as well as transfer printing processes for synthetic fibers (see Chapter V), make the distinction between the two groups of dyes even less apparent.

The difference between pigments and solvent dyes is the insolubility of pigments in organic solvents. This difference, however, is not absolute, but relative. Most commercial pigments still have some solubility in organic solvents. For practical purposes, however, they are incorporated into materials by dispersion and are in the colloidal form rather than in true solution in the substrate. In application, both pigments and solvent dyes are competing with each other in inks, coatings, mass coloration of synthetic polymer compositions, etc. Special requirements of application will decide which one will be selected. The relative merits of solvent dyes and pigments have been reviewed.[1–3] Structures of many solvent dyes and pigments are very similar. Thus CI Solvent Yellow 14 and CI Pigment Orange 2 are aniline and *o*-nitroaniline → 2-naphthol.

Some solvent dyes were discovered over 100 years ago: CI Solvent Yellow 1 (Aniline Yellow) in 1861, CI Solvent Black 5 and 7 (Nigrosine) in 1867, and CI Solvent Violet 8 (Methyl Violet) in 1862. Most earlier solvent dyes were simple azo colors or free bases of basic dyes. In 1920–1930 IG commercialized the amine salt of acid dyes as well as spirit-soluble metal complex dyes as Zapon Fast dyes. This increased the range of application and improved the fastness properties of earlier solvent dyes. Later research on solvent dyes has concentrated on developing a line of liquid dyes for petroleum products and new dyes for ballpoint pen inks or other specialty inks. More recent research has emphasized new colors for polymeric materials and for daylight-fluorescent pigments.

Solvent dye production in the United States rose from 8.5 million pounds in 1964 to close to 14 million pounds in 1973. Table I shows the United States production data for some important solvent dyes in 1964, 1968, and 1973. The statistics on individual solvent dyes are far from being complete. This is due to the policy of the U.S. Tariff Commission that statistics for an individual chemical are given only where there are three or more producers, none of whom is predominant.

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[1] J. Koerner, *Plast. Mod. Elastomeres* **26**, 139 (1974).

[2] S. Bonnie, *Plast. Technol.* **3**, 633 (1957).

[3] C. Musgrave, *Plastics* (*London*) **31**, 1129 (1966).

TABLE I

UNITED STATES SOLVENT DYE PRODUCTION (IN 1000 LB)[a]

Dye	1964	1968	1973
Total solvent dyes	8,547	11,400	13,988
Solvent Yellow Dyes (total)	1,136	1,151	1,381
Solvent Yellow 14	747	695	564
Solvent Orange Dyes (total)	365	460	646
Solvent Red Dyes (total)	1,192	1,571	2,243
Solvent Red 24	293	343	213
Solvent Red 26	300	326	206
Solvent Violet Dyes (total)	541	335	—
Solvent Violet 8	378	206	—
Solvent Blue Dyes (total)	—	1,324	4,003
Solvent Blue 38	—	126	157
Solvent Green Dyes (total)	193	—	—
Solvent Green 3	146	—	217
Solvent Brown Dyes (total)	65	89	88
All other solvent dyes	5,055	6,470	5,410

[a] United States Tariff Commission, Synthetic Organic Chemicals, United States production and sales.

The data nevertheless reveal that while total production of solvent dyes is increasing over the years, the production of old-line solvent dyes is actually decreasing.

B. TYPES AND USES OF SOLVENT DYES

Based on the solubility characteristics, solvent dyes can be further divided into the following types.

1. *Dyes Soluble in Hydrocarbons and Other Less Polar Solvents*

This type of dye is more soluble in aliphatic or aromatic hydrocarbons, chlorinated hydrocarbons, oils, fats, and waxes. It is usually used to color these solvents or a great variety of materials containing such solvents. Names for commercial solvent dyes of this type include Oil (many companies), Calco (ACY), Sudan (G), Organol (Fran), Ceres (FBy), Waxoline (ICI), Petrol (PAT).

2. *Dyes Soluble in Spirit and Other More Polar Solvents*

This type has more solubility in alcohols and ketones. It is used for lacquers, stains, and varnishes; for flexographic and gravure inks; for ballpoint pen inks. Commercial names of this type include Calcofast (ACY), Azosol (G), Orasol (Ciba), Iosol (NAC), Intracetyl (Fran), Irgacet (Gy), Spirit Soluble (NAC), Luxol (DUP), Methasol (ICI), Zapon (FH), Neozapon (BASF).

3. *Dyes That Have Relatively Low Solubility in Most Solvents*

These dyes can be used for mass coloration of synthetic polymer compositions and various other end uses. Commercial dyes of this type include Plasto (NAC), Thermoplast (BASF), Amaplast (AAP), Hytherm (PAT), Solvaperm (FH).

C. CHEMICAL CONSTITUTION AND SOLUBILITY CHARACTERISTICS OF SOLVENT DYES

Chemical constitution can be designed or modified from other classes of colors to obtain solvent solubility. They can be achieved by using the following.

1. *Dyes with Low Molecular Weight*

Most simple azo or anthraquinone dyes have good solubility in organic solvents. Many are good solvent dyes.

2. *Dyes with Long Aliphatic Side Chains*

High-molecular-weight colors that have poor solubility in organic solvents can be made soluble by introducing long side chains. For instance, CI Vat Green 1 (16,17-dimethoxyviolanthrone) has very poor solubility in solvents, but Zapon Fast Green B (CI 59840) in which the methoxyl groups are replaced by $OCH_2CH_2OC_4H_9$ is used as a solvent dye. Also, copper phthalocyanine has been converted to solvent-soluble dyes by introducing long-chain sulfonamide groups (CI Solvent Blue 89, CI 74340).

3. *Metal Complex Dyes*

The most common metal complex dyes are chromium or cobalt complexes of azo dyes, e.g., CI Solvent Yellow 21 (Cr complex of the dye anthranilic acid → 1-phenyl-3-methyl-5-pyrazolone). Selected metal complex dyes have good solubility in alcohols, glycols, and ketones, but they are relatively insoluble in lipophilic substances such as oils, fats, and waxes. The solubility of these dyes can be further improved by treating these classic metal complex dyes with solubilizing amine.[4]

4. *Salts of Acid or Basic Dyes*

Usually, an aliphatic amine salt of acid dyes or a fatty acid salt of basic dyes can be used as solvent dyes. Normally, they also have more

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[4] BASF, *DBP* 1,226,727; 1,263,947.

solubility in polar solvents such as alcohol. Selected dyes of this type, however, have good all-around solubility in many organic solvents.

D. Chemical Classification

Solvent dyes can be generally classified into the following groups.

1. *Azo Dyes*

Azo dyes used for solvent dyes generally do not have a water-solubilizing group. They provide many yellow, orange, and red colors. Although they are cheap and have many uses, they generally have poor fastness and are gradually being replaced by other types of solvent dyes in more demanding applications.

2. *Azo Metal Complex Dyes*

This group also provides many yellow, orange, and red colors. Due to their good fastness and solubility characteristics, their use in printing inks and transparent lacquers has steadily increased.

3. *Triarylmethane and Related Dyes*

This group provides important reds, violets, blues, greens, and blacks. Although they are among the earliest dyes discovered, the free bases as well as their fatty acid salts are still widely used in many applications due to their high color strength and brilliance of shade.

4. *Amine and Basic Dye Complexes of Acid Dyes*

Sulfonated acid dyes, usually azo or copper phthalocyanines, form solvent soluble dyes with organic bases of high molecular weight such as diarylguanidines and dicyclohexylamine. Copper phthalocyanine derivatives are especially important spirit-soluble blue dyes.

5. *Anthraquinones and Related Dyes*

Anthraquinones provide important blues and greens. Many newer patents are based on this group, and the newer products are used in mass coloration of polymer compositions.

6. *Fluorescent Dyes*

This group consists of dyes with various chemical structures, but all show fluorescent characteristics. They are being used in increasingly important daylight-fluorescent colorants.

7. *Miscellaneous Dyes*

Many well-known colors, such as quinophthalones and the newer phthaloperinones, belong to this group. Many have become important dyes for plastic materials.

II. Chemistry and Properties of Solvent Dyes

A. Azo Dyes

Azo dyes along with some free bases of basic dyes were the earliest discovered solvent dyes. Most of the earlier so-called oil colors belong to this series. Because of their low cost and good solubility in many solvents, they are still being widely used for many applications. Probably the single most important application today is in the coloring of petroleum products, which are colored so that different kinds or grades of products can be distinguished by refiners, deliverers, and users. It is also necessary to satisfy some governmental regulations since the same petroleum product may be taxed differently in different end uses. Fastness properties are usually not a big problem. Solubility and ease of application are main concerns. Azo dyes are found to be well suited in these applications.

Almost all the earlier oil colors were in powder form. They have been modified to pellet form by mixing a molten stream of dyes with vigorously agitated water[5,6] or to flake form by allowing the molten dyes to cool over a flaking device.[6] More recent patents have emphasized making such dyes in liquid forms so that refiners may use automatic metering systems to color their products. Such liquid forms can be obtained by using selected solvents, such as isopropyl or other alkyl phenols,[7] or by dissolving in other petroleum additives such as a liquid corrosion inhibitor[8] or surfactant.[9] These liquid petroleum dyes can also be obtained by modified dye structures, which will be discussed later. Azo dyes provide most of the yellows, oranges, and reds. The products are almost always isolated and used without any diluent.

1. *Azobenzene Derivatives*

These dyes are mostly yellows. The more important colors are Solvent Yellow 1(4-NH_2), 2(4-NMe_2), 3(4-NH_2-3,2'-Me_2), 56(4-NEt_2) and Solvent Orange 1[2,4-$(OH)_2$] and 3[2,4-$(NH_2)_2$]. Solvent Yellow 2 is gradually being replaced by the diethyl derivative Solvent Yellow 56. Both Solvent Yellow 2 and 56 have rather poor solubility in alcoholic solvents, and mixtures of dyes similar to Solvent Yellow 56 are used to improve solubility.[10] Solvent Yellow 3, with two nuclear

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[5] Allied, *USP* 3,071,815.

[6] ACY, *USP* 3,049,533; 3,356,443.

[7] William, *Neth. Appl.* 65,012,904; Allied, *Japan Appl.* 7002–660–R.

[8] BASF, *BP* 1,133,414.

[9] Komitau, *FP* 2,028,637.

[10] ICI, *Neth. Appl.* 66,012,344.

methyl groups and a free amino group, has much better all-round solubility. Solvent Orange 3, free base of Basic Orange 2 (Chrysoidine), also has excellent all-round solubility in organic solvents.

To improve the solubility in petroleum products, a number of patents use alkyl-substituted intermediates, e.g., heptylnaphthol, octyl- or *p*-nonylphenol,[11,12] and *N*-butylaniline[13] as a coupler. Mixed amines with 2–10-carbon alkyl- or alkoxyanilines are used as diazo components to couple with phenol and naphthol to give replacements of Solvent Orange 1.[14] Also, *N*-(2-nitro-1-phenylethyl)aniline has been used to give yellow to red oil-soluble colors.[15]

2. *Monoazo Naphthalene Dyes*

The most important dye in this group is Solvent Yellow 14 (1-phenylazo-2-naphthol), comprising one-half of Solvent Yellows produced in the United States. It is a reddish yellow, some commercial products being called Oil Orange, and is extensively used in petroleum products. When aniline is replaced by *o*-toluidine or 2,4-xylidine, the product is Solvent Orange 2 or Solvent Orange 7, respectively. Solvent Orange 7 has better solubility than Yellow 14 but is much redder and is called Oil Scarlet in some commercial products. It is also widely used in petroleum products.

When *o*-anisidine is used as a diazo component to couple with 2-naphthol, the product is Solvent Red 1. It has somewhat restricted solubility, which is improved by using *o*-phenetidine and mixing with an alkylphenol, e.g. nonylphenol, to give a liquid composition containing up to 50% dye.[16] Also, alkyl-2-naphthols with C_5–C_{12} alkyl substituents have been used for liquid dyes with improved solubility.[17,18]

Another way to obtain solvent dyes is by converting an azo dye with a sulfonic group to an amide or ester through the sulfonyl chloride.[19] Dyes containing a carboxyl group similarly have been converted to solvent soluble dyes (I) and (II).[20,21] These dyes have somewhat

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[11] Nitto Boseki Co., *USP* 3,208,813.

[12] R. B. Orelup, *BP* 1,180,854.

[13] EKCo., *USP* 2,925,333.

[14] FH, *BP* 1,407,059.

[15] FBy, *DBP* 927,286.

[16] Allied, *Neth. Appl.* 66,011,126.

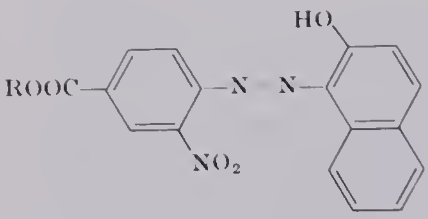
[17] BASF, *DBP* 836,383.

[18] Morton Int., *USP* 3,690,809.

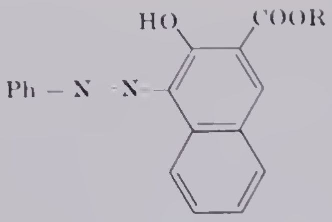
[19] CIBA, *BP* 779,880.

[20] CIBA, *BP* 790,797.

[21] CIBA, *USP* 2,888,452.



(I)



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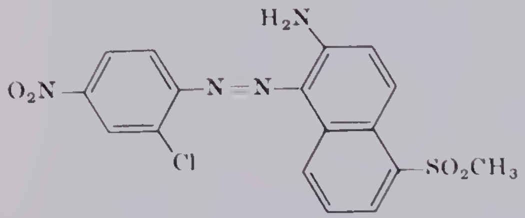

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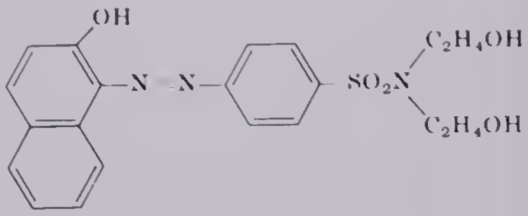

(IV)

better fastness and are recommended for lacquers. Other dyes in this series but with sulfone and sulfonamide groups (III and IV) are recommended for polymeric materials.[22,23]

Another group of dyes is made by using α-naphthylamine as a diazo component to couple with β-naphthol (Solvent Red 4), α-naphthylamine (Solvent Brown 3), or α-naphthol (Solvent Brown 5).

3. *Disazo Dyes*

Most disazo dyes start from aminoazobenzene derivatives and are red dyes. A few disazo dyes with conjugation interrupted by aliphatic carbon are yellow dyes.

Solvent Yellow 29, 31 (analog of Solvent Yellow 29 using *p-tert*-butylphenol) and to some degree Solvent Yellow 30 have good solvent solubility and improved lightfastness. They are recommended for spirit varnishes and inks. A similar yellow uses the same diazo component as Solvent Yellow 29 but 1-benzyl-3-methyl-5-pyrazolone as the coupler to give a highly soluble dye for ballpoint pen inks.[24]

The most important group of colors in this series is made by using various aminoazobenzene derivatives to couple with β-naphthol to give Solvent Red 23 through 27 (CI 26100, 26105, 26110, 26120, 26125). The following five 4-aminoazobenzenes are used, respectively: unsubstituted, 3,2′-Me_2,2,3′-Me_2, 2,5,2′-Me_3, mixed xylylazoxylidines. Solvent Red 24 and 26 are widely used in petroleum products.

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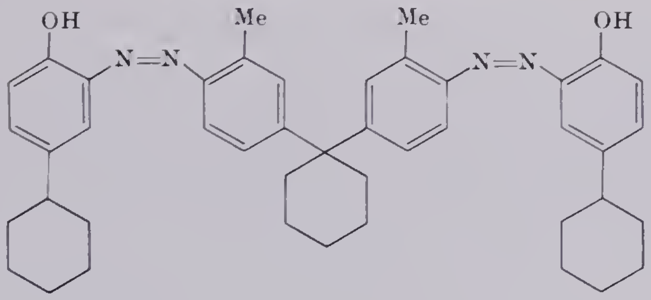
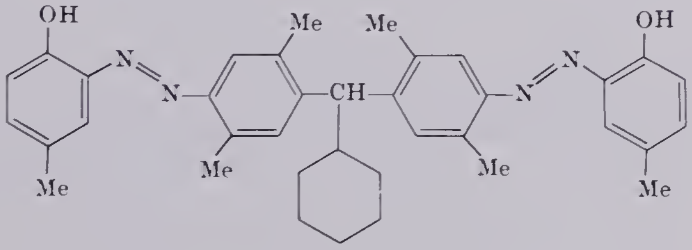
[22] Gy, *BeP* 630,024.

[23] FH, *BP* 1,217,351.

[24] FBy, *USP* 3,577,403.



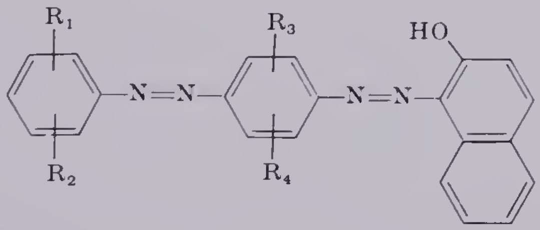
CI Solvent Yellow 29



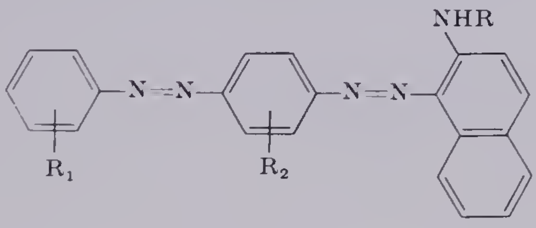
CI Solvent Yellow 30

Mixed primary amines, e.g., various toluidines, xylidines, and alkoxyanilines, are used to produce a mixture of aminoazobenzene intermediates, which are used for preparing disazo dyes of the general structure (V), which are hydrocarbon-soluble liquid dyes.[25]

Other hydrocarbon-soluble liquid red dyes, made from 2-alkylaminonaphthalene as a coupler, have the general structure (VI),



(V)



(VI)

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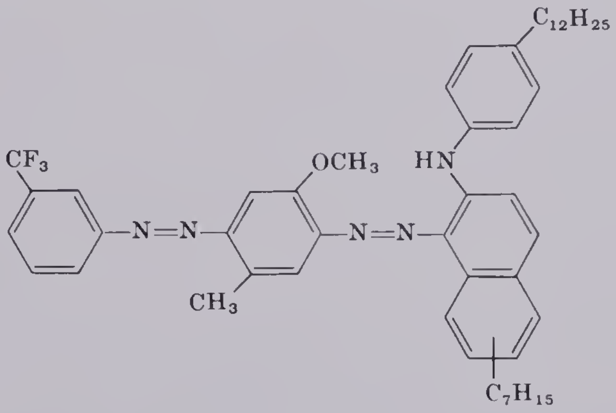
[25] Allied, *USP* 3,494,714.

where R may be a mixture of ethyl and isopropyl,[26] 2-ethylhexyl, *n*-octyl, etc.[27]

One drawback of some Solvent Reds when used in petroleum fuels is that they can be removed by common adsorbents such as clays, charcoal, and alumina. Disazo dyes (VII) with resistance to adsorption have been made to avoid the possibility of large-scale tax evasion.[28]



(VII)

Another solvent dye with considerable commercial importance is Solvent Black 3 (CI 26150; aniline → 1-naphthylamine → acetonide of 1,8-diaminonaphthalene).

4. *Other Azo Dyes*

Acetoacetic esters and acetoacetanilides have been used as couplers to give solvent dyes, such as (VIII)[29] and (IX).[30,31] Dye (IX) is recommended for coloring varnishes and is another example of the use of a sulfonamide group to impart solvent solubility.

1-Phenyl-3-methyl-5-pyrazolone has been used as a coupler and gives Solvent Yellow 16, 18, and 23 with aniline, 2,4-xylidine, and 4-amino-2-nitrotoluene as diazo components, respectively. Other pyrazolone dyes such as the analog of *o*-benzylaniline and (X) are claimed to be good solvent dyes.[32,33] Electronic spectra of some

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[26] FBy, *DBP* 1,645,876.

[27] BASF, *Ger. Offen*, 2,361,758; 2,413,369.

[28] Morton-Norwich, *USP* 3,862,120.

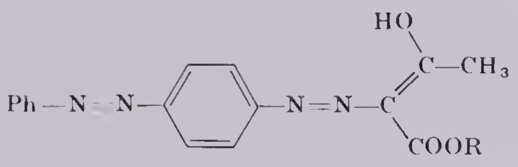
[29] Fran, *FP* 1,225,841.

[30] FH, *USP* 2,729,632.

[31] FH, *DBP* 1,021,104.

[32] CFM, *DBP* 818,221.

[33] FBy, *USP* 2,634,262.



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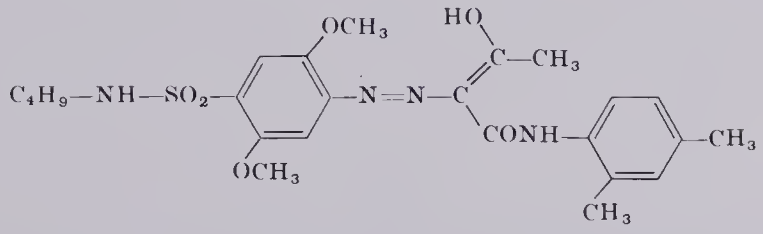
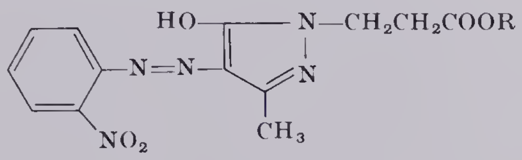


(IX)

substituted arylazopyrazolone dyes have been calculated and compared with experimental data.[34]



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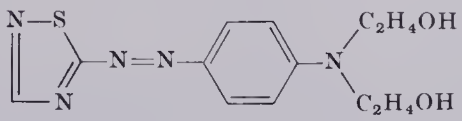

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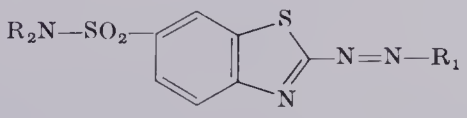

(XII)

Acetoacetanilide and pyrazolone dyes are more important as components for metal complex dyes rather than the simple azo dyes.

Many heterocyclic compounds have been used as either diazo or coupling components. Dyes made from 5-amino-1,2,4-thiadiazole (XI)[35] and from 2-aminobenzothiazole (XII)[36] are recommended for lacquer and plastic materials. Also, dyes made from 3,7-diaminodibenzothiophene dioxide (benzidine sulfone, *CSD I*, p. 130) are used as

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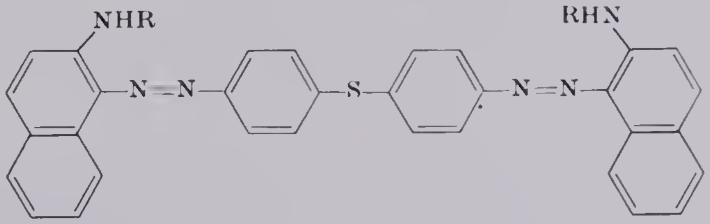
[34] J. Arriau, J. P. Campillo, and J. Deschamps, *Tetrahedron* **30**, 1353 (1974).

[35] FBy, *BP* 760,618.

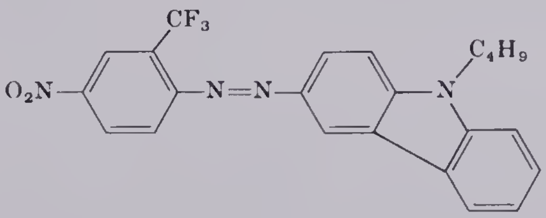
[36] S, *BP* 851,910.

solvent dyes.[37] A red liquid dye (XIII) can be obtained by tetraazotizing bis(4-aminophenyl) sulfide and coupling with C_6–C_{18} alkylaminonaphthalene.[38]



(XIII)

In addition, carbazole and pyridine derivatives have been used as couplers to give dyes (XIV)[39] and (XV).[40] Both are recommended as



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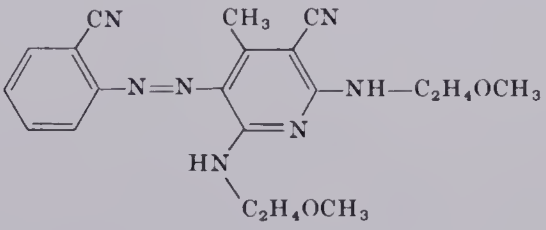


(XV)

heat- and light-stable colors for rigid plastic materials such as polystyrene.

Also, dyes with the general formula (XVI)[41] are recommended for printing inks and formula (XVII)[42] for light-stable olefin resin.

A disazo dye (XVIII) for alcohol-based printing inks is made by condensing Chrysoidine base with formaldehyde.[43]

[37] Allied, *USP* 2,879,266.

[38] Fran, *Ger. Offen.* 2,523,268.

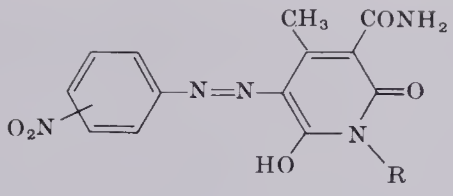
[39] AAP, *USP* 3,897,203.

[40] BASF, *Ger. Offen.* 2,409,754.

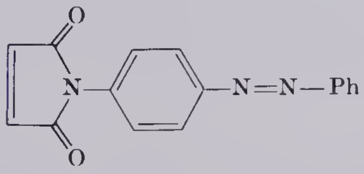
[41] ICI, *Ger. Offen.* 2,216,207.

[42] EKCo., *USP* 3,361,707.

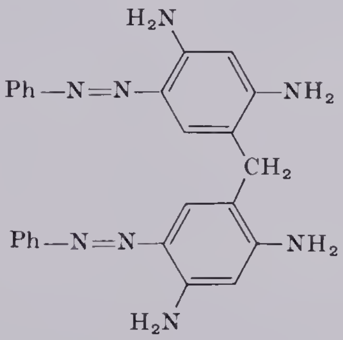
[43] Williams Hounslow Ltd., *Ger. Offen.* 2,419,821.



(XVI)



(XVII)



(XVIII)

Polyazo dyes are generally not suitable for solvent dyes due to poor solubility. However, the product obtained by coupling 2 moles of diazotized aminoazobenzene with 1 mole of resorcinol is claimed to be a useful solvent dye for polymethyl methacrylates.[44]

B. Azo Metal Complex Dyes

The first prechromed dyes appeared in 1912 with the introduction of the Ergans (BASF). These were azosalicylic acid derivatives. Soon Neolan (Ciba) and Palatine Fast (BASF) were developed. They were 1:1 chromium complexes of *o*,*o*′-dihydroxyazo dyes and were precursors of the metal complex dyes that are used today as solvent dyes. The range of premetallized azo dyes was further extended by the development of 2:1 chromed neutral dyeing colors such as Irgalan (Gy), Perlon (FBy), Cibalan (Ciba), Capracyl (DUP), and Lanamid (Allied). The earlier-developed premetallized dyes were used for dyeing textile fibers but were soon found to be useful solvent dyes. Some of the Zapon Fast dyes introduced by IG around 1930 for the coloring of transparent lacquers

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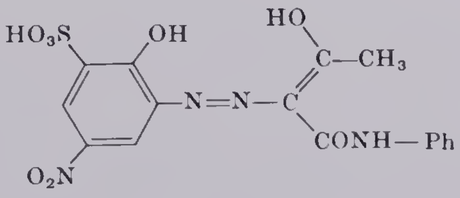
[44] AAP, *USP* 3,350,383.

were the first metal complex dyes used for nontextile applications. More recently, the solubility of these metal complex dyes was further improved by modifying the classic metal complex dyes with solubilizing amine. Neozapon dyes (BASF) represent this type of solvent dye.[45] Due to high color strength, brilliant shades, good fastness, and solubility, their use in printing inks and lacquers has increased steadily. Price (*CSD III*) has recently reviewed the chemistry of the metal complex dyes. Only chromium and cobalt are used in making solvent dyes.

1. *Acetoacetanilide Dyes*

Two of the earlier Zapon Fast colors were CI Solvent Yellow 19 and CI Solvent Orange 45. The former is the Cr complex of (XIX), and the latter the Co complex of the analog without the sulfonic group.



Cr complex

(XIX)

Solvent Yellow 19 is still an important color, used not only as a self shade, but also as an acid component for Solvent Red 36, 79, and 109. The Co complex of (2-aminophenol-4-sulfonamide → acetoacetanilide) is a solvent dye.[46]

2. *Pyrazolone Dyes*

Chromium complexes of dyes made from 1-phenyl-3-methyl-5-pyrazolone provide important yellows, oranges, and reds. Solvent Yellow 21 (CI 18690), made from diazotized anthranilic acid is a reddish yellow. It has good lightfastness and is used extensively in spirit lacquers, alcohol-based inks, wood stains, etc. The chlorinated derivatives have also been made.[47,48] Solvent Orange 5 (2-amino-4-nitrophenol-6-sulfonic acid →) is also used extensively in spirit solvents. Solvent Orange 62 (2-amino-4-nitrophenol →) and Red 8 (2-amino-5-nitrophenol →) are isomers; mixtures of the two are known as Solvent Red 100 and 142.

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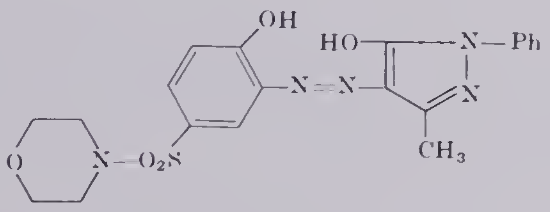
[45] G. Rieder and H. Sixtus, *Br. Ink Maker* 12. 133 (1970).

[46] Fran, *USP* 2,840,552.

[47] S, *BP* 807,695.

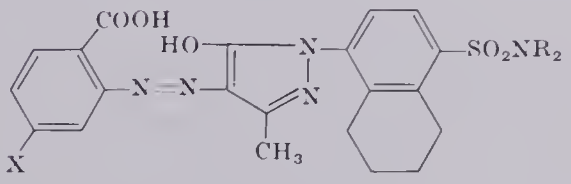
[48] BASF, *BP* 823,393.

Various sulfonamide groups have been introduced either into the diazo component as in (XX)[49] or into the pyrazolone component as in (XXI).[50] Many related colors have been reported.[51] In addition, metal complex dyes have been made from 1-phenyl-5-pyrazolone 3-carboxylic acid,[52] its amide,[53] 1-aryl-3-alkyl-4-pyrazolones[54] and 1-phenyl-3-methyl-5-aminopyrazole.[55]



Cr complex

(XX)



Cr complex

(XXI)

3. *Phenol and Naphthol Dyes*

Although metal complex dyes have been made by using phenols (e.g., 2,4-dichlorophenol and 4-methoxyphenol),[56] they are generally weak in color strength and are not as important as the red, violet, and black 2:1 metal complexes of the dyes from β-naphthol. CI Solvent Red 102 is the Cr complex of the dye from diazotized 2-aminophenol-4-sulfonamide. Solvent Violet 1 and Black 34 are the Co and Cr complexes, respectively, of the dye from diazotized 2-amino-5-nitrophenol. Solvent Black 35 is a mixture of Black 34 and the isomer from 2-amino-4-nitrophenol.

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[49] GAF, *USP* 2,834,772.

[50] S, *USP* 2,839,522.

[51] ICI, *BP* 793,712; S, *BP* 795,417; CIBA, *DBP* 1,110,349; *USP* 2,897,189; Saul and Co., *USP* 2,864,814; BASF, *BP* 793,136; FBy, *DBP* 957,871.

[52] FH, *DBP* 1,020,425.

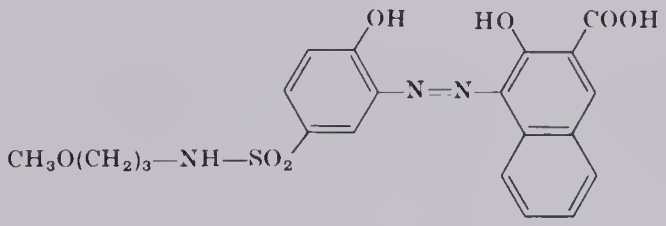
[53] CIBA, *BP* 838,657.

[54] BASF, *DBP* 1,060,522.

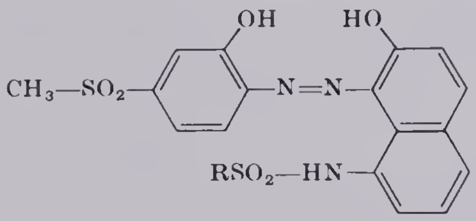
[55] S, *BP* 837,716.

[56] BASF, *BP* 794,473; 865,410; Fran, *FP* 1,191,027; CIBA, *SP* 329,046; 340,285.

Various *N*-substituted sulfonamide groups have been introduced to modify the solubility character,[57] as in dyes (XXII)[58] and (XXIII).[59]

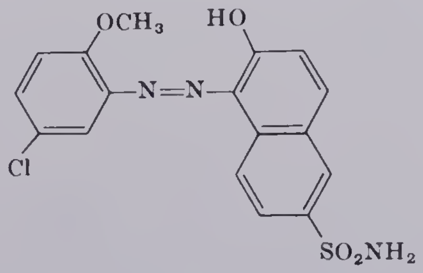


Cr complex
(XXII)

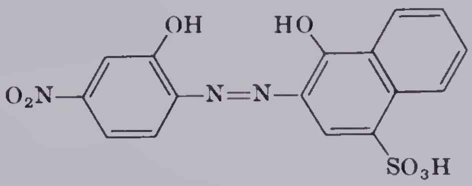


Cr complex
(XXIII)

Also, metal complex dyes have been made from 2-naphthol substituted by acetamido[60] and sulfonamide groups.[61] When the dyes (XXIV)



(XXIV)



(XXV)

[57] FBy, *BP* 948,837; S, *BP* 835,772; BASF, *USP* 2,954,370; Gy, *USP* 2,933,490.

[58] S, *BP* 805,217; Gy, *DBP* 1,110,786.

[59] Fran, *FP* 1,095,561.

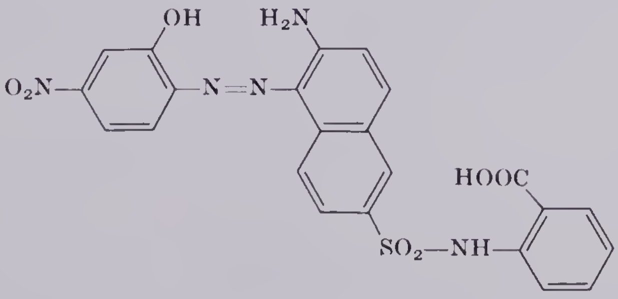
[60] Gy, *BP* 838,791; S, *SP* 327,162.

[61] S, *USP* 2,909,515.

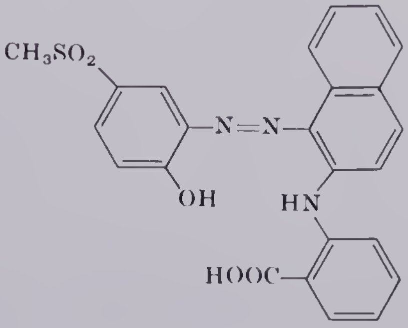
and (XXV) are metallized, the methyl and sulfonic groups, respectively, are lost.[62,63]

4. *Miscellaneous Types*

Metal complex dyes have been prepared from *o*-aminoazo derivatives, such as (XXVI)[64] and (XXVII).[65] These are olive to blue-gray dyes recommended for nitro and vinyl lacquers.



Cr, Co complex
(XXVI)



Cr, Co complex
(XXVII)

Metal complex dyes have been made from acenaphthene[66] and thianaphthene.[67] An interesting method for making such azo dyes (e.g., XXVIII) is to condense an arylhydrazine with acenaphthenequinone.[68]

Solvent Red 99, a yellowish red color used for lacquer, is a 1:1 chromium complex (XXIX) made from 2,4-quinolinediol. Solvent

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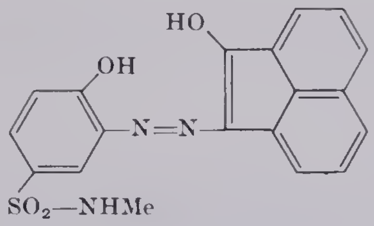
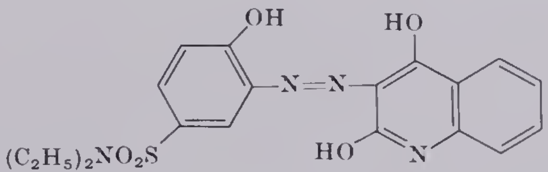
[62] BASF, *DBP* 1,060,520.
[63] BASF, *DBP* 931,061.
[64] S, *SP* 384,108.
[65] Gy, *USP* 2,822,360.
[66] Fran, *FP* 1,199,729.
[67] BASF, *BP* 824,300.
[68] S, *USP* 2,928,823.



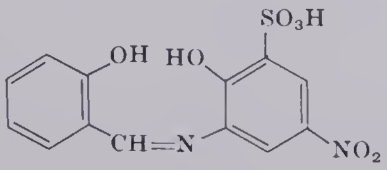
(XXVIII)

Yellow 32 is an azomethine dye (XXX) from salicylaldehyde. Similar azomethine dyes have been made from 2-hydroxy-1-naphthaldehyde.[69]



Cr complex

(XXIX)



Cr complex

(XXX)

C. Triarylmethane and Related Dyes*

The free bases are used as solvent dyes, and for this purpose they can be further divided into xanthenes, triarylmethanes, azines, and thiazines.

1. *Xanthene Dyes*

These dyes are mostly red. They can be divided into hydroxy- and aminoxanthenes. Most hydroxyxanthenes are acid dyes. The free acids or their esters are used as solvent dyes, but they are less important. Fluorescein (Solvent Yellow 94), Eosine (Solvent Red 43), Phloxine (Solvent Red 48), and a few others are still used as biological stains. Some are also used as drug and cosmetic colors. Eosine is used as D & C Red No. 21, Phloxine as D & C Red No. 27, Solvent Red 72 as D & C Orange No. 5, and Solvent Red 73 as D & C Orange No. 10. They are

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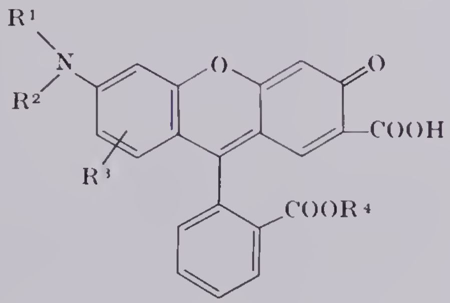
*See *CSD II* and *IV*.

[69] Gy, *Ger. Offen.* 2,025,111.

not as widely used as the aminoxanthenes. Mixed amino- and hydroxyxanthene dyes are also used. An interesting solvent dye (XXXI) is made by converting such xanthenes to a chromium complex with 3-(2-ethyl hexyloxy)propylamine, and it is recommended for aluminum coating.[70]



Cr complex
(XXXI)

Rhodamine dyes dominate the aminoxanthene series. In addition to many uses in alcohols, fatty acids, lacquers, and inks, they are used as daylight-fluorescent colors, which require that they fluoresce at wavelengths similar to those that are normally reflected. Thus, the color that reaches the eye contains not only the light normally reflected from the illumination, but also light from fluorescence. This gives an intense color with a dominant wavelength of extreme purity. Rhodamine B base (Solvent Red 49) and Rhodamine 6GDN base (CI 45160, Rhodamine 6GDN, Basic Red 1, is an ethyl ester) have such fluorescent character so that they are used extensively in daylight-fluorescent colors.[71]

Rhodamine B is available as a solution containing an organic acid, water, and a solvent such as acetonitrile.[72] Rhodamine 6GDN is also converted to liquid form in glycol.[73] The modified rhodamine dye (XXXIIA) is obtained by treating the free base with ethyl- or methylsulfuric acid in alcohol.[74] The product is water insoluble and is recommended for ballpoint pen inks. The free base can also be treated with diethyl sulfate in glycol or glycol ether to give the liquid rhodamine dye (XXXIIA and B).[75]

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[70] Taoka Dyestaff Mfg. Co., *JP* 124,124/74; *CA* 83, 81224.

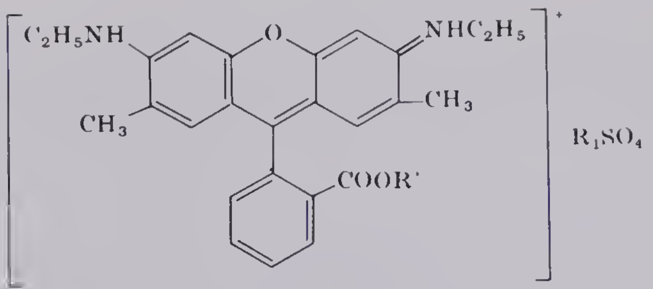
[71] Hercules, *Ger. Offen.* 2,452,870. Sherwin-Williams, *BP* 1,191,483; Japan Fluorescent, *JP* 24,515/73; *CA* 80, 110037.

[72] BASF, *USP* 3,346,322.

[73] DUP, *USP* 3,767,358.

[74] BASF, *USP* 3,708,499.

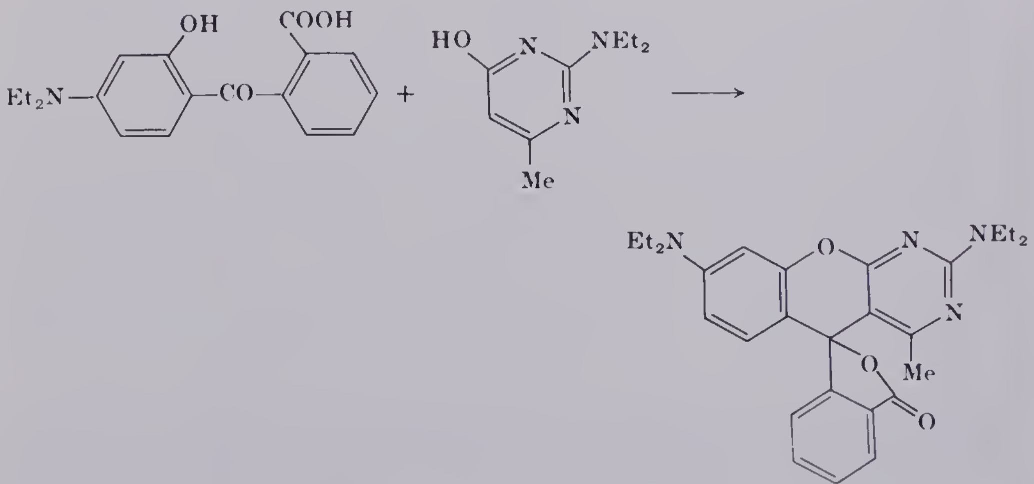
[75] BASF, *USP* 3,849,065.



(XXXIIA) $R, R_1 = CH_3$ or C_2H_5
(XXXIIB) $R = CH_2CH_2OR_1$
$R_1 = CH_3$ or C_2H_5

The diazaxanthene dye (XXXIII, Chart 1) is recommended for color precursors.[76]

Chart 1



(XXXIII)

2. *Triarylmethane Dyes*

The free bases provide solvent violets, blues, and greens. Methyl Violet base (Solvent Violet 8) is an important color in this series. Crystal Violet base (Solvent Violet 9), Victoria Blue bases (Solvent Blue 4, 5, and 6), and Malachite Green base (Solvent Green 1) also find important uses as solvent dyes.

It should be noted that most of the free bases are in the colorless carbinol structure, especially in the pure state. By the loss of one H_2O, some of the free bases are in weak red quinone forms such as Victora Pure Blue B0 base (CI 42595, XXXIV). In either case, an acid will

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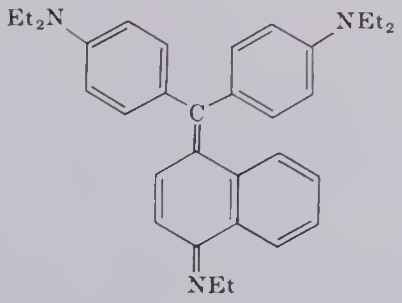
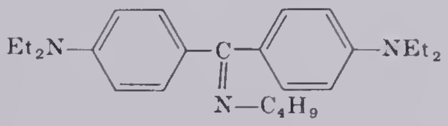
[76] BASF, *USP* 3,896,128.



(XXXIV)



(XXXV)

convert them to the salts with the original hue. They have good solubility in fatty acids, but rather poor solubility in many other solvents. For these reasons, fatty acids are usually included in their formulation when these dye bases are used for typewriter ribbons, copying papers, ballpoint pen inks, printing inks, and lacquers. In order to improve the solubility in alcohols and glycols, many modified salts have been made. These include nitrate,[77] organic salts of benzenesulfonic acid,[78] 3-methylphenol-2,4-disulfonic acid,[79] stilbene disulfonic acid,[80] salicylic acid,[81] 4,5′-bis(*p*-hydroxyphenyl)pentanoic acid, and[82] orthophosphate.[83]

Among the diarylmethanes Auramine base (CI 41000:1) is used as a solvent dye. A modified *N*-substituted Auramine dye (XXXV) is recommended for printing ink.[84] Some of the leuco Auramine derivatives are stable colorless compounds.[85] They turn a deep color when brought into contact with an acid like the carbinols of triarylmethanes. This unique property is being used to develop colorless copy paper and other thermo- or pressure-sensitive recording systems (see *CSD IV*, p. 103).[86]

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[77] BASF, *USP* 3,682,979.

[78] LBH, *FP* 1,355,969.

[79] Hodogaya, *JP* 24,667/70; *CA* **73**, 131990.

[80] B. V. Zychlinski, *DBP* 1,195,887.

[81] FBy, *DBP* 930,168.

[82] Interchemical, *USP* 3,353,972.

[83] J. S. Staedtler, *BP* 1,214,349.

[84] BASF, *Ger. Offen.* 2,158,954.

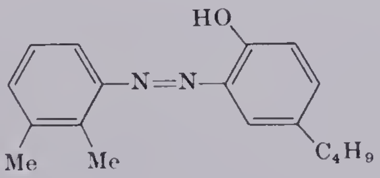
[85] Allied, *USP* 2,948,753; 2,981,733; 2,981,738; 2,983,756.

[86] Fuji Photo, *Ger. Offen.* 2,142,173; see also R. Garner, *Rep. Prog. Appl. Chem.* **57**, 135 (1973).

3. *Azines and Thiazines*

Mauve, the first synthetic dye, made in 1856, is an azine. Today, two important solvent dyes are similar but more complex azines. Induline (Solvent Blue 7, CI 50400) is usually a mixture of trianilino and tetraanilino derivatives; the latter gives a greener shade. Nigrosines (Solvent Black 5 and 7, CI 50415) are various mixtures of complex azines mixed with some oxazines. The shades vary from bluish black to deep black, depending upon the manufacturing conditions. Both Indulines and Nigrosines are used as the free bases for oil- and wax-soluble solvent dyes and also as the chlorides for alcohol-soluble solvent dyes. Because of their low cost, Nigrosines are the largest-volume solvent dyes. Although their production is not listed in recent U.S. Tariff Commission Reports, the estimated use in plastics alone was 2.5 million pounds in 1974.[87]

To improve fat and wax solubility, a process has been developed involving the addition of fatty acid during the fusion of Nigrosine dyes.[88] Extra pure Nigrosine or Induline colors can be made by heating the finely divided color bases with dilute mineral acid to remove impurities.[89] Stable glycol-based inks can be made by converting the Nigrosine or Induline to C_1–C_8 organic acid salts.[90] Heat absorbency and stability of polyethylene film are improved by adding 0.5% Nigrosine and 0.01% cobalt acetylacetone.[91] A modified black azine dye can be obtained by fusing aniline salt with the azo compound (XXXVI).[92] Also, a modified granule Nigrosine dye with better solubility can be obtained by reacting aniline with 4-butylnitrobenzene.[93]



(XXXVI)

The only well-known thiazine dye is Methylene Blue (CI 52015), more important as a basic dye (Basic Blue 9). Its free base is Solvent Blue 8, which is a greenish gray shade that is not as widely used as

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[87] *Mod Plast.* 52, 49 (1975).

[88] BASF, *DBP* 890,104.

[89] BASF, *BP* 1,045,129.

[90] ICI, *BP* 934,356.

[91] EKCo. *USP* 3,592,792.

[92] Taoka, *JP* 52,825/73; *CA* 79, 12739.

[93] Taoka, *JP* 148,427/75; *CA* 84, 75708.

triarylmethane blue bases. The *N*-benzoyl derivative of leuco Methylene Blue is used for felt-tipped markers.[94]

D. Amine and Basic Dye Complexes of Acid Dyes

As mentioned earlier, Zapon Fast dyes were the first group of colors especially developed for solvent dyes. Some of them are metal complex dyes, but most are organic amine salts of dyes with acid groups. Since their development many new colors have been promoted by different manufacturers. They represent an improvement over the simple oil colors in the following respects:

1. They generally have better fastness to light.
2. They show much improved sublimation and migration characteristics over oil colors. Due to their larger molecules and their ionic nature, they remain fixed in the area where they are applied.
3. They give brilliant, deep shades that are not available with oil-soluble colors, particularly in the yellow and red range.
4. They have excellent solubility in a variety of solvents. In this respect, the amine salts are better than classic metal complex dyes, which are generally limited to use in alcoholic solvents. The selected amine salts can be made soluble not only in alcohols and ketones, but also in benzene and toluene. They are not very soluble in mineral spirits and vegetable oils and therefore show no tendency to bleed through dry oil, varnish, or enamel coatings.

The composition of earlier Zapon colors has been reported in *CSD II*. The amines used in earlier dyes were cyclohexylamine, dicyclohexylamine, diarylguanidines, and diisoamylamine.[95] Diarylguanidines and dicyclohexylamine are still being used in many colors.

1. *Amine Salts of Azo Acid Dyes*

Pyrazolone dyes (XXXVII) are often chosen for yellows (Table II).[96–100] Dye (XXXVIII) is a Solvent Orange, but aminoazobenzene and its derivatives are more often used in making red dyes such as Solvent Red 30, 31, and 32 (CI 27291, 27306, and 26766). Solvent Red 30, a yellowish red and the most important, is the dicyclohexylamine

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[94] National Cash Register, *USP* 3,769,066; see also *CSD IV*, p. 158.

[95] GAF, *USP* 1,800,300; DUP, *USP* 1,674,128; Allied, *USP* 2,095,077.

[96] ACY, *USP* 2,721,111.

[97] FH, *DBP* 946,732.

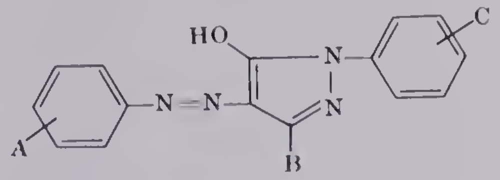
[98] Fran, *FP* 1,199,654.

[99] FH, *USP* 2,816,886.

[100] CGY, *Ger. Offen.* 2,106,085.

TABLE II

Amine Salts of Pyrazolone Dyes



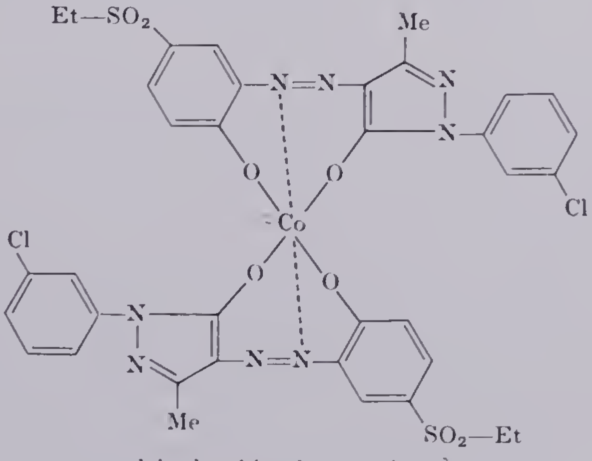
(XXXVII)

Dye	*A*	*B*	*C*	*Amine*	*Reference*
Solvent Yellow 15	2-SO_3H	COOH	2-SO_3H	Dicyclohexylamine	CI 19120:1
	H	CH_3	2-Cl,5-SO_3H	Rosin amine	96
	2-NO_2	CH_3	2-SO_3H	Dicyclohexylamine	97
	4-$CONHC_6H_{11}$	CH_3	4-SO_3H	Dicyclohexylamine	98
XXXVIII	4-$C_6H_4N{=}N$	COOH	2-SO_3H	Dicyclohexylamine	99
	2-SO_3H	$COOC_2H_5$	4-CH_3,2-SO_3H	Dicyclohexylamine	100

salt of the dye (4-aminoazobenzene → G-acid). Modified dyes, using other amines such as dibutylamine[101] or 1-(β-ethylhexoxy)-3-aminopropane[102] have good solubility in alcohol, improved migration stability, and heat resistance. Therefore, they are suitable for bulk dyeing of polypropylene.

Most azo dyes give yellow to red solvent dyes. However, Solvent Blue 37 (CI 13390), a navy blue, is the salt of CI Acid Blue 92 (H-acid → *N*-phenyl periacid) with an organic base.

Classic 2:1 metal complexes derived from *o,o′*-dihydroxyazo dyes are usually in the form of sodium salts. The solubility of these dyes can be further increased by converting them to amine salts. Thus, Solvent Yellow 82 is such a converted product of CI 18690, and Solvent Red 122 is that of CI 12716. Similar amine salts, such as (XXXIX)[103] have been made.[104]



dehydroabietylammonium$^{\oplus}$

(XXXIX)

Metal complexes containing sulfonic acid groups have also been converted to amine salts for better solubility. Solvent Orange 56 is converted from CI 18745:1, and Solvent Yellow 81 from CI 13900:1. Other dyes having good solubility and fastness properties, such as (XL),[105] have been made.[106]

A novel method of preparation of organic solvent-soluble dyes from water-soluble acid dyes is to use an emulsifier such as the acid phosphate

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[101] FBy, *USP* 3,640,994.

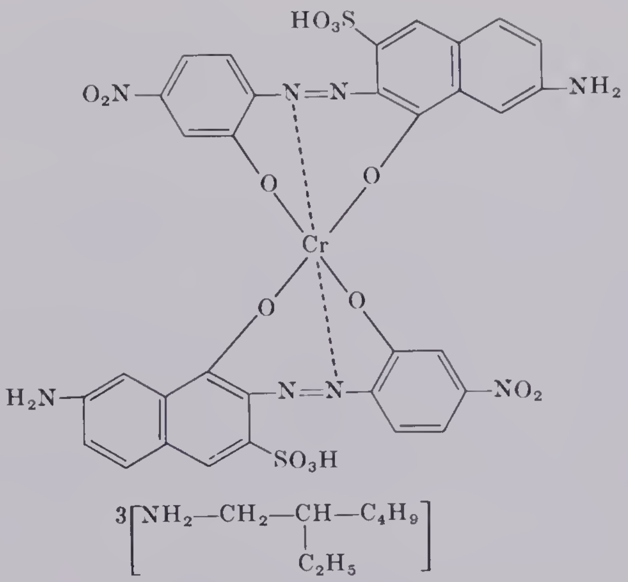
[102] BASF, *USP* 3,828,020.

[103] Gy, *USP* 3,551,170.

[104] Taoka, *JP* 124,120/74; 116,126/74; *CA* 83, 116926; 195206.

[105] Hodogaya, *JP* 123,146/75; 10,323/75; *CA* 83, 81192.

[106] ACY, *USP* 2,937,165; CGY, *Ger Offen.* 2,238,773.



(XL)

of the nonionic condensation product of a dialkylphenol or an alkanol and ethylene oxide.[107] Acid Yellow 116 and Acid Green 23 are made soluble in perchloroethylene by this method.

Instead of using a colorless organic base to solubilize acid dyes, free bases of basic dyes have been used to give alcohol-soluble dyes. Solvent Red 35, 36, 79, and 109 and Solvent Violet 2 all use Rhodamine bases (CI 45160 and 45170) to form salts with different acid dyes. They are brighter than acid dyes and have better lightfastness than basic dyes. Various combinations of this type are recommended for ballpoint pen inks[108] and felt-tipped marker inks.[109] Blue and green solvent dyes of this type are usually anthraquinones (Solvent Blue 74, CI 63005), azines (Solvent Blue 49, CI 50315 and Solvent Blue 50, CI 50320), or phthalocyanines.

2. *Amine Salts of Phthalocyanine Dyes and Related Colors*

The most important Solvent Blues are derived from copper phthalocyanine (CuPc), because of the reasonable cost, superior fastness, and the pleasing turquoise shade. Many molecular modifications have been made in converting this pigment into a soluble dye. The CI colors are listed in Table III.

All the dyes in Table III are derived from sulfonated copper phthalocyanine. Solvent Blue 24 and 38 are made by converting the sulfonic

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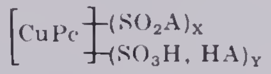
[107] Pechiney-Saint-Gobain, *USP* 3,915,630.

[108] Gillette, *USP* 3,597,244; B. V. Zychlinski, *FP* 1,397,267.

[109] ACY, *USP* 3,705,045.

TABLE III

Copper Phthalocyanine Dyes

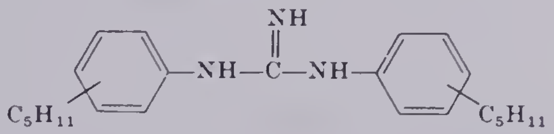


$$\left[\mathrm{CuPc}\right]\begin{matrix}-(SO_2A)_X\\-(SO_3H,\ HA)_Y\end{matrix}$$

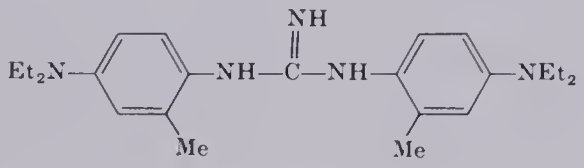
(XLI)

CI Solvent	*CI*	*HA*	*X*	*Y*
Blue 24	74380	Dimethylamine	0	2–4
Blue 25	74350	Isohexylamine	2–3	1–2
Blue 38	74180	Organic bases	0	2–3
Blue 55	74400	Isoundecylamine	2–3	1
Blue 89	74340	Organic base	3	0

acids to amine salts. Among many methods developed for converting the insoluble copper phthalocyanine to a solvent dye,[110] this is one of the earliest and is still an effective way to get a good alcohol-soluble solvent dye at a reasonable cost.[111] Solvent Blue 38 is especially popular. It has slightly different compositions among the many commercial products, with various degrees of sulfonation and use of slightly different amines. Most commercial Solvent Blue 38 dyes are probably the diarylguanidine salts. Inorganic sulfate contamination can be removed by treatment with calcium or barium chloride to give a grit-free color for inks.[112] Modified guanidines, such as (XLII) and (XLIII), have been used.[113] Again, free bases of some basic dyes may be used to replace the guanidines to give various shades of color for



(XLII)



(XLIII)

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[110] F. H. Moser and A. L. Thomas, "Phthalocyanine Compounds." Van Nostrand-Reinhold, Princeton, New Jersey, 1963.

[111] ICI, *USP* 2,150,741; DUP, *USP* 2,153,740; GAF, *USP* 2,187,816.

[112] ACY, *USP* 3,010,970.

[113] Allied, *USP* 3,470,200–1.

ballpoint pen inks.[114] Another interesting approach for obtaining a solvent-soluble dye is to use copper phthalocyanine derivatives containing basic substituents to form a salt with acid triarylmethane dyes[115] or other acid dyes.[116] The latter approach may give more lightfast products by using selected acid dyes.

To modify the solubility and bleeding character, copper phthalocyanine with mixed sulfonyl chloride and sulfonic acid is used to react with various amines to give mixed amides and amine salts. Solvent Blue 25 and 55 are such products. Other amines used for this type of product are $R—NH(CH_2)_x—NH—CH_2CH_2NH_2$,[117] $C_{12}H_{25}O(CH_2)_xNH_2$,[118] $HO—R—NH_2$,[119] and 2-iminohexahydropyrimidine.[120]

When copper phthalocyaninesulfonyl chloride is reacted with selected amines, the resulting amides may have the character of oil-soluble dyes. Solvent Blue 89 is this type of color. The amines used could be 2-ethylhexylamine,[121] 3-methoxypropylamine,[122] 2-acetoxyethylamine,[123] isopentoxypropylamine,[124] or dimethylaminopropylamine.[125] When the last amine is used, the product not only has good solubility in a glycol solvent, but also can be made water-soluble by converting it into a salt and using it as a basic dye. CI Solvent Blue 51 may be obtained in this way. More recently, a similar dye has been made by using dibutylaminopropylamine for condensation.[126]

Instead of using an amine, an alkyl- or alkoxyphenol may be used to react with copper phthalocyanine tri- or tetrasulfonyl chloride to give $CuPc(SO_3Ar)_{3-4}$. The product is recommended for coloring varnishes, fuels, and waxes.[127]

A special vanadium phthalocyanine containing $SO_2N(C_4H_9)_2$ groups is used for coloring plastic material in protective goggle lenses, face shields, etc.[128]

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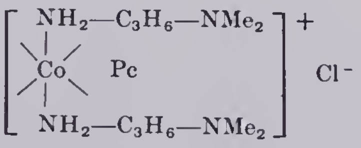
[114] DUP, *USP* 2,950,286; BASF, *BP* 902,110.
[115] Zychlinski, *DBP* 1,132,275.
[116] BASF, *DBP* 1,248,835.
[117] Gy, *USP* 3,057,873.
[118] Hodogaya, *JP* 059,586/67.
[119] FBy, *BP* 1,059,457.
[120] Gy, *USP* 3,082,213.
[121] S, *SP* 341,591; *USP* 3,136,777.
[122] CIBA, *USP* 2,897,207.
[123] ICI, *BP* 883,807.
[124] BASF, *DBP* 1,203,404.
[125] FBy, *USP* 2,863,875.
[126] Allied, *USP* 3,954,392.
[127] FBy, *USP* 3,634,451.
[128] ACY, *USP* 3,853,783.

A very interesting solvent-soluble dye is made by treating cobalt phthalocyanine with an oxidizing agent in the presence of an anion and with an aliphatic amine to give a coordinatively hexavalent complex salt of trivalent cobalt, such as (XLIV).[129] The product is alcohol-soluble and is used for lacquers and ballpoint pen inks.



(XLIV)

Another way to introduce solvent-soluble character is by chloromethylation of copper phthalocyanine followed by reacting the intermediate with an amine[130] or a thio compound[131]; but this approach will not be commercially important in the future, since the reagent, bischloromethyl ether, was found to be carcinogenic.[132]

E. Anthraquinone and Related Dyes

While azo dyes supply most solvent yellows, oranges, and reds, anthraquinones provide most solvent violets, blues, and greens. The lightfastness and chemical resistance of anthraquinone dyes are generally superior to these of azo colors. This is especially true of α-alkyl- or arylaminoanthraquinone in which the amino hydrogen is strongly bonded with a quinone carbonyl. These α-substituted derivatives are readily available from sulfonated or halogenated anthraquinones or from leucoquinizarin. The simple 1,4-bisalkylaminoanthraquinones are used for coloring petroleum products, oils, waxes, etc. Many newer anthraquinone solvent dyes are being introduced to color plastic materials where the requirements for lightfastness and thermal and chemical resistance are more demanding.

CI 58840, 1,8-bisphenylthioanthraquinone, misplaced in CI as a pigment, is a yellow solvent dye. In its lightfastness and heat stability in polystyrene and polymethyl methacrylate, it is far superior to conventional azo solvent yellows. In addition, it is not affected by peroxide catalyst and exhibits no anticatalyst effect when used in monomer prior to polymerization.[133]

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[129] FBy, *USP* 3,636,040.

[130] ICI, *USP* 3,042,683; GAF, *USP* 2,547,972; 2,859,219.

[131] BASF, *USP* 2,759,950.

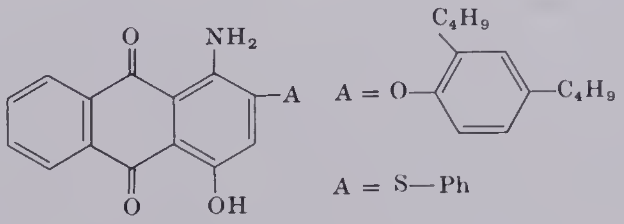
[132] B. L. Van Duuren, A. Sivak, B. M. Goldschmidt, C. Katz, and S. Melchionne, *J. Nat. Cancer Inst.* **43**, 481 (1969).

[133] Allied, *USP* 3,441,536.

Solvent Red 111, 1-methylaminoanthraquinone, initially used in plastic materials, has been replaced by newer anthraquinone reds in some applications. 1-Cyclohexylaminoanthraquinone, a slightly bluer red, has better lightfastness and heat stability in polystyrene and methyl methacrylate.[134] 1-(2-Hydroxyethylamino)anthraquinone also shows better heat resistance in polystyrene.[135] 1-(4-Butylanilino)-anthraquinone has been shown to have excellent heat stability in fluorocarbon refrigerants and is recommended for leak detecting refrigeration compositions.[136] Most of these products are prepared by the condensation of 1-chloroanthraquinone with amines. Many substituted 1-arylaminoanthraquinones have been made this way and the factors influencing the color of the dyes have been discussed.[137,138] 1-α-Anthraquinonylamino-3,5-diphenoxy-*s*-triazine is recommended for coloring ABS resin yellow.[139]

CI Solvent Violet 11 (1,4-diaminoanthraquinone), a bright violet, has good lightfastness even at low concentrations. It is used in cellulose acetate and other plastic materials. CI Solvent Violet 13 (CI 60725, 1-hydroxy-4-*p*-toluidinoanthraquinone) is used as a tracer for some petroleum fuels.

1-Amino-4-hydroxyanthraquinone is a weak color with poor lightfastness, but the 2-substituted derivatives (XLV A and B) have been recommended for polymeric material.[140]



(XLVA)

(XLVB)

These dyes are normally obtained from 1-amino-4-bromoanthraquinone-2-sulfonic acid. Recently an interesting process has been developed by a different route[141]; the phthalimide (XLVI) yields the corresponding 1-aminoanthraquinone (XLVII) by heating with sulfuric and boric acids at 100°–180°. Previous attempts to make substituted aminoanthraquinones directly through Friedel–Craft reactions were

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[134] Allied, *USP* 3,312,655.

[135] MCI, *JP* 29,614/71; *CA* 77, 35693.

[136] DUP, *USP* 3,770,640.

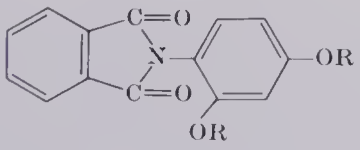
[137] W. M. Lord and A. T. Peters, *J. Chem. Soc.* p. 2305 (1973).

[138] T. Hayashi and M. Matsuo, *Bull. Chem. Soc. Jpn.* **35**, 1500 (1962).

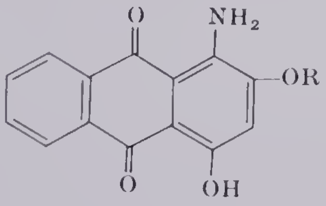
[139] KYK, *JP*, 60,569/75; *CA* **83**, 165135.

[140] DUP, *USP* 3,536,735; FBy, *FP* 2,057,018.

[141] FBy, *USP* 3,947,477.



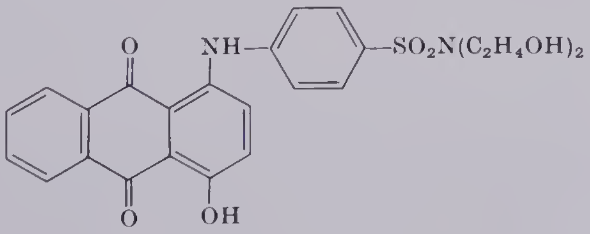
(XLVI)



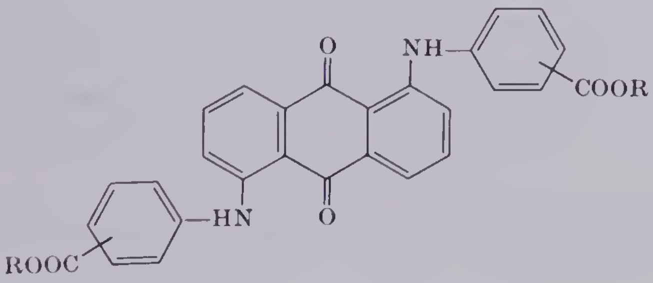
(XLVII)

not very successful. Solvent Violet 14 (CI 61705) (1,5-and some 1,8-bis-*p*-toluidinoanthraquinone) has better heat resistance and lightfastness in thermoplastic resins. Modified products with halogenated anilino groups[142,143] as well as 1,8 isomers[144] are both recommended for mass coloring of polymers.

Other related anthraquinone dyes having the anilino group substituted with a sulfonamide group such as (XLVIII) or ester group (XLIX) are used for spin-dyeing of polyesters.[145]



(XLVIII)



(XLIX)

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[142] CGY, *Ger. Offen.* 2,418,379.

[143] Oriental, *JP*, 31,240/73; *CA* 79, 67353.

[144] Fuji Photo, *JP* 059,673/68.

[145] GAF, *USP* 2,730,534; CIBA, *USP* 3,522,264; *BP* 928,619; ICI, *USP* 3,424,708; FBy, *BP* 803,525.

When both 1- and 4-positions of anthraquinone are substituted with alkyl or arylamino groups, the shade shifts to the blue-green range. 1,4-Bisalkylaminoanthraquinones constitute many Solvent Blues, Solvent Blue 36 (1,4-bisisopropylaminoanthraquinone) probably being the most popular. Most of these dyes are used for coloring petroleum products, but they may also be used for lacquer stain and resin materials.

Solvent blues used especially for petroleum products have also been made in liquid forms. This can be done by dissolving a mixture of 1,4-bisbutylaminoanthraquinone and 1,4-bis-3-(2-ethylhexoxy)propylaminoanthraquinone in dehydronorbornyl methyl ketone,[146] or by condensing leucoquinizarin with at least two different amines such as 3-(2′-ethylhexoxy)propylamine, 2-ethylhexylamine, and 3-methoxypropylamine.[147]

The fastness properties of these 1,4-bisalkylaminoanthraquinones are generally not adequate for some thermoplastic materials, and improved colors substituted by arylalkylamines such as 2-phenylethylamine[148] and alkoxybenzylamine[149] are recommended.

Also, when one alkylamino is replaced by an arylamino group, the fastness often improves. Solvent Blue 11 (CI 61525), a green blue, and Solvent Blue 12 (CI 62100), a redder blue, made by reacting *p*-toluidine with 1-methylamino-4-bromoanthraquinone and 1-amino-2,4-dibromoanthraquinone, respectively, have better fastness properties and are more suitable for thermoplastic materials.

When leucoquinizarin is condensed with 2 moles of *p*-toluidine, the product is the blue-green Solvent Green 3 (CI 61565), used extensively for coloring glycol-type antifreezing liquid. It has good all-round fastness and can be used in many applications. Solvent Green 3 can be further chlorosulfonated or chloromethylated and the products treated with alkylamine or phenol to give greens with good fastness.[150] 1,4-Bis-(biphenylamino)anthraquinone, made from either leucoquinizarin or 1,4-dichloroanthraquinone and 4-aminobiphenyl, is a pure grass green with excellent light- and heatfastness in thermoplastics.[151]

1,4-Bismesidinoanthraquinone is recommended for use in aminoplast resin.[152] The steric effect of two adjacent methyls in the mesidino

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[146] BASF, *FP* 1,548,181.

[147] BASF, *USP* 3,597,254.

[148] BASF, *BeP* 672,688.

[149] Fran, *USP* 3,845,081.

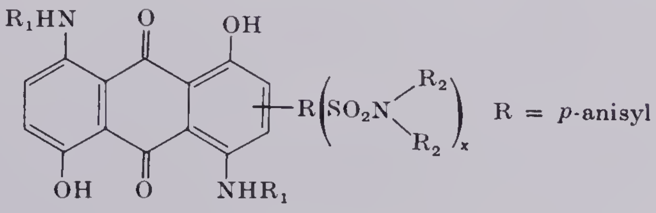
[150] S, *USP* 2,852,535; GAF, *USP* 2,677,694.

[151] Allied, *USP* 3,388, 094.

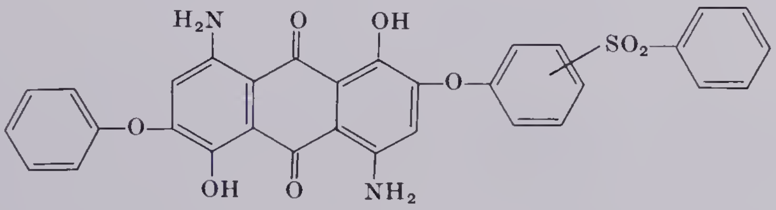
[152] NSK, *JP* 06,215/75.

group makes this a much redder color. Spectroscopic studies of many bisarylaminoanthraquinones have been reported.[153]

Solvent Blue 18 (CI 64500) and 69 (CI 62500) are 1,4,5,8-tetrasubstituted anthraquinones [$(NH_2)_4$ and 1,4-$(NHCH_2CH_2OH)_2$-5,8-$(OH)_2$]. Improved dyes with additional substitution such as (L) and (LI) are recommended for spin dyeing and coloring rigid plastic substrates.[154]



(L)

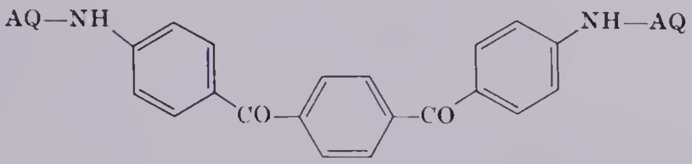


(LI)

Dye (LI) is made by the Friedel–Crafts reaction of benzenesulfonyl chloride and aluminium chloride with the corresponding diphenoxy dye.[155]

Dimeric aminoanthraquinones such as (LII, AQ = 1-anthraquinonyl)[156] and 1,1′-anthrimides containing SR groups are used for mass coloration of thermoplastic materials; e.g., pentantrhimide (*CSD II*, p. 894) substituted by SPh in the central ring is a jet black dye for polymethacrylate.[157]

CI Solvent Red 52 (LIII, A = *p*-toluidino)[158] is a bluish red with excellent lightfastness and heat resistance in polystyrene, polymethyl



(LII)

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[153] T. Hayashi and T. Tokumitsu, *Bull. Chem. Soc. Jpn.* **38**, 916 (1965); *Senryo to Yakuhin* **13**, 427 (1968); *CA* **70**, 116213.

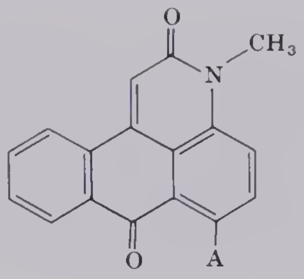
[154] CGY, *DAS* 1,644,518.

[155] AAP, *USP* 3,840,567; 3,923,454.

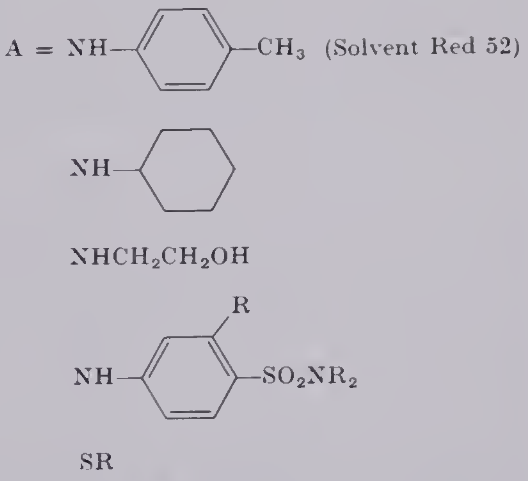
[156] CGY, *USP* 3,923,727.

[157] AAP, *USP* 3,439,002.

[158] *CSD II*, p. 853; *CSD V*, p. 125.



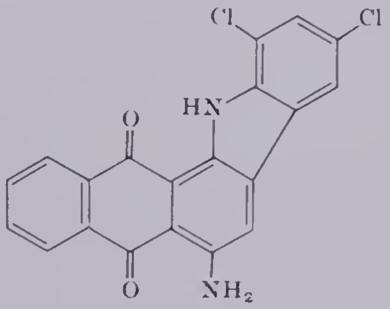
(LIII)



methacrylate,[159] and polyester film.[160] Many modified dyes have been made; instead of *p*-toluidine, other amines as indicated can be used.[161–164]

CI Solvent Red 114 (CI 68415, Lumogen L Red Orange),[165] a yellowish red, is used for thermoplastic resins. A similar dye, Fluorol 242,[165] is used for coloring oils.

Other heterocyclic derivatives made from anthraquinone are the carbazole (LIV)[166] and the acridone (LV),[167] suggested for use in



(LIV)

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[159] FBy, *DBP* 1,295,193.

[160] C. S. Hunter, *USP* 3,853,807.

[161] NSK, *JP*, 20,744/74; *CA* **82**, 99269x.

[162] AAP, *USP* 3,324,131.

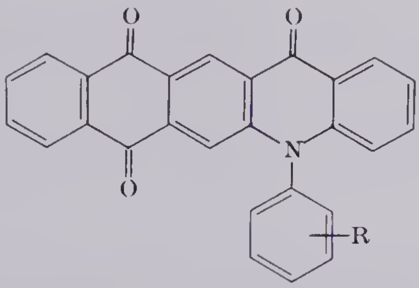
[163] FBy, *Ger. Offen.* 2,421,375.

[164] Sumitomo, *JP* 37,577/73; *CA* **82**, 87107.

[165] *CSD II*, p. 999.

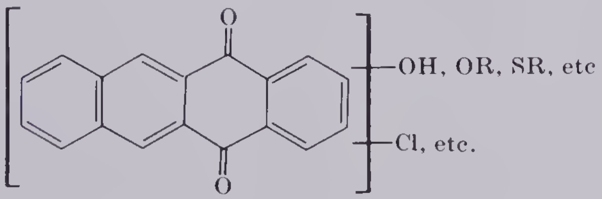
[166] FH, *FP* 1,365,744.

[167] FH, *BeP* 649,151.



(LV)

lacquers, varnish, and plastic materials. A series of 5,12-naphthacenedione derivatives (LVI) have been recommended as fast yellows and oranges for polystyrene, polypropylene, etc.[168]



(LVI)

F. FLUORESCENT DYES

Solvent-soluble fluorescent dyes have been known in the literature for a long time. Earlier Lumogen colors,[169] activated only by ultraviolet light, are now obsolete. Some Solvent Greens listed in CI have greenish fluorescence in mineral oils and petroleum products. Solvent Green 4 (Fluorol 5G; *CSD II*, p. 747), Solvent Green 5 (CI 59075; isobutyl ester of perylene 3,9-dicarboxylic acid) and Solvent Green 6 (distearate of leuco-16,17-dimethoxyviolanthrone, cf. CI 59845) have limited use in coloring lubricating oils. Solvent Green 5, despite its name, has been found to be a bright fluorescent yellow in thermoplastic resins with good light and heat stability. A related color, 3,9-bismesitoylperylene, is made by reacting 3,9-perylene dicarbonyl chloride with mesitylene in the presence of aluminum chloride.[170] It is also an excellent yellow, but without fluorescence. The steric effect of the mesitoyl group probably quenches fluorescence.

Fluorescent solvent dyes have become important after the development of daylight fluorescent pigments,[171] usually made by molecularly

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[168] MDW, *JP* 81,440/74; 65,539/75; *CA* **83**, 115804; **83**, 194459.

[169] *FIAT*, **1313** III.

[170] Allied, *USP* 3,316,205.

[171] R. W. Voedisch and D. W. Ellis, *Kirk-Othmer*, *Encyc. Chem. Technol. 2nd Ed.* **9**, 483 (1966).

dissolving the dye in either thermosetting or thermoplastic resin while the resin is in liquid form. The resin is then allowed to harden by cooling or curing and is then crushed to obtain pigment particles. The dyes used in these pigments exhibit visible fluorescence when activated by short-wavelength visible light as well as by UV light.

Earlier pigments, developed by Switzer Brothers, used substrates of urea or melamine formaldehyde resins, which have been gradually replaced by a modified sulfonamide resin matrix.[172] Many improvements have been made during the past twenty years in lightfastness, heat stability, fineness of pigment, and bleeding characteristics. As a result, these fluorescent colors have been rapidly employed in many new applications, including coatings, inks, and plastics to impart brilliant color and conspicuousness to bodies and surfaces.[173–176]

So far, improvements of this type of color have been obtained mainly through the additives[177] or by modification of resin substrates.[177,178,179] Until recently, little progress was made in developing new dyes for this type of application. Solvent Yellow 44 is usually used for yellow and Rhodamines for reds. Oranges and scarlets are usually obtained by mixtures. Green is obtained by shading a fluorescent yellow with a green toner or pigment. Many new dyes, however, have been proposed for this type of application in the last few years. It appears that daylight fluorescent pigments will be further improved in the future.

4-Aminonaphthalimide type dyes are probably still the most important yellow components for daylight fluorescent pigments. 4-Butylamino-*N*-butylnaphthalimide (LVII, $R_1 = R = n$-butyl), made by reacting *n*-butylamine with 4-sulfonaphthalic anhydride was used in earlier developments. It was soon replaced by Solvent Yellow 44 (CI Disperse Yellow 11, CI 56200, LVII, R_1 = 2,4-xylyl, R = H). These can be made from acenaphthene through nitration, sulfonation, or halogenation routes.[180] When the nitration route is used the final product is obtained by reduction. An amine replacement reaction will give a product having either a free amino group or a substituted amino group at the 4-position when the sulfonation or halogenation

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[172] Switzer Brothers, *USP* 2,809,954.

[173] J. Richter, *Soc. Plast. Eng., Tech Pap.* **19**, 225 (1973).

[174] W. R. Duncan, *Am. Inkmaker* **39**, 46 (1961).

[175] W. Geib, *Am. Inkmaker* **49**, 22 (1971).

[176] T. J. Gray, *Plast. Eng.* **31**, 39 (1975).

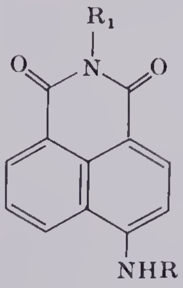
[177] Switzer Brothers, *USP* 2,851,423–4.

[178] Sherwin-Williams, *USP* 3,518,205.

[179] Hercules, *USP* 3,682,854.

[180] *CSD II*, p. 1189; *CSD V*, p. 616.

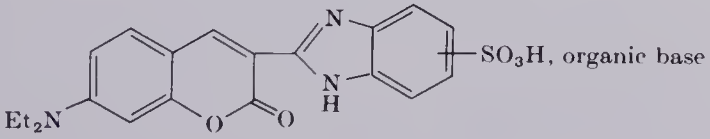
route is used.[181] Stepwise condensation with two different amines is possible, since the anhydride group will react under much milder conditions.



(LVII)

Some modifications have been proposed, such as using mesidine (LVII, R_1 = mesityl, R = H)[182] or trifluoromethylaniline (LVII, R_1 = trifluoromethylphenyl, R = H)[183] for the imide group or ethanolamine at the 4-position (LVII, R_1 = xylyl, R = NHC_2H_4OH).[184] Analogs of (LVII) with R_1 = butoxy or amino and alkoxy substituents in the 4,5-positions have been suggested as fluorescent dyes.[185–187]

Many other structures have been developed for fluorescent dyes. Coumarins have been used as fluorescent brightening agents for some time, and substituted coumarins, such as (LVIII), are green-yellow fluorescent dyes.[188] Also, 2-imino-7-amino-substituted coumarins



(LVIII)

(LIX), synthesized as in Chart 2, can be used for preparing yellow daylight-fluorescent pigments.[189] The imino group in (LIX) can be further reacted with amines to give *N*-substituted iminocoumarin dyes.[190] Styryl and stilbene derivatives (LX), (LXI), and (LXII) are

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[181] FH, *Ger. Offen.* 2,423,546.

[182] Allied, *USP* 3,371,092.

[183] D. G. Pereyaslova *et al.*, *Zh. Prikl Spektrosk.* **21**, 704 (1974).

[184] FH, *USP* 3,939,093; *Ger. Offen.* 2,360,705; 2,360,787.

[185] BASF, *Ger. Offen.* 2,415,027.

[186] Mitsubishi, *JP* 08,465/72.

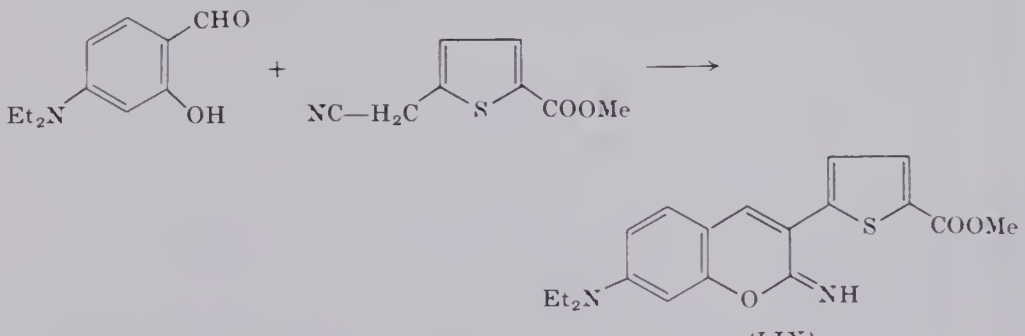
[187] Nippon Kayaku, *JP* 18,556/75.

[188] BASF, *Ger. Offen.* 2,006,517.

[189] BASF, *USP* 3,801,602.

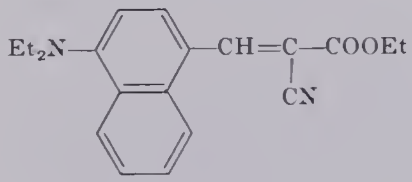
[190] BASF, *USP* 3,910,912.

CHART 2

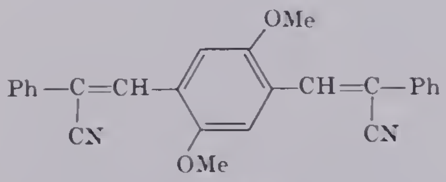


(LIX)

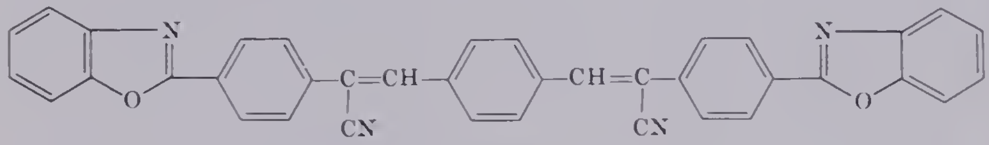
also proposed as yellow to orange fluorescent dyes.[191–193] A tetrazaindene (LXIII) reported earlier shows strong yellow-red fluorescence in solvents.[194] More recently, the tetracyclic pentaza compound (LXIV) was recommended as a yellow fluorescent dye.[195] The conjugated heterocyclic dyes (LXV) show green-yellow fluorescence in plastic materials.[196] The bisisoquinolinedione derivatives (LXVI), made



(LX)



(LXI)



(LXII)

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[191] GAF, *USP* 2,914,551.

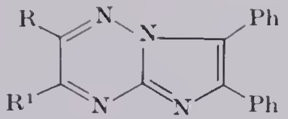
[192] Showa Chem. Industries, *JP* 80,316/75; *CA* **83** 149105.

[193] EKCo., *USP* 3,458,506.

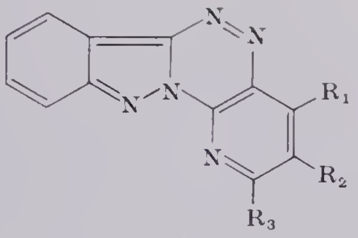
[194] S. Rossi and R. Trave, *Quim. Ind.* (*San Paulo*) **40**, 827 (1958); *CA* **53**, 7194.

[195] FH, *Ger. Offen.* 2,360,986.

[196] V. E. Bondarenko *et al.*, *RP* 244,607; *CA* **72**, 44486.

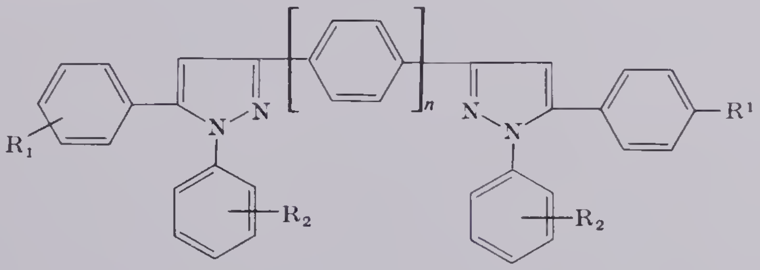


(LXIII)



(LXIV)

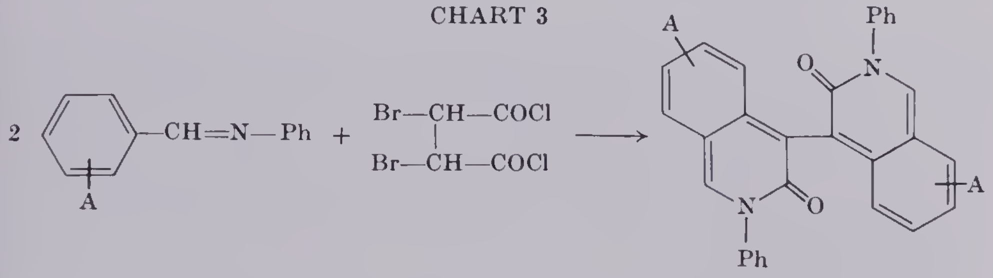
as in Chart 3, are fluorescent greenish yellow to reddish yellow dyes with good fastness.[197]



(LXV)

Perhaps the most extensive search for new fluorescent dyes has been made by FH on benzoxanthene and thiobenzoxanthene dicarboxylic acid derivatives. The required benzoxanthene dicarboxylic acid is prepared from either 4-phenoxy-5-aminonaphthalic acid or 4-(2′-aminophenoxy)naphthalic acid via the diazonium salt. The anhydride is converted to the imides (LXVII), which are strong yellows with greenish fluorescence and have very good fastness to light.[198] Many substituted benzoxanthene dicarboxylic imides and their derivatives for making yellow to red daylight-fluorescent pigments have been described.[198] It will be interesting to see the impact of this series of dyes on the future of fluorescent pigments.

CHART 3



(LXVI)

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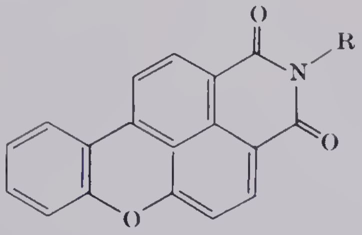
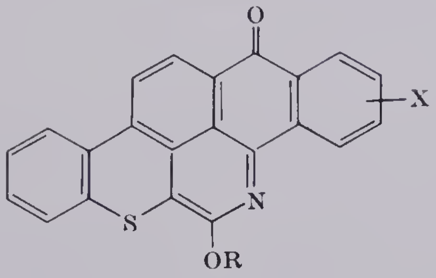
[197] CGY, *USP* 3,751,419.

[198] FH, *USP* 3,741,971; 3,748,330; 3,749,727; 3,769,229; 3,772,333; 3,781,302; 3,785,989; 3,812,051–4; 3,845,075; 3,853,884.



(LXVII)

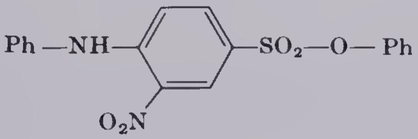


(LXVIII)

Polycyclic fluorescent dyes have been made from benzanthrone,[199] violanthrone,[200] and isoviolanthrone.[201] The dibenzo-4-aza-6-thiapyrene derivatives (LXVIII) are violet fluorescent dyes.[202]

G. Miscellaneous Dyes

Solvent Orange 53 is 2,4-dinitro-4′-aminodiphenylamine. A related dye (LXIX), obtained from 4-chloro-3-nitrobenzenesulfonyl chloride, is an oil-soluble yellow.[203] C_5–C_{18} alkyl-substituted nitrodiphenylamines are also solvent dyes.[204] Indophenols such as Solvent Blue 22 (CI 49705) and the amino-1,4-naphthoquinones (LXX) are used as solvent dyes.[205] 1,3-Perinaphthindandione (2,3-dihydrophenalene-1,3-dione) treated with aldehydes in presence of formic acid, gives solvent



(LXIX)

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[199] S. *BeP* 0,737,846.

[200] ACY, *BeP* 0,738,326.

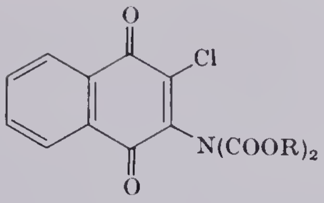
[201] N. F. Levchenko *et al.*, *RP* 231,794; *CA* **70**, 78838.

[202] Montedison, *Ger. Offen.* 2,500,487.

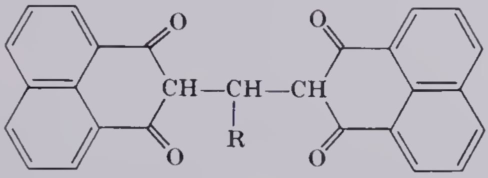
[203] CIBA, *USP* 2,796,422.

[204] Saul, *USP* 2,879,269.

[205] Schenley Industries, *USP* 2,913,453.

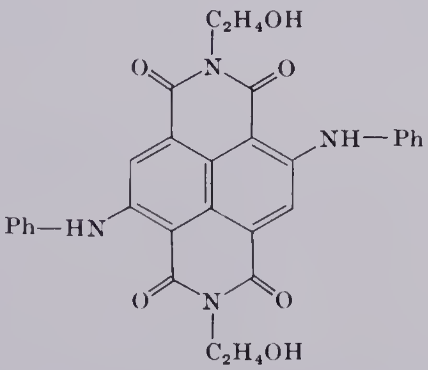


(LXX)



(LXXI)

yellows (LXXI) used for inks and similar applications.[206] 2,6-Dichloronaphthalene-1,4,5,8-tetracarboxylic dianhydride has been converted by successive condensation with ethanolamine and aniline to the blue dye (LXXII) for mass coloration of polyester with excellent fastness properties.[207]



(LXXII)

Quinophthalones are a group of important solvent yellows (see *CSD III*, p. 455). The simplest, made by condensing quinaldine with phthalic anhydride, is Solvent Yellow 33 (CI 47000). Many substituted derivatives and benzo derivatives have been made and their chemistry reviewed.[208] As a solvent dye, Solvent Yellow 33 is weak with fair fastness properties, but it is still being used in many applications. When trimellitic anhydride is used instead of phthalic anhydride, the

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[206] BASF, *BP* 712,166.

[207] ICI, *USP* 3,507,871.

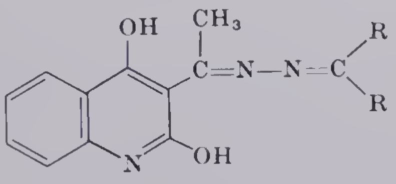
[208] A. R. Patil, G. G. Patkar, and T. Vaidyanathan, *Bombay Technol.* **24**, 26 (1974).

product and its esters are recommended for mass coloring polyesters.[209] When 8-aminoquinaldine is condensed with 2 moles of phthalic anhydride, the resulting phthalimidoquinophthalone has better lightfastness and heat stability.[210]

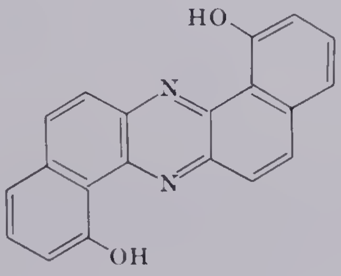
Better lightfastness is obtained when a 3-hydroxy group is introduced into the quinophthalone molecule by condensing 3-hydroxyquinaldine 4-carboxylic acid with various aromatic *o*-dicarboxylic anhydrides. Decarboxylation occurs during condensation. The hydrogen bonding of the 3-hydroxyl group may contribute to the improved fastness. When phthalic anhydride, naphthalene 2,3-dicarboxylic anhydride or trimellitic anhydride derivatives are used, all the resulting yellow dyes are useful for thermoplastic materials.[211]

1-Phenylthio-4-nitroacridone is a strong yellow dye for polyester fiber and lacquers and for mass coloration of polymeric materials.[212] Other examples of heterocyclic compounds useful as solvent dyes for plastic materials are esters of 3-amino-5-nitrothianaphthene 2-carboxylic acid,[213] 2,4-dihydroxyquinolines such as (LXXIII)[214] and dihydroxydibenzophenazine (LXXIV).[215]

Phthaloperinone is another group of heterocyclic compounds receiving considerable attention as solvent dyes for plastic materials. It is generally made by condensing 1,8-naphthalenediamine with



(LXXIII)



(LXXIV)

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[209] ICI, *USP* 3,417,048.

[210] BASF, *DAS* 1,770,960.

[211] MCI, *Ger Offen.* 2,456,125; *JP* 115,133/74; *CA* 83, 29115; *JP* 35,241/75; *CA* 83, 98460.

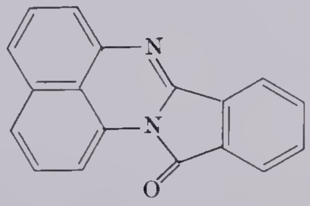
[212] CGY, *USP* 3,541,099; 3,624,255.

[213] FB, *USP* 3,659,004.

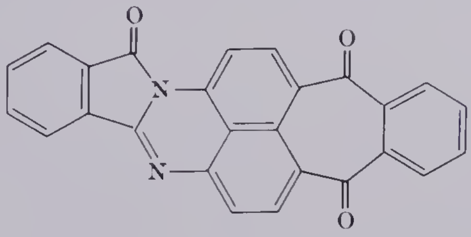
[214] BASF, *USP* 3,715,360.

[215] FB, *USP* 3,833,536.

phthalic anhydride or its derivatives in a high-boiling solvent. Phthaloperinone itself (LXXV)[216] is a lightfast and heat-stable orange in polymethyl methacrylate and polystyrene. Tetrahydrophthaloperinone, made from tetrahydrophthalic anhydride, is a somewhat redder amber, also having excellent fastness, but better tinctorial value and better solubility in styrene and methyl methacrylate monomers.[217] When trimellitic anhydride is used instead of phthalic anhydride, the phthaloperinone contains a carboxyl group that can be converted to an orange to red ester[217a] or amide.[218] Other phthaloperinones can be made from pyromellitic dianhydride,[219] 3,3′,4,4′-benzophenone tetracarboxylic dianhydride or tetrabromophthalic anhydride.[220] Tetrabromophthaloperinone is recommended as a flame-retardant dye for coloring polystyrene.



(LXXV)



(LXXVI)

When phthaloperinone is chlorosulfonated and condensed with dibutylamine, the resulting yellow-orange dye can be used in polyvinyl chloride without the undesirable blooming.[221] A number of other derivatives have been made from phthaloperinone; Friedel–Crafts reaction with phthalic anhydride gives a dye (LXXVI) that can be used in plastic material.[222]

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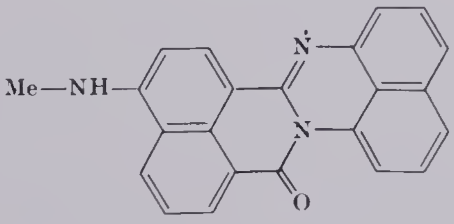
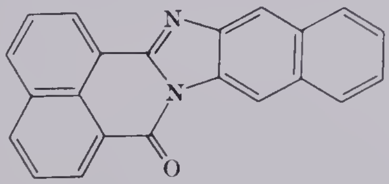
[216] Fran, *FP* 1,075,110; 1,108,109; 1,251,445.
[217] Allied, *USP* 3,299,065.
[217a] ICI, *USP* 3,410,821.
[218] MCI, *JP* 07,036/73; *CA* 79, 6787.
[219] Japan Chem, *JP* 34,424/72; *CA* 78, 137954.
[220] BASF, *USP* 3,538,095; 3,544,573.
[221] ACY, *USP* 3,909,442.
[222] ICI, *USP* 2,884,422; 2,889,327; *DBP* 1,077,353.

Other perinones, such as the red (LXXVII),[223] can be made from 1,8-naphthalic anhydride and 1,8-naphthalenediamine; 2,3-naphthalenediamine gives the yellow (LXXVIII).[224]

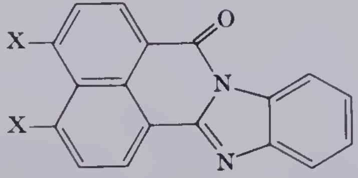


(LXXVII)



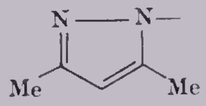
(LXXVIII)

The perinones made from *o*-phenylenediamine and substituted naphthalic anhydrides are usually yellow to orange solvent dyes such as (LXXIX A,B,C), with good fastness on plastic materials.[225–227]



(LXXIX)

one X = NHR (A)



(B)

COOR (C)

Dye (LXXIX B) is prepared from 4-hydrazinonaphthalic anhydride giving hydrazinoperinone, which is further condensed with acetylacetone to form the pyrazole ring.

The naphthyridinedione (Ciba Lake Red B, CI 73095), obtained by reacting indigo with phenylacetyl chloride, has been shown to be a brilliant pink with good fastness in polyamide.[228] The yields in such

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[223] KYK, *JP* 140,548/75.

[224] FH, *DBP* 1,121,750.

[225] Fran, *BP* 1,189,196.

[226] MCI, *JP* 05,871/73.

[227] FBy, *USP* 3,953,452.

[226] CIBA, *USP* 2,993,024.

condensations are usually not very good. An improved process using a mixture of arylacetyl halide, aroyl halide, and thionyl halide has been developed.[229]

III. Application, Evaluation, and Analysis of Solvent Dyes

There is a great variety of applications for solvent dyes. Some properties required are similar to those for dyes for other uses; for example, shades and color strength are always evaluated. Many other properties, however, vary according to different applications and substrates. One of the important properties that may be unique for solvent dyes is their solubility in organic solvents. An ideal solvent dye should have good solubility in the solvent in which it will be applied, but no solubility or poor solubility in other solvents. Solubility data are therefore very important for the evaluation of a solvent dye for new applications. A solubility guide for many common solvent dyes in nonaqueous systems is presented in Table IV. These data are given as a guide in developmental work. It should be noted that the solubilities for the same dye made by different manufacturers may vary considerably. The solubility is affected by the testing method and the presence of isomeric and homologous dyes or other impurities. The figures given in the table only indicate the order of solubility to be expected.

In actual application, more concentrated color solutions may be made by heating the solvent. Mixed solvent systems will also increase the dye solubility. Many other special properties and requirements of solvent dyes in various applications are scattered in the literature. Good reviews of solvent dyes used for colored signal smokes,[230,231] for inks,[232] for printing inks,[45] and for ballpoint pen inks[233] are available. Ballpoint pens, popular after the second World War, require dyes having high tinctorial value and exceptional solvent solubility. A considerable number of new dyes have been developed for this purpose during the last twenty years. Satisfactory dyes are available at the present time, producing well over a billion units per year of such pens in the United States.[234] Application research has shifted to other types of inks, such as felt-tip and other marking pen inks,[235] ink for

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[229] Allied, *USP* 3,580,919.

[230] Chemical Warfare Service, *Chem. & Eng. News* **22**, 1990 (1944).

[231] J. W. Orelup, *USP* 2,478,418–9.

[232] E. A. Wich, *Am. Inkmaker* **44**, 30 (1966).

[233] N. L. Anderson, *Am. Inkmaker* **35**, 38 (1957).

[234] *Consumer Bulletin* April (1969).

[235] National Cash Register, *FP* 2,143,051.

TABLE IV

SOLUBILITY GUIDE FOR SOLVENT DYES IN NONAQUEOUS SYSTEMS[a]
(grams of dye per 100 grams of solvent)

CI Solvent	*Methanol*	*Ethanol*	*Acetone*	*Methyl ethyl ketone*	*Ethyl acetate*	*Carbitol*	*Cellosolve*	*Diethylene glycol*	*Toluol*	*Xylol*	*Oleic acid*	*Stearic acid*	*Kerosene*	*Bleed into water*
Yellow 3	6.0	4.5	25.0	22.0	20.0	12.0	15.0	12.0	10.0	8.0	6.0	6.0	1.8	SB
Yellow 14	0.3	0.4	3.5	5.0	4.0	2.4	1.5	HB	5.5	5.4	4.0	3.0	1.8	NB
Yellow 33	HB	HB	0.1	0.2	0.1	0.2	0.2	0.2	0.2	0.2	0.6	HB	0.2	SB
Yellow 40	0.1	0.1	1.0	1.5	1.2	0.3	0.5	0.2	3.8	2.5	1.0	1.0	0.4	SB
Yellow 42	8.0	27.0	33.0	8.0	10.0	12.0	9.0	18.0	22.0	7.0	10.0	10.0	I	SB
Yellow 44	0.2	0.2	1.1	0.8	0.2	1.6	0.7	0.5	I	I	HB	1.0	I	SB
Yellow 45	50.0	17.0	11.5	10.0	2.2	5.0	4.5	5.0	0.5	0.2	HB	0.1	I	CB
Yellow 56	0.1	0.2	19.0	23.0	10.0	1.8	4.0	0.1	31.0	22.0	6.0	2.0	0.5	SB
Orange 3	16.0	9.0	19.0	16.0	13.0	7.0	12.0	50.0	2.5	1.5	3.0	5.0	SB	CB
Orange 7	1.3	1.8	6.5	6.0	7.0	2.5	5.0	HB	10.0	9.0	2.0	7.0	1.8	SB
Orange 23	30.0	28.0	28.0	16.0	15.0	8.5	23.0	18.0	12.0	6.0	15.0	10.0	I	SB
Orange 31	1.0	1.5	5.0	6.5	5.0	2.0	4.0	HB	10.0	9.0	5.0	4.0	0.2	AB

Red 24	0.1	0.2	3.4	3.0	2.5	0.3	0.7	0.4	5.0	4.0	2.0	3.0	0.8	SB
Red 26	0.1	0.1	0.8	1.3	1.0	0.3	0.5	0.4	2.5	2.4	2.0	3.0	1.0	SB
Red 27	0.1	0.2	2.7	3.0	1.2	1.5	1.0	0.4	7.0	6.8	2.0	3.0	0.2	SB
Red 68	16.0	20.0	22.0	4.0	6.0	10.0	6.0	18.0	9.0	9.0	25.0	10.0	I	CB
Red 74	10.0	5.0	16.0	11.0	18.0	9.0	2.0	3.0	7.5	6.5	2.0	10.0	I	SB
Red 75	25.0	25.0	5.0	5.0	HB	100.0	100.0	10.0	SB	SB	I	0.5	I	HB
Violet 17	0.2	0.3	1.2	1.5	0.6	2.5	1.0	0.5	0.1	0.1	0.5	HB	I	NB
Blue 12	I	I	I	AB	I	I	I	0.2	0.1	0.1	HB	SB	0.5	SB
Blue 16	0.6	1.0	4.0	4.0	3.0	2.6	2.7	0.5	3.3	3.8	4.0	5.0	0.2	SB
Blue 36	0.4	0.5	2.5	3.0	3.0	0.6	2.0	1.0	6.0	5.0	1.0	2.0	0.1	NB
Blue 38	6.5	3.0	0.1	0.1	I	100.0	100.0	1.0	I	I	I	I	I	HB
Blue 43	20.0	20.0	10.0	AB	HB	100.0	100.0	10.0	I	I	0.1	1.0	I	HB
Green 3	I	I	AB	0.1	0.1	HB	HB	0.2	0.5	0.5	0.5	30.0	0.5	NB
Black 3	1.0	1.0	4.0	3.5	0.5	0.5	0.5	0.7	3.5	3.0	1.0	1.5	0.2	NB
Black 5	2.2	2.1	0.7	0.5	0.3	2.0	3.0	3.0	0.6	0.4	15.5	10.0	SB	NB
Black 7	0.2	0.5	1.5	2.5	2.0	1.0	2.5	3.0	0.7	0.5	72.0	50.0	SB	SB
Black 12	0.1	0.1	4.5	10.5	4.5	3.0	5.5	I	9.0	11.0	2.0	1.5	0.2	SB
Black 13	9.0	15.0	15.0	6.0	1.3	2.4	3.0	18.0	0.5	HB	1.0	10.0	I	SB

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[a] Data given in *TSC* No. 15 Rev., Technical Service, Allied Chemical Corp.

I = insoluble, AB = appreciable bleed, NB = no bleed, SB = slight bleed, CB = considerable bleed, HB = heavy bleed.

recorders,[236] for transfer sheets,[237,238] for electrostatic reproduction,[239,240] and other electrophotographic uses.[241–244]

Perhaps the most challenging problem facing solvent dyes is their use in newer plastic materials. Although solvent dyes have been used in phenolic thermoset resins for years, their use in thermoplastics causes many problems. Among all the plastic materials made in the world, an estimated 90% are colored.[245] Dyes are used in only about 20% of these colored plastics.[246] Most of the coloring is done with pigments. The advantages of solvent dyes used for plastic materials are brightness, high tinctorial strength, excellent transparency, low cost, and ease of incorporation.

Some of the disadvantages (poor migration and lower lightfastness, hiding power, heat resistance, and resistance to chemicals in comparison with pigments) are gradually being overcome by the new solvent dyes. Heat-stable dyes that can withstand 500°–600°F process temperatures and chemically inert dyes that will not be affected by the peroxide in acrylate polymers or the reducing environment of polyamides are available. Lightfastness has been improved, so that some solvent dyes are actually being used for outdoor signs, automobile tail lights, etc. Today, solvent dyes are being used in many thermoplastic materials, including acrylics, polystyrenes, cellulose acetate, polyamide, and rigid vinyls.

Two deficiencies remain that hinder the use of solvent dyes in other plastic materials. Many solvent dyes have poor hiding power and migrate badly in flexible thermoplastics in the presence of plasticizer. Both deficiencies are actually due to the solvent-soluble character of dyes of this class. However, dye manufacturers have not done enough to meet this challenge. Recent patents claiming improved dye compositions,[221] as well as mass coloration methods[247] giving satisfactory migration properties in polyvinyl chloride, indicate that research can pay off in this area.

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[236] Teletype, *Ger. Offen.* 2,046,491.

[237] Columbia Ribbon & Carbon, *Ger Offen.* 2,116,902.

[238] Burroughs Corp., *Ger. Offen.* 2,117,075.

[239] A. B. Dick, *FP* 2,075,210.

[240] Xerox, *FP* 2,056,400.

[241] Mita Industrial Co., *BP* 1,282,058.

[242] A. B. Dick, *USP* 3,717,463.

[243] Xerox, *Ger. Offen.* 2,260,027.

[244] IBM, *Ger. Offen.* 2,306,003–4.

[245] L. J. Zukor, *Plast. Technol.* 8, 27 (1962).

[246] A. L. Baseman, *Plast. Technol.* **12**, 37 (1966).

[247] S, *USP* 3,536,658.

Many reviews on coloring plastic materials are available.[248] Recent patents disclose improved processes for mass coloration of polystyrene,[249] polyester,[250] and polyvinyl using spirit-soluble dyes with *N*-vinyl-2-pyrrolidone.[247] Instead of using mass coloration, the plastic articles can also be colored by surface dyeing. This will not only reduce the dye cost, but also permit the plastic manufacturer to make uncolored articles and to dye different shades as needed. Most of these recent dyeing processes use solvent dyes with an organic solvent system,[251] such as hydrocarbon,[252] a molten wax bath,[253] or a butanol solution of polyvinyl pyrrolidone for dyeing of polyolefins[254]; an aromatic hydrocarbon for dyeing polyvinyl chloride[255]; a volatile ketone for plasticized polyvinyl chloride[256]; and an alcoholic solvent for polyurethane foam.[257] Sometimes, the process involves surface modification before dyeing.[258]

Another approach for applying solvent dyes to plastic articles, such as polystyrene foam,[259] polycarbonate resin,[260] and polypropylene,[261] is to use a solvent–water emulsion with an emulsifier. Solubilization of some solvent dyes in water by detergents[262] and during the production of polystyrene latexes has been studied in some detail. In general, the solubility increases with increasing temperature and surfactant concentration.[263]

Methods for coloring polymers using dyes with polymerizable groups have been studied.[264] Many compositions of the so-called polymeric

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[248] J. Simpson, *Mod. Plast.* **40**, (3) 142 (1962); P. J. Papillo, *ibid.* **45**, 131 (1967); A. L. Baseman, *Plast. Technol.* **13**, 31 (1967); J. Koerner, *Kunstst.-Rundsch.* **20**, 117 (1973).

[249] MDW, *JP* 07,852/73; *CA* **80**, 71672.

[250] ICI, *USP* 3,846,369.

[251] Société Quillery, *FP* 1,460,901.

[252] Triangle Conduit & Cable, *BP* 918,588.

[253] Avisun Corp., *USP* 3,447,883.

[254] Owen-Illinois, *USP* 3,625,731; 3,707,347.

[255] Toppan, *JP* 07,870/75; *CA* **83**, 29158.

[256] B. J. Rosenberger & E. Czypionka, *USP* 3,830,626.

[257] GAF, *USP* 3,635,652; Fran, *USP* 3,901,648.

[258] General Mills, *USP* 3,594,111; Keuffel & Esser, *USP* 3,467,481.

[259] Foster Grant, *USP* 3,632,288; Koppers, *USP* 3,399,025.

[260] AAP, *USP* 3,514,246.

[261] MacDermid Inc., *USP* 3,533,727.

[262] F. Tokiwa, *Bull. Chem. Soc. Jpn.* **43**, 939 (1970).

[263] I. P. Knyaginina, E. M. Aleksandrova, *et al.*, *Tr. Mosk. Khim.-Tekhnol. Inst.* **66**, 256 (1970); **67**, 194 (1970); **70**, 205 (1972); *CA* **75**, 141521; 130425; **79**, 19600.

[264] F. N. Stepanov and L. A. Zosim, *Ukr. Khim. Zh.* **35**, 186 (1969); *CA* **71**, 4072p; S. V. Vinogradov and I. P. Antonova-Antipova, *Prog. Polim. Khim.* p. 375 (1968). *CA* **72**, 13237u.

reactive dyes are given.[265] Most are acryloyl derivatives. These, in theory, will give nonmigration products after polymerization, but they have not achieved commercial success so far.

Quality tests for solvent dyes are relatively simple because of the solvent solubility characteristics and the fact that they are usually free of diluents or additives. For many established dyes, a melting point test versus standard gives sufficient indication of the quality of the dye. Percentage of solvent insoluble is also a good indication of quality. Spectral strength versus standard is another common test for quality. In addition, a test for shade and strength is usually performed to ensure quality of the product. This can be done by using a paper pour-out of a colored solution or making a draw-down of colored ink or resin for comparison with standard. For evaluation of a new solvent dye, or for a new application of an old dye, the dye will have to be tested in the materials and under the conditions in which it is intended to be used. In addition to shade, strength and solubility information, lightfastness, heat stability, resistance to migration, resistance to chemicals, and bleed tests are often examined to determine the suitability of the dye for a particular application. These tests are similar to those for pigments discussed in *CSD V*, pp. 459–474. For a solvent dye in liquid form, an extra storage stability test under various temperatures and conditions is usually made.

A method has been described for the numerical characterization of the hue of solvent-soluble dyes.[266] Some problems of the colorimetric method for solvent dyes have been discussed.[267] Visual assessment of the luminosity of daylight fluorescent colors and their relation to colorimetric qualities shows that a linear relationship exists between these two data.[268] By a simple acid–base treatment of blue ballpoint pen inks, a visual observation can be used to differentiate between various solvent dyes.[269]

Paper electrophoresis in 5 N acetic acid[270] and gas–liquid chromatography[271] can be used to identify some simple azo and anthraquinone

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[265] Ivanov Chem-Tech Inst., *RP* 193642–3; Dainichiseika Color and Chemicals, *BeP* 637,190; BASF, *BP* 877,402; 920,390; S. Horiguchi and M. Nakamura, *USP* 3,563,931.

[266] I. F. Trotter, *J. Soc. Dyers Colour.* 78, 79 (1962).

[267] L. Gall, *Kunstst.-Rundsch.* **20**, 129 (1973); V. S. Kenkare, *Text. Dyer & Printer* **1**, 47 (1968).

[268] R. Thielert and G. Schliemann, *J. Opt. Soc. Am.* **62**, 137 (1972).

[269] D. A. Crown, J. V. P. Conway, and P. Kirk, *J. Crim. Law. Criminol. Police Sci.* **52**, 338 (1961).

[270] T. Fukuda and R. Kaneda, *Eisei Kagaku* **16**, 267 (1970); *CA* **75**, 50385.

[271] J. B. Terrill and E. S. Jacobs, *J. Chromatogr. Sci.* 8, 604 (1970).

dyes. Solvent dyes can be identified by paper chromatography,[272–274] and by reverse-phase TLC on cellulose acetate.[275] Thin-layer chromatography on silica gel,[274,276–278] polyamide,[279] and a mixture of the two[280] is more commonly used to separate and identify solvent dyes. Finally, special isolation and analytical techniques for identifying solvent dyes in coating materials and lipsticks,[279] foods,[278,281,282] and drinks[283] have been described.

[272] I. Shimizu, *Yukagaku* **17**, 35 (1968); *CA* **68**, 70895.

[273] H. Tajiri, *Kogyo Kagaku Zasshi* **61**, 1572 (1958); *CA* **56**, 3597.

[274] N. Mesicek, M. Perpar, and S. Cimperman, *Kem. Ind.* **22**, 233 (1973).

[275] R. A. Hoodless, J. Thomson, and J. E. Arnold, *J. Chromatogr.* **56**, 332 (1971).

[276] M. Kamikura, *Shokuhin Eiseigaku Zasshi* **7**, 45 (1966); *CA* **67**, 118071.

[277] M. R. Verma and J. Rai, *Am. Inkmaker* **44**, 97 (1966); M. R. Verma, P. K. Gupta, and J. Rai, *Res. Ind.* **12**, 233 (1967).

[278] P. K. Bose, B. R. Roy, and S. N. Mitra, *J. Food Sci. Technol.* **7**, 112 (1970).

[279] G. Lehmann, H. Einschuetz, and P. Collet, *Z. Lebensm-Unters.-Forsch.* **143**, 187 (1970).

[280] H. C. Chiang, L. C. Hau, and S. L. Pan, *Tai-wan Yao Hsueh Tsa Chih* **21**, 8 (1969). *CA* **75**, 147549t.

[281] R. S. Silk, *J. Assoc. Off. Agric. Chem.* **42**, 427 (1959).

[282] W. Reiners, *Fresenius' Z. Anal. Chem.* **229**, 406 (1967).

[283] P. K. Bose, *J. Inst. Chem., Calcutta* **42**, 176 (1970).

CHAPTER IV

NEW DEVELOPMENTS IN TEXTILE COLORATION

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I. Use of Solvents in Dyeing

Solvents have been employed in dyeing processes in two ways—as a dyebath additive to augment the dyeing rate or as a medium that replaces water in the system.

A. SOLVENTS AS ADDITIVES

Many solvents have been examined (e.g., butyl alcohol, *n*-amyl alcohol, pyridine) as accelerators for dyeing various fibers (e.g., nylon, polyester, cellulose triacetate, and wool). The solvents are added in relatively small quantities and may be miscible with water, although more often they are only partially miscible.[1,2] The major interest in solvent addition (2–4%) lies in the possibility of dyeing wool at temperatures below the boil when the presence of the solvent is claimed to improve the levelness of the dyeing[3]; dyeing has been successfully carried out in the presence of benzyl or amyl alcohols using times as short as 30 minutes at 70°–80°.[4] Some data showing the marked increases in rate of uptake particularly at the lower temperatures[5] are given in Fig. 1. The solvent (benzyl alcohol) has a low affinity but is rapidly adsorbed by wool and is not effective until it diffuses into the fiber[6]; its equilibrium sorption properties follow a solution process as judged by the linear nature of the isotherms.[5]

The action of the solvent is likely to be that of a plasticizer and hence is likely to increase the rate of diffusion in the cortex.[7] But because the wool fiber is heterogeneous, the solvent may modify one or more of the different regions of the fiber. The solvent may also help to remove some of the hydrophobic materials from the surface of the fiber and hence to reduce the resistance to the entry of dye and minimize variations in hydrophobic character of the fiber surface.

Addition of solvents has been used for the dyeing of nylon, with the advantage of improved coverage of the barré effect.[8] In a recent examination of the problem, the effects of additions of *n*-butanol have been examined.[9] Better penetration of dye was achieved, presumably because of the faster dyeing rate, and the barré effects using a specially designed fabric were less marked even for some dyes (e.g., directs and some selected acid dyes) noted for their sensitivity to changes in fiber structure. In this work, it was shown that a concentration of not less

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[1] L. Peters and C. B. Stevens, *Dyer, Text. Printer. Bleacher Finish.* **115**, 327 (1956); *J. Soc. Dyers Colour.* **72**, 100 (1956); J. Delmenico, *Text. Res. J.* **28**, 899 (1957); J. W. Bell, P. J. Smith, and C. V. Stevens, *J. Soc. Dyers Colour.* **79**, 305 (1963); H. Stern and S. V. F. Fachorgan, *Textilveredlung* **15**, 582 (1960); R. J. Peirent, J. Casey, and G. Dadoly, *Am. Dyest. Rep.* **49**, 41 (1960); W. Beal and G. S. A. Corbishley, *J. Soc. Dyers Colour.* **87**, 329 (1971).

[2] Y. Takasi, T. Ogawa, and K. Shibata, *Sen'i Gakkaishi* **21**, 147 (1965); V. A. Blinov, E. N. Anishchuk, and Y. F. Komarova, *Tekst. Promst. (Moscow)* **22**, 57 (1962); H. R. Hirsbrunner, *Text. J. Aust.* **37**, 1398 (1962); B. N. Mel'nikov and I. B. Kotova, *Izv. Vyssh. Vchebn. Zaved., Tekhnol. Tekst. Promsti* **26**, 106 (1962).

[3] C. Hobday and G. Siegrist, *Melliand Textilber.* **41** 1119 (1960).

[4] W. Beal, E. Bellhouse, and K. Dickinson, *J. Soc. Dyers Colour.* **76**, 333 (1960).

[5] L. Peters, C. B. Stevens, J. Budding, B. C. Burdett, and J. A. W. Sykes, *J. Soc. Dyers Colour.* **76**, 543 (1960).

[6] M. Kärholm, *J. Text. Inst.* **51** T1323 (1960).

[7] A. B. Cassie, *J. Soc. Dyers Colour.* **76**, 617 (1960).

[8] W. Beal and G. S. A. Corbishley, *J. Soc. Dyers Colour.* **87**, 329 (1971).

[9] A. N. Derbyshire, F. D. Harvey, and D. Parr, *J. Soc. Dyers Colour.* **91**, 106 (1975).

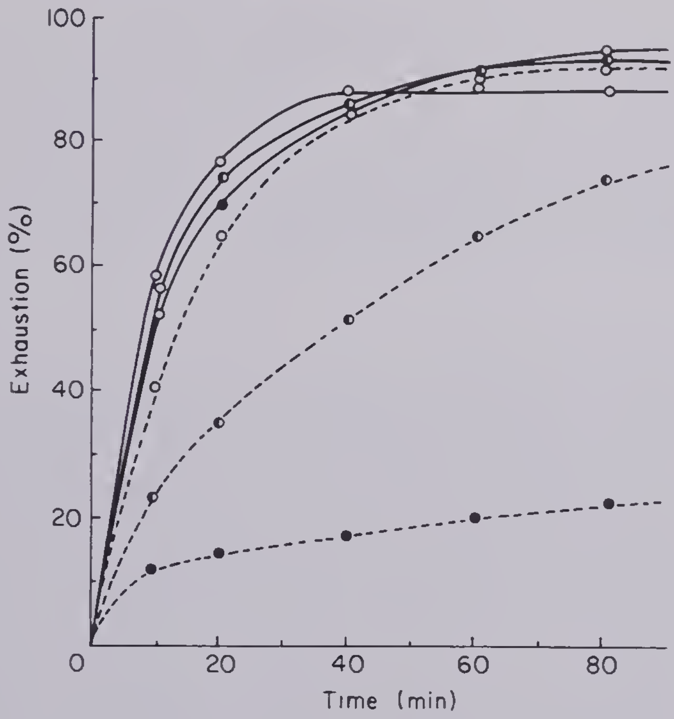
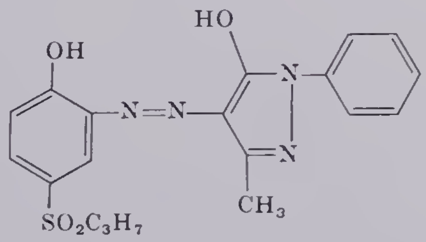


FIG. 1. Effect of benzyl alcohol on the rate of dyeing of wool.[5] – – –, 3% benzyl alcohol addition; ——, without benzyl alcohol, (○) 95°; (◐) 80°; (●) 60°. Dyeing was with the chromium complex of



than 4% in the bath was required. Additions of 5% were taken to be generally satisfactory; the method was confirmed in bulk trials. A wide range of solvents was examined (alcohols, ketones, esters); most were ineffective to lesser or greater extents, and only benzyl alcohol and *n*-butanol were shown to be useful.

n-Butanol has also been shown to accelerate the sorption of dyes by polyester fibers with the concomitant advantage that the dyeings are more level. The improvement brought about by this solvent has been shown to be similar to that with a conventional carrier (benzyl benzoate) when the latter is used at a lower concentration (2 g/liter).

In another study[10] of the addition of solvents in the dyeing of polyester, solvents (e.g., 2-phenoxyethanol, benzyl alcohol) were added

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[10] J. K. Skelly, *J. Soc. Dyers Colour.* **91**, 177 (1975).

in sufficient amount to form a two-phase system. Dyes were readily soluble in the solvent phase. On immersion of the fabric, the solvent phase transferred quickly and uniformly to the fiber phase, and on raising the temperature to 100° or 120°, dyeing was rapid. Since these solvents with solubility parameters close to that of the fiber act as plasticizers, the success of the operation must depend on the fact that the large amount of plasticizer present is able to reduce the T_g dramatically.

B. DYEING FROM SOLVENTS

The possibility of replacing water in a dyeing system has significant attractions,[11] particularly because of the potential shortage of water and the low heats of vaporization of many solvents compared with that of water. It has also been noted that the rates of desorption and adsorption on polyester are faster, and better levelness and covering of barré effects are achieved compared with aqueous systems.[12,13] Interest in the use of solvents as dyeing media goes back many years; in 1928, alcohol–water mixtures were suggested for dyeing cellulose acetate.[14] Although many solvents might be used, e.g., ethylene glycol and recently methanol–water mixtures,[15] attention has been mainly

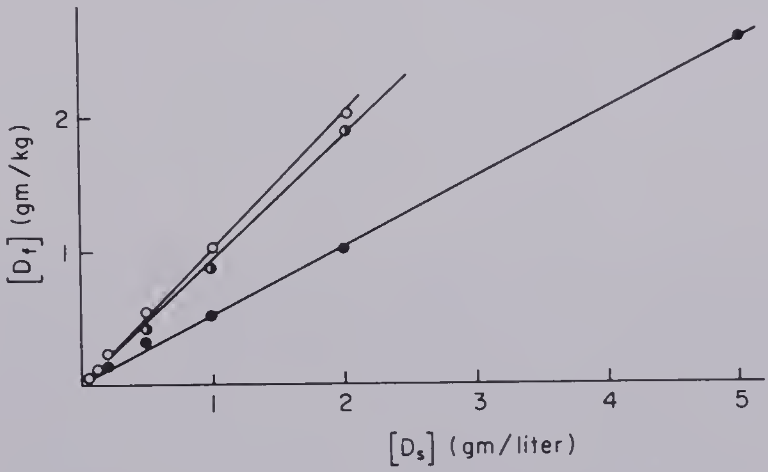

FIG. 2. Partition coefficient of CI Disperse Yellow 65 in a polyester–perchlorethylene system as a function of temperature, (○) 75°; (◑) 90°; (●) 121°.[18]

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[11] J. J. Willard, *Text. Chem. Color.* **4**, 62 (1972).

[12] D. Hildebrand, *Bayer Farben Rev.* **17**, 18 (1969).

[13] W. Langmann, *Melliand Textilber.* **53**, 565 (1972).

[14] P. C. Duggan, *Am. Dyest. Rep.* **44**, 202 (1955).

[15] H. von der Eltz, W. Birke, and F. Schön, *Text. Solvent Technol.-Update '73, AATCC Symp., 1973* p. 44 (1973).

devoted to the chlorinated hydrocarbons because of their nonflammability and the experience already available from their use for scouring and dry cleaning.[16] Of the two common chlorinated hydrocarbons tri- and perchloroethylene, the latter is perhaps the more interesting because of its higher boiling point. The chlorinated hydrocarbons are aprotic and able to wet almost all fibers rapidly and efficiently. After dyeing, they can be removed from the fabric in hot air and steam.[17]

1. *Adsorption Isotherms*

In general, isotherms for the adsorption of dyes are linear on cellulose triacetate, nylon, and polyester fibers (Fig. 2).[18–22] Only one or two dyes give curved isotherms.[23] The mechanism of dyeing may therefore be considered to occur in a manner similar to that in aqueous systems and hence to be of a solution type, with the partition coefficients decreasing and the saturation limits increasing with increases in temperature. The mechanism is confirmed by the independence of dye sorption when dyes are applied in admixture.[23] The partition coefficients of most dyes are small, being two orders of magnitude lower than those observed in aqueous systems, as shown by results for polyester fibers (Table I).[18,22] This has been confirmed with a range of some forty-two dyes using cellulose triacetate and polyester fibers employing

TABLE I[a]

Dye	*Saturation sorption* By fiber (gm/kg)	*Saturation sorption* By solvent (gm/liter)	*Partition coefficient*
1-Aminoanthraquinone	3.33	1.39	2.40
1,4-Diaminoanthraquinone	11.74	3.27	3.59
1,5-Diaminoanthraquinone	2.66	1.53	1.74
1,8-Diaminoanthraquinone	11.63	3.47	3.35
1,4,5,8-Tetraaminoanthraquinone	4.13	0.42	9.84

[a] From B. Miličevič.[18]

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[18] R. Senner and J. Merkel, *Textilveredlung* **4**, 487 (1969).

[17] B. Milićevič, *J. Soc. Dyers Colour*, **83**, 503 (1971).

[18] B. Milićevič, *Text. Chem. Color.* **1**, 87 (1970).

[19] R. C. R. Sheth, M.Sc. Thesis, Manchester University, (1969).

[20] W. S. Perkins and D. M. Hall, *Text. Res. J.* **43**, 115 (1973).

[21] Y. Suda, M. Suzuki, and F. Nakajima, *Bull. Res. Inst. Polym. Text. (Jpn.)* **99**, 43 (1972).

[22] A. Katakaya, Y. Kitano, and N. Kuroki, *Sen'i Gakkaishi* **28**, 302 (1972).

[23] K. V. Datye, S. C. Pitkar, and U. M. Purao, *Textilveredlung* **6**, 593 (1971).

perchlorethylene as a solvent; with few exceptions, the values of the partition coefficients are less than ten[23] and are not greatly influenced by raising the dyeing temperature or addition of carriers.[24,25] The color yield may be improved by adding small quantities of water.[26] The partition coefficients vary from solvent to solvent, and recently the sorption properties and diffusion coefficients have been shown for polyethylene terephthalate to be dependent on the solubility parameter of the solvent relative to that of the fiber (Fig. 3).[27] Those solvents with solubility parameters different from the fiber show the greater partition coefficients and the lower diffusion coefficients, the situation being reversed as the solubility parameter of the solvent approaches that of the fiber. For a series of disperse dyes on cellulose acetate, an inverse relation between partition coefficient and solubility in perchloroethylene has been demonstrated.[28] The commercial disperse dyes

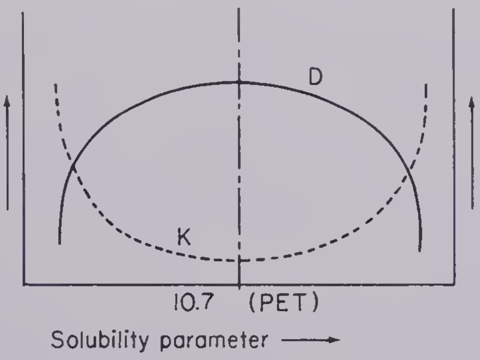
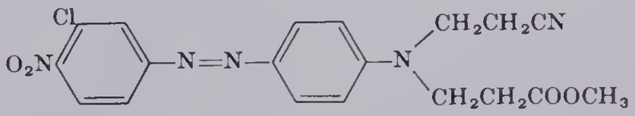
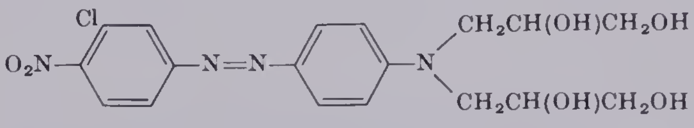


FIG. 3. Correlation between solubility parameter and diffusion (D) and partition (K) coefficients, in poly(ethylene terephthalate).[27]



(I)



(II)

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[24] K. Gebert, *J. Soc. Dyers Colour*, **87**, 509 (1971); W. Langmann and G. Sturzenacker, *Text. Asia* **3**, 7 (1972).

[25] R. Kuchni, *Text. Solvent Technol.-Update '73, AATCC Symp., 1973* p. 36 (1973).

[26] W. Kothe, *Text. Solvent Technol.-Update '73, AATCC Symp. 1973* p. 127 (1973).

[27] F. O. Harris and T. Guion, **42**, 626 (1972).

[28] Y. Suda and K. Akiyama, *Bull. Res. Inst. Polym. Text.* (*Jpn.*) 8, 19 (1973).

that are available are in general too soluble for use in perchloroethylene. Improvements in the partition can, however, be made by making the dye more hydrophilic. Thus, dye (I) gives a very low yield of 8%, but the introduction of the hydroxyl groups in dye (II) raises this to 40%.[25]

The partition coefficients of the disperse dyes indicate that poor color yields are obtained in practice from exhaustion dyeing. However, reduction of the liquor ratio from 1:30 to 1:10 raises the exhaustion in a typical case from about 50% to 90%[18]; naturally, the success of this depends on the solubility of the dye.[26]

Measurements of the heats of solution and heats of dyeing of the dyes may be determined from the changes with temperature in solubility of the dyes in the solvent and in the substrate. The heat of dyeing may be determined from the difference. Examples of the results are shown in Table II.[25,29] These examples are in line with those found in aqueous systems, namely positive heats of solution and negative heats of dyeing.

Only few results may be quoted for nylon dyeing. It seems that in contrast to the rapid rates of dyeing observed on polyester, sorption on nylon from chlorinated solvents is not very rapid.[30] This presumably arises from the inability of the solvent to modify the fiber properties sufficiently. However the partition coefficients of the dyes are also in general too small.

2. *Kinetics*

The diffusion into the more hydrophobic polymers, namely, cellulose triacetate, polyethylene terephthalate, and nylon 6, has been shown to be governed by constant diffusion coefficients.[29–32] The speed of dyeing varies with the solvent as indicated above, but for cellulose acetate and polyester, it is rapid.[19,29,33] The sorption of the solvent by the fiber will reduce the glass transition temperature to an extent depending on how close the solubility parameter of the solvent matches that of the substrate. A comparison between the rates of dyeing from water and perchloroethylene is shown in Fig. 4.[32] The diffusion coefficients are decreased with increasing molecular weight as shown in Fig. 5.[32]

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[29] R. H. Peters, "Textile Chemistry," Vol. III. Elsevier, Amsterdam, 1975.

[30] W. S. Perkins and D. M. Hall, *Text. Res. J.* **44**, 528 (1974).

[31] A. Katakaya, Y. Kitano, and N. Kuroki, *Sen'i Gakkaishi* **28**, 308 (1972).

[32] K. V. Datye, S. C. Pitkar, and U. M. Purao, *Teint. Apprets* **128**, 7 (1972).

[33] B. Milićević, *Textilveredlung* **4**, 231 (1969).

TABLE II

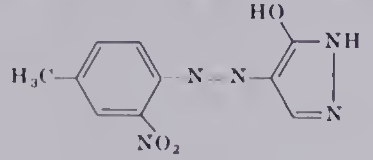
CHANGE IN ENTHALPY AND ENTROPY IN DYEING FROM PERCHLOROETHYLENE[a]

	Poly(ethylene terephthalate)[b]				*Cellulose triacetate*		
Dye[c] *no.*	ΔH_s (*kcal/mole*)	ΔH_f^0 (*kcal/mole*)	$-\Delta H^0$ (*kcal/mole*)	ΔS^0 (*cal/mole/deg*)	ΔH_f^0 (*kcal/mole*)	$-\Delta H^0$ (*kcal/mole*)	ΔS^0 (*cal/mole/deg*)
1	11.62	3.94	7.68	16.5	5.52	6.10	12.59
2	17.21	9.15	8.06	19.3	10.48	6.73	15.56
3	17.85	11.62	6.23	12.1	12.91	4.94	7.83
4	10.8	6.41	4.39	7.7	7.93	2.87	3.44
5	10.98	5.86	5.12	9.7	4.62	6.36	13.24
6	19.13	10.98	8.15	15.9	10.0	9.13	16.56

[a] From K. V. Datye, S. C. Pitkar, and U. M. Purao, *Textilveredlung* **6** 593 (1971).

[b] ΔH_s = heat of solution in the solvent; ΔH^0 = heat of dyeing; ΔH_f^0 = heat of solution in the fiber.

[c]



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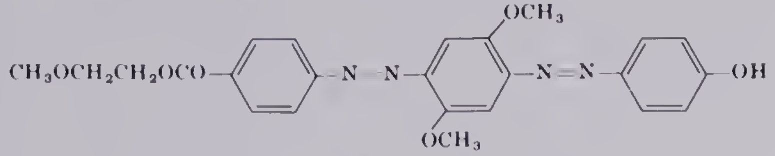

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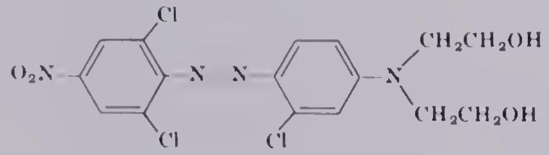

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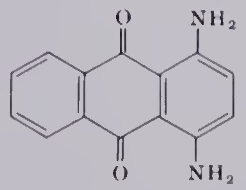

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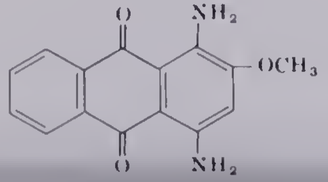

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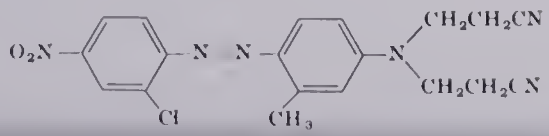

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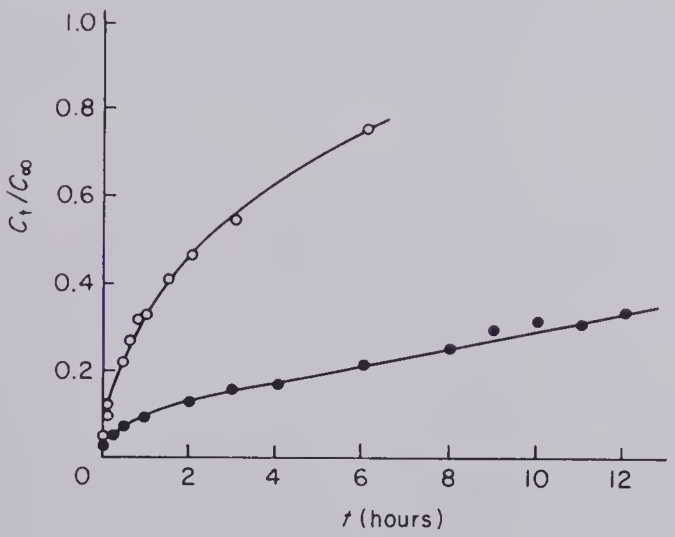

FIG. 4. Rates of dyeing, at 95°, in perchloroethylene (○) and in water (●).[32]

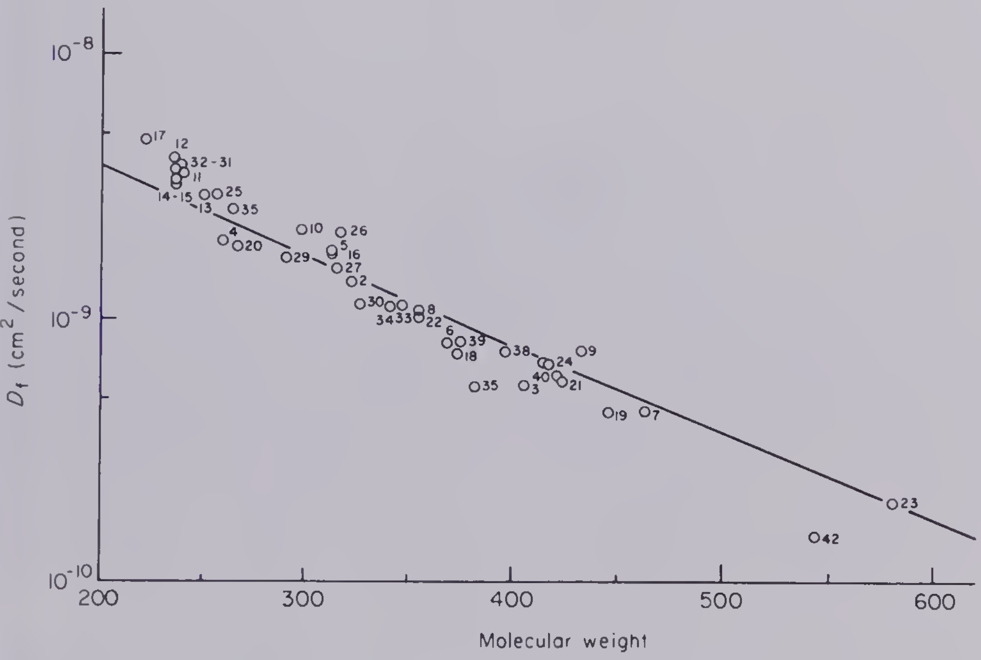

FIG. 5. Correlation between diffusion coefficient (D_f) and molecular weight of dyes in polyester film (perchloroethylene at 121°).[32]

TABLE III

Diffusion Coefficients and Activation Energy of Dyes on Poly(ethylene Terephthalate) Film from Perchloroethylene Bath[a]

	M	*Diffusion coefficients (cm²/second × 10⁻¹⁰) at:*						*Activation*
Dye[b]	*W*	91°*C*	95°*C*	101°*C*	110°*C*	115°*C*	121°*C*	*energy (kcal)*
1	261	0.538	0.723	1.81	3.78	7.50	19.4	33.94 ±2.36
2	464	0.064	0.098	0.325	0.893	1.63	4.44	40.08 ±2.28
3	434	0.107	0.211	0.551	1.91	.253	7.48	39.11 ±0.85
4	238	0.97	1.34	2.40	7.19	10.4	25.0	29.63 ±3.49
5	268	0.856	0.948	1.92	3.52	8.18	18.57	34.97 ±3.75
6	383	0.15	0.183	0.478	0.85	2.33	5.56	30.22 ±1.92

[a] From K. V. Datye, S. C. Pitkar, and U. M. Purao, *Textilveredlung* **6**, 593 (1971).

[b] See Table II for key to numbers.

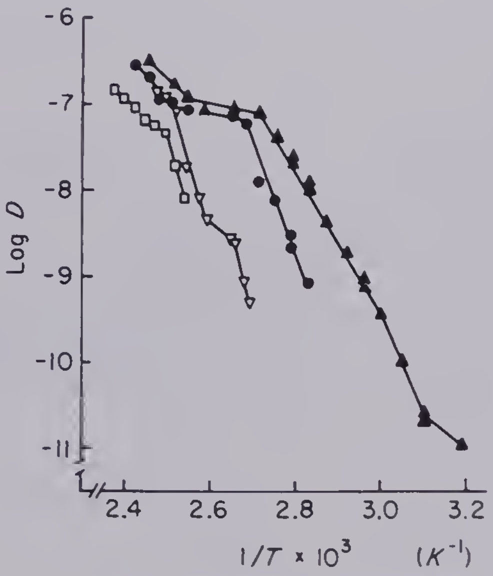

Fig. 6. Arrhenius plot of diffusion coefficients in PET from the TCE or water dyebath. Violet 1: (▲) from TCE, (▽) from water, Violet 8: (●) from TCE, (□) from water.[34]

The process of diffusion is temperature sensitive, and the activation energies are large, being similar in magnitude to those found in aqueous systems (Table III).[23,34] Moreover, as with aqueous systems, a plot of the logarithm of the diffusion coefficient versus the reciprocal of the absolute temperature shows similar transitions, albeit at a different temperature (Fig. 6).[34]

3. *Interaction of Solvents with Fibers*

Sorption of the solvent by the fiber can be rapid. In the case of polyester, cellulose acetate and triacetate, and nylon 6, equilibrium was reached in 1–2 minutes using trichloroethylene at 87° and perchloroethylene at 120°. The extent to which sorption occurred varied with the fiber, but was in the region of 5–10%.[35] However, with these particular solvents, the absorption of solvent was not significant for nylon 66, wool, or polyacrylonitrile.

The absorption of the solvent can cause considerable changes in the mechanical properties of the fibers and may in the case of polyesters cause fissures to develop in the fiber surface.[36] With fibers such as rayon or nylon, the solvent may raise or lower the initial modulus and shorten or extend the plastic flow region of the load extension curves. However, the majority of solvent–fiber interactions cause a lowering of the initial modulus.[37,38] Correlations of these changes with the solubility parameter of the solvent were not good; it was concluded that rather specific interactions occurred, e.g., changes in hydrogen bonding or hydrophobic interaction between chains.

The sorption of solvent usually causes shrinkage, which may then be followed by crystallization to give small crystalline regions without necessarily increasing the perfection of the system.

A comprehensive study of the interaction of some twenty-six solvents with polyester fiber has been made.[39] The yarns were treated in solvents and their load extension curves determined in the same solvents. With some solvents (e.g., perchloroethylene, acetone, methylene chloride), a significant plastic flow region was observed together with some irreversible shrinkage. Various physical properties of the fibers –

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[34] Z. Morita, R. Kobayashi, K. Uchimura, and H. Motomura, *J. Appl. Polym. Sci.* **19**, 1095 (1975).

[35] M. Capponi, J. Moreau, and F. Somm, *Am. Dyest. Rep.* **63**, 36 (1974).

[36] H. Weigmann and M. G. Scott, *Text. Res. J.* **45** 554 (1975).

[37] H. Weigmann and A. S. Ribnick, *Text. Solvent Technol.-Update '73, AATCC Symp., 1973* p. 24 (1973).

[38] H. Weigmann and A. S. Ribnick, *Text. Res. J.* **44**, 165 (1974).

[39] B. H. Knox, H. D. Weigmann, and M. G. Scott, *Text. Res. J.* **45**, 203 (1975).

shrinkage, swelling, glass transition temperature, crystallinity—were related to the total solubility parameter of the solvent relative to that of the polyester (10.7); i.e., the changes were at a maximum when the solubility parameter of the solvent was in the region of 10.7.

When examined in more detail, the changes in properties when plotted against the solubility parameters showed large changes for values of the latter in the two regions 8.5–11 and 12–13. These two maxima are likely to be the result of specific interactions of the solvent with the —COC_6H_4CO— unit of the chain and the methylene groups in the —OCH_2CH_2O— unit, respectively. Thus the physical effects of solvents can be very complex, although it is likely from the dyeing point of view that the lowering of the glass transition temperature is the major factor in determining the dyeing rate in any particular solvent. The reductions in this property vary from solvent to solvent (Table IV).[40]

TABLE IV

EFFECT OF SOLVENT ON POLYESTER GLASS TRANSITION[a]

Solvent	T_g(°C)
Water	80–85
Butanol	~70
Perchloroethylene	~60
Acetone	~40
Trichlorethylene	33–36
Chloroform	~10
Methylene chloride	~ −10

[a] From R. Weingarten, *Text.-Prax.* **28**, 231 (1973).

It is interesting to note in this connection that additives to the solvent may cause changes in the dyeing rate and the glass transition of the fiber. Water is particularly important from this point of view. An example is the increased rate of dyeing of cellulose triacetate from an isooctane solvent when water is added.[41] In the case of acrylic fibers, addition of water to benzyl alcohol solutions increases the dyeing rate and lowers the glass transition temperature.[42]

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[40] R. Weingarten, *Text.-Prax.* **28**, 231 (1973).

[41] C. R. Ramachandran, R. McGregor, and R. H. Peters, *J. Soc. Dyers Colour.* **84** 9 (1968).

[42] Z. Gur-Arieh and W. C. Ingamells, *J. Soc. Dyers Colour.* **90**, 8 (1974).

4. *Practical Aspects*

Solvent dyeing has with some exceptions been concerned with dyeing from the chlorinated hydrocarbons, with the main emphasis on polyesters.[43] With batchwise processing or exhaustion dyeing, the partition coefficients of normal commercial dyes between pure solvent and polyester are very low,[24] and attempts have been made to design more suitable dyes. Unfortunately, the number of these available is small. The dyes are in general too soluble for good exhaustion; for success, the dyes must be only slightly soluble and in the correct dispersed form.[24] Complementary efforts to solve these problems have led to developments on the machinery side.[43]

One way of improving the exhaustion is to mix the perchloroethylene with an inert medium. In one process,[43,44] the solvent is diluted with 75–80% of a silicone fluid, the introduction of which increases the exhaustion and hence the apparent partition coefficient and reduces the solubility of the dye. After dyeing and subsequent discharge of the exhausted dyebath, the fabric is rinsed with perchloroethylene or acetone, the latter being preferred, since this facilitates drying.

Continuous dyeing processes that are essentially based on padding followed by a fixation process require high solubility of the dyes. To ensure this, co- or booster solvents are added. These are polar aprotic substances such as *N*,*N*-dimethylacetamide.[18,45] Many normal dyes have been shown to be suitable for continuous dyeing.[46]

Continuous dyeing of polyester has been examined in some detail.[35] A distinction may be made between the two main phases of continuous dyeing, application and fixing. The dye liquor may take one of three forms: (1) a solution in perchloroethylene using a booster solvent, (2) an emulsion of water in perchloroethylene, standard commercial dyestuffs being used as a dispersion or solution in the water, or (3) a dispersion of the dye in perchloroethylene.

The first of these suffers *inter alia* from difficulties of separation of the booster from the solvent in subsequent recovery and the substantial migration that occurs during drying. The emulsion process gives good results in many cases, but its application is limited by the solubility of the dye when it is of the water-soluble type. In this process, it is necessary to operate with a water content of between 5 and 20%. The stability of the emulsion has been shown to be good except when

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[43] R. V. Love, *Rev. Prog. Color. Relat. Top.* **6**, 18 (1975).

[44] J. P. Coats, *BP* 1,386,072 (1975).

[45] B. Milićevič, *Textilveredlung* **4**, 766 (1969).

[46] N. L. Anderson and J. N. Capone, *Text. Solvent Technol.-Update '73, AATCC Symp., 1973* p. 65 (1973).

the temperature is in the boiling range. For this reason, to reduce condensation losses, additions of lithium chloride or acetamide have been suggested.[47] The addition of water to the system does not alter the linearity of the isotherm, although the addition of the emulsifier decreases the value of the partition coefficient.[13]

Using a dispersion technique, it is possible to dye continuously the more hydrophobic fibers, but not wool or cotton. Dyes can be fixed in hot air, in superheated steam, by contact heat, or even in solvent vapor. Of these, superheated steam is the most effective. Examples of rates of fixation curves are given in Fig. 7.[35]

One novel solvent proposed is liquid ammonia. The cloth is padded through a solution of the dye in the liquid and subsequently steamed for dye fixation. No additives to the bath are required, and it is claimed

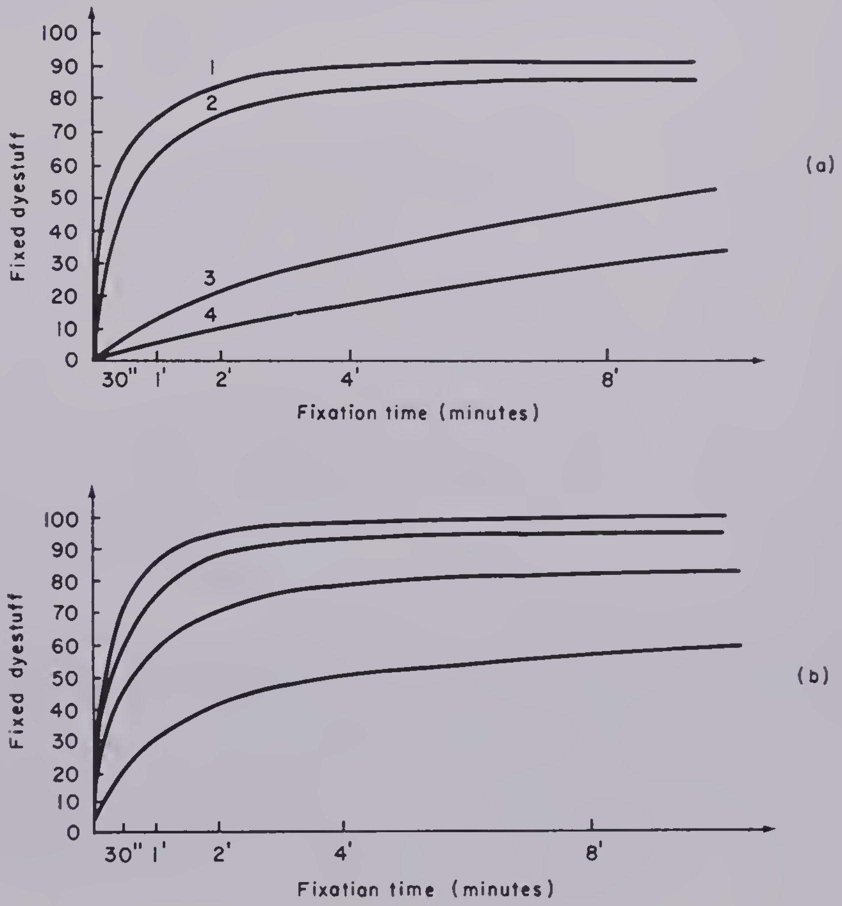

FIG. 7. Fixation curve for (a) Polyacryl Orange 2 on Orlon and (b) Polyester Red 34 on acetate.[35]

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[47] R. Menold, *Kolloid-Z. & Z. Polym.* **250**, 711 (1972).

that with the exception of wool and cellulose acetate all fibers may be treated in this way.[48]

a. Ionic Dyes. Batchwise dyeing of nylon, wool, and cellulosic fibers with ionic dyes poses different problems, because the dyes are insoluble in perchloroethylene. To initiate dyeing, small quantities of water need to be introduced, usually in emulsion form. The water swells the fibers and assists in ionizing the dyes. Effectively, dyeing occurs from an aqueous bath of very low liquor ratio, and dyeing is carried out at normal dyeing temperatures as in aqueous processing. Such a system has some disadvantages, e.g., danger of emulsion breakdown, need for pressure dyeing equipment for dyeing above the boiling point (87°) of the water perchloroethylene azeotrope.[43] Emulsion systems have been described for the dyeing of nylon with acid, metal complex, or reactive dyes.[49] Such systems have also been suggested for wool dyeing.[50,51] It is interesting to note that in the water perchloroethylene system at 80°, the saturation values correlated well with the number of amine end groups in nylon 6.[52]

Emulsions have been used for dyeing acrylic fibers with basic dyes, but it is necessary to dye under pressure at temperatures above the boiling point of the azeotropic mixture in order to obtain good color yields.[50,51]

When combined with a rather hydrophobic ion of opposite charge, an ionic dye will form a complex capable of dissolving in organic solvents. For basic dyes, these complexes have been manufactured as dry powders, which may be dissolved in perchloroethylene with the aid of a booster solvent.[13,53,54] The acrylic fiber may then be padded and passed through heated solvent vapor. The dyed fabric possesses excellent fastness to solvents, so that some ion exchange is likely to have occurred in the solvent vapor with the rejection of the solvent–soluble anion. Using a bath of perchloroethylene or *m*-xylene with additions of tetrahydrothiophene 1,1-dioxide, it was shown that cationic dyes were sorbed in quantities nearly equivalent to the number of available acid groups in the fiber.[54]

In an analogous way, acid dyes may be solubilized by the addition

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[48] S. Kane, *Am. Dyest. Rep.* **62**, 27 (1973); *Melliand Textilber.* **55**, 162 (1974).

[49] D. Hildebrand, *Bayer Farben Rev., Spec. Ed.* **13**, 2 (1971); D. Hildebrand and R. Kuth, *Melliand Textilber.* **53**, 569 (1972).

[50] D. Hildebrand and R. Kuth, *Melliand Textilber.* **53**, 569 (1972).

[51] D. Hildebrand and R. Menold, *Text.-Ind.* (*Moenchen-Gladbach, Ger.*) **73**, 278 (1971).

[52] K. H. W. Weible and J. P. Merminod, *Text. Solvent Technol.-Update '73, AATCC Symp., 1973* p. 178 (1973).

[53] F. Sievenpiper, E. Bement, and R. Dawson, *Text. Chem. Color.* **3**, 469 (1971).

[54] E. A. Duffy and E. S. Olson, *J. Appl. Polym. Sci.* **16**, 1539 (1972).

of triethanolamine oleate. Isotherms for nylon are linear, suggesting that the complex is dyeing like a disperse dye.

The mechanism of dyeing seems to be an ionic one. Examination of the sorption properties of acid dyes complexed with amines carrying long aliphatic chains showed that the uptake by wool and nylon was very small until water was added.[55] This observation has led to the suggestion that the complex hydrolyzes prior to being taken up by the fiber. Confirmation of this came from the distribution of the complex between perchloroethylene and water when significant quantities of the dye dissolved in the aqueous layer. Moreover, on this test, those dye complexes that possessed the shorter aliphatic chains hydrolyzed to a greater extent and were absorbed to greater extents by the fibers.

b. Cellulose Dyeing. These fibers are difficult to dye from normal solvents, since ionic dyes are only absorbed if the fiber is in the swollen state. On a laboratory scale, however, it has been shown that dyeing may take place from dimethylformamide or mixtures of this solvent with perchloroethylene.[56] Other workers have suggested the use of direct dyes in a mixture of water/glycerol (100% weight of goods) together with an emulsifying agent, which is then diluted with perchloroethylene to give a liquor ratio of 10:1.[57] Using reactive dyes, the introduction of cotton preswollen with caustic soda into a bath containing dimethylformamide and trichloroethylene has been suggested.[58]

C. CARRIER DYEING

Some fibers, notably polyesters and acrylics, are troublesome to dye because they dye very slowly below their glass transition temperatures (T_g); these transitions occur, under dyeing conditions, in the region of 60°–80°. Adequate rates are only achieved when the temperature is in excess of the T_g. For polyethylene terephthalate fibers, economic speeds of dyeing are achieved by using high temperatures (~130°). An alternative method is to add a carrier or plasticizer to the bath, when more normal dyeing temperatures may be employed. Many types of chemical compounds act in this way, e.g., phenols, amines, esters; the choice of compound has been made by trial and error.[59]

Carriers have been of most value in the dyeing of polyesters, although

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[55] Y. Nemoto, K. Mose, H. Funahashi, and K. Katama, *Text. Solvent Technol.-Update '73, AATCC Symp., 1973* p. 58 (1973).

[56] AATCC Delaware Section, *Text. Chem. Color.* 5, 60 (1973).

[57] H. M. Silver, *J. Soc. Dyers Colour.* **90**, 111 (1974).

[58] R. B. Chavan, *J. Soc. Dyers Colour.* **91**, 59 (1976).

[59] H. Murray and K. Mortimer, *Rev. Prog. Color. Relat. Top.* **2**, 67 (1971).

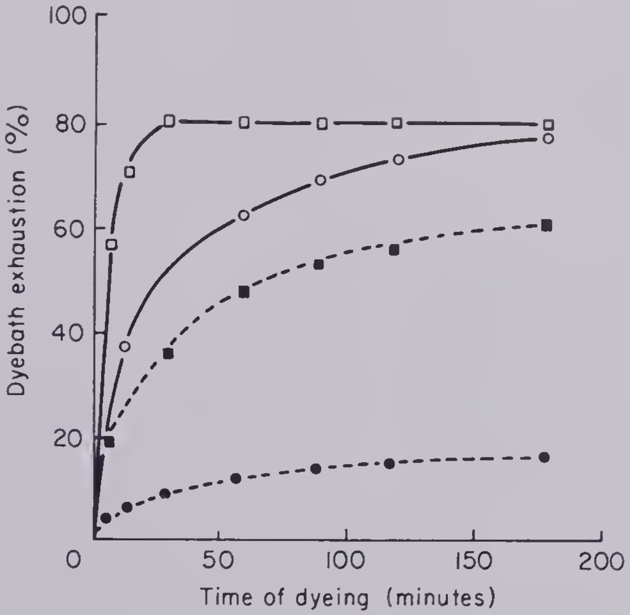

FIG. 8. The effect of Tumescal D on the rate of dyeing of Dispersol Fast Scarlet B 150. (●) no carrier at 85°; (■) no carrier at 100°; (○) 8.0% Tumescal D at 85°; (□) 8.0% Tumescal D at 100°.[62]

they have been recommended for dyeing cellulose triacetate with some of the more slowly dyeing dyes and are essential for dyeing Qiana. They have also been recommended as assistants in high-temperature dyeing.[60]

For polyester, the most popular compounds are *o*-phenylphenol, diphenyl, and chlorinated benzenes, although the last suffer from being volatile. Among the range of compounds suggested, some have high water solubility (e.g., phenol, benzoic acid) whereas others (e.g., diphenyl) are almost insoluble and are added to the bath as emulsions.[61]

i. Rate increases on carrier addition. An example of the way[62] in which additions of carriers increase the rate of dyeing is shown in Fig. 8. However, the different carriers vary markedly in their effectiveness, low water solubility being an advantage. This is related to the degree to which they are absorbed by the polyester, as shown by the partition coefficients (Table V).[63] The absorption isotherms for carriers are linear,

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[60] J. K. Skelly, *Textilveredlung* **8**, 102 (1973).

[61] C. L. Zimmerman, J. M. Mesco, and A. J. Carlino, *Am. Dyest. Rep.* **44**, 296 (1955).

[62] I. M. S. Walls, *J. Text. Inst.* **45**, 258 (1954).

[63] D. Balmforth, C. A. Bowers, J. W. Bullington, T. H. Guion, and T. S. Roberts, *J. Soc. Dyers Colour*, **82**, 405 (1966).

TABLE V

PARTITION OF CARRIERS BETWEEN POLYESTER AND WATER[a]

Compound	*Solubility (gm/liter)*	*Partition coefficient*
Diphenyl	0.164	574
Phenyl salicylate	0.223	473
o-Phenylphenol	2.26	90
Benzoic acid	73.0	3.7

[a] From D. Balmforth, C. A. Bowers, J. W. Bullington, T. H. Guion, and T. S. Roberts, *J. Soc. Dyers Colour.* 81, 405 (1966).

and hence their mechanism of sorption is similar to that of disperse dyes.[64]

ii. Mechanism of carrier action. The above observations suggest that for a carrier to be effective, it must be sorbed by the fiber, and hence the action results from fiber modification.[65] Indeed, many carriers for polyester are solvents or induce crystallization of the amorphous polymer.[66] Using a set of aromatic carboxylic acids as carriers for polyester, it was shown that the carrier reduces the dynamic modulus and the orientation of the fiber but increases the crystallinity.[67] With others (e.g., methyl salicylate, *o*-phenylphenol) little or no change in the crystallinity occurs, although there is considerable disorientation.[68,69] Some, when used in excess (e.g., *o*-cresol, diphenyl), can penetrate the crystalline structure as shown by changes in the X-ray picture.[70] Moreover, the sorption of carriers modifies the dimensions of the fiber, which may swell or contract in length[70–72]; however no correlation between carrier action and swelling has been established.[73]

As an example, swelling polyester in mixtures of trichloroacetic acid (85%) and water at 23°–24° produced marked increases in dye

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[64] F. Fortess and V. S. Salvin, *Text. Res. J.* **23**, 1009 (1958).

[65] V. S. Salvin, *Am. Dyest. Rep.* **49**, 600 (1960).

[66] J. H. Lemons, S. S. Kakar, and D. M. Cates, *Am. Dyest. Rep.* **55**, 76 (1966).

[67] V. N. Zashta, M. Sotton, and J. Jacquemart, *Bull. Inst. Text. Fr.* **11**, 277 (1974).

[66] T. Vickerstaff, *Melliand Textilber.* **35**, 765 (1954).

[69] A. H. Brown and A. T. Peters, *Am. Dyest. Rep.* **57** 281,284 (1958).

[70] P. Senner, V. Schwair, W. Morgenstern, and D. Sandner, *Melliand Textilber.* 48, 789 (1967).

[71] AATCC, Piedmont Section, *Am. Dyest. Rep.* **48**, 23,37 (1959).

[72] F. M. Ravicz, D. Cates, and H. A. Rutherford, *Am. Dyest. Rep.* **59**, 320 (1961).

[73] R. Rochas and M. Courmont, *Int. Conf. IFATCC*, London (1959).

TABLE VI

PARTITION OF CI DISPERSE RED 15 BETWEEN POLYESTER FIBER AND BATH AT 95° IN PRESENCE AND ABSENCE OF CARRIERS [a]

	Equilibrium carrier concentration		
Carrier	*In fiber (gm/kg)*	*In bath (gm/liter)*	*Partition coefficient*
Biphenyl	0.0	0.0	633
	23.3	0.0407	845
	46.6	0.0814	923
	69.9	0.1221	1000
o-Phenylphenol	0.0	0.0	633
	45.0	0.50	878
	67.5	0.75	1000
	90.0	1.00	1138
Phenyl salicylate	0.0	0.0	633
	45.8	0.105	700
	68.7	0.157	768
	87.0	0.199	857
Benzoic acid	0.0	0.0	633
	16.92	4.58	535
	33.84	9.16	460

[a] From D. Balmforth, C. A. Bowers, J. W. Bullington, T. H. Guion and T. S. Roberts, *J. Soc. Dyers Colour*, **82**, 405 (1966).

uptake, which were greater for fabrics treated under tension and for fabrics previously heat set.[74]

The relaxation of the structure brought about by the carrier has an advantage in practice, namely, a reduction in the differences in the dyeing properties of the yarn, and hence a more uniform dyeing is obtained.[75]

iii. Effects of carriers on the equilibrium sorption of dyes. The linearity of the isotherms of disperse dye sorption is not modified by the presence of the carrier, but the partition coefficient is altered (Table VI).[63,76] In the presence of hydrophobic carriers, the partition coefficient increases, whereas the more hydrophilic carriers reduce it.

A partial explanation of the increase in dye uptake is offered by

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[74] G. A. Byrne, *J. Soc. Dyers Colour.* **89**, 215 (1973).

[75] J. K. Skelly, *J. Soc. Dyers Colour.* **89**, 349 (1973).

[76] E. Waters, *J. Soc. Dyers Colour.* **55**, 609 (1950); M. J. Schuler and R. Remington, *Discuss. Faraday Soc.* **16**, 201 (1954).

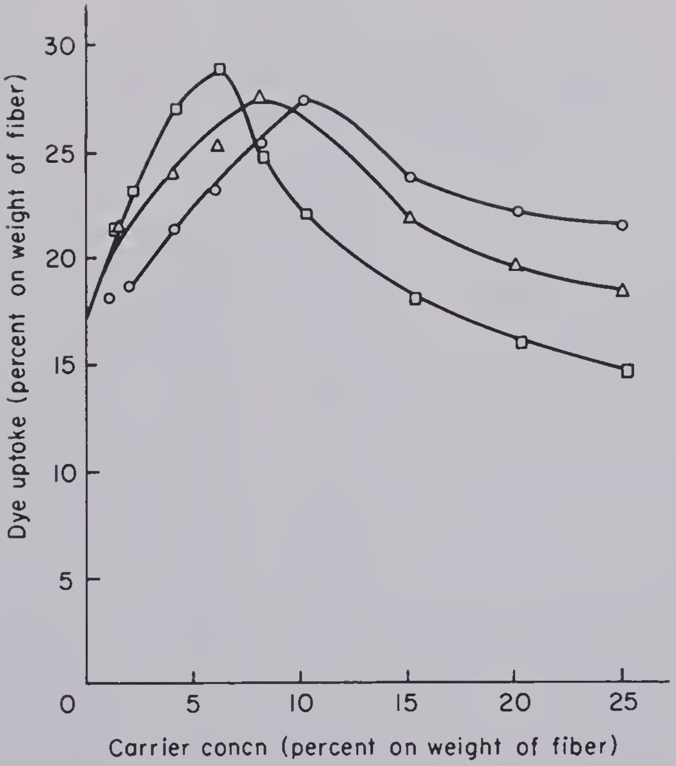

FIG. 9. Effect of carrier concentration (% on weight of fiber) on the uptake of Amacel Fast Blue AGF Conc. at 100°. □, Biphenyl; ○, phenyl salicylate; △, *o*-phenylphenol.[63]

the suggestion that the carrier present in the fiber phase augments the solubility in the fiber by the quantity of dye that dissolves in the absorbed carrier. Some evidence for association of the dye with the carrier comes from the spectral changes of the dye that occur when nitrobenzene is used.[77] Analysis of the position is complicated by the fact that water dissolves in the carrier and carrier in the water; this will modify the solubilities of the dye in the carrier and water phases as compared with those in the pure phases.[78]

The decrease in the partition coefficient when benzoic acid is used as a carrier may be explained conversely by the low partition coefficient of the latter and the high solubility of the dye in the benzoic acid solution. The latter may be regarded as acting as a hydrotrope. It may be noted that with the hydrophobic carriers, sorption of dye increases with carrier concentration to a maximum and then decreases (Fig. 9). The maximum value appears to occur when the system is saturated

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[77] F. Nakajima and Y. Suda, *Bull. Res. Inst. Polym. Text.* (*Jpn.*) **9**, 63 (1969); Y. Suda, F. Janijima, and H. Ujigawa, *ibid.* p. 71.

[78] R. Weingarten, *Chemiefasern* [N.S.] **28**, 397 (1973).

TABLE VII

Diffusion Coefficient of Dyes in Dacron Fiber[a]

	D (cm²/second × 10^{11})		
Dye	*Without carrier*	*Benzoic acid*	*Trichlorobenzene*
1,8-Dihydroxyanthraquinone	0.62	13.0	18.0
1,4-Dihydroxyanthraquinone	0.6	23.0	14.0
1-Hydroxy-3-bromo-4-aminoanthraquinone	6.28	9.5	33.0
1-Hydroxy-2,3-dichloro-4-aminoanthraquinone	0.10	4.5	23.0
1,5-Dihydroxy-4,8-diaminodibromoanthraquinone	0.1	3.1	9.5
1-Hydroxy-4-anilinoanthraquinone 2-carboxylamide	0.17	1.8	1.5
1-Hydroxy-4-toluidinoanthraquinone	0.07	2.8	1.1
4-Hydroxy-2′,4′-dinitrodiphenylamine	0.34	6.2	22.0
p-Aminoacetanilide → *p*-cresol	0.06	2.3	18.0
2-Chloro-4-nitro-6-bromoaniline → 3-chloro-*N*-dihydroxyethylaniline	0.6	2.3	2.3

[a] From O. Glenz, H. Beckmann, and W. Wunder, *J. Soc. Dyers Colour.* **75**, 141 (1959).

with carrier; further increase in the latter leads to the formation of a third phase in which the dye is very soluble.[78]

iv. Kinetics. The dramatic increases in rate of dyeing are shown quite clearly, for addition of two carriers, in Table VII.[79] The diffusion coefficients of disperse dyes in fibers pretreated with carriers are time and concentration independent, which suggests that a solution mechanism is operative.[41] Simultaneous sorption of the carrier and dye presents a more complicated picture, since the carrier as it penetrates modifies the structure and the now rapidly diffusing dye will be the main diffusing component in the modified polymer structure. For most carriers, the diffusion of the carrier is faster than the dye.[78,80] If the relaxation processes resulting from the interaction of the carrier with the structure are slow, the dye may diffuse at a speed determined by the speed of the carrier. The diffusion process of the carrier is expected to be anomalous, since it is accompanied by alterations in the structure of the fiber that may be time dependent.

v. Relation of carrier action to fiber structure. In general terms, the speed of diffusion of a dye may be correlated with the mechanical

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[79] O. Glenz, H. Beckmann, and W. Wunder, *J. Soc. Dyers. Colour.* **75**, 141 (1959).

[80] H. Rath and P. Senner, *Text. Ind.* (*Moenchen-Gladbach, Ger.*) **69**, 77 (1967).

properties of the fiber, such as modulus, stress relaxation, and shrinkage. When the fibers are treated with carriers, shrinkage or extension occurs and the glass transition temperature of the fiber is lowered.[29,81] Such observations suggest that the major change in the fiber properties results from the plasticizing effect of the carrier rather than from swelling. Indeed, it has been shown from studies of the acrylic fiber Acrilan that the increases in diffusion coefficients brought about by various carriers were related to the glass transition lowering[42] but not to the swelling of the fiber.

Below the glass transition temperature, little dye and even little typical carrier is sorbed,[69] and it is not until the dyebath temperature is in excess of the T_g that substantial sorption occurs.[82] If the dye

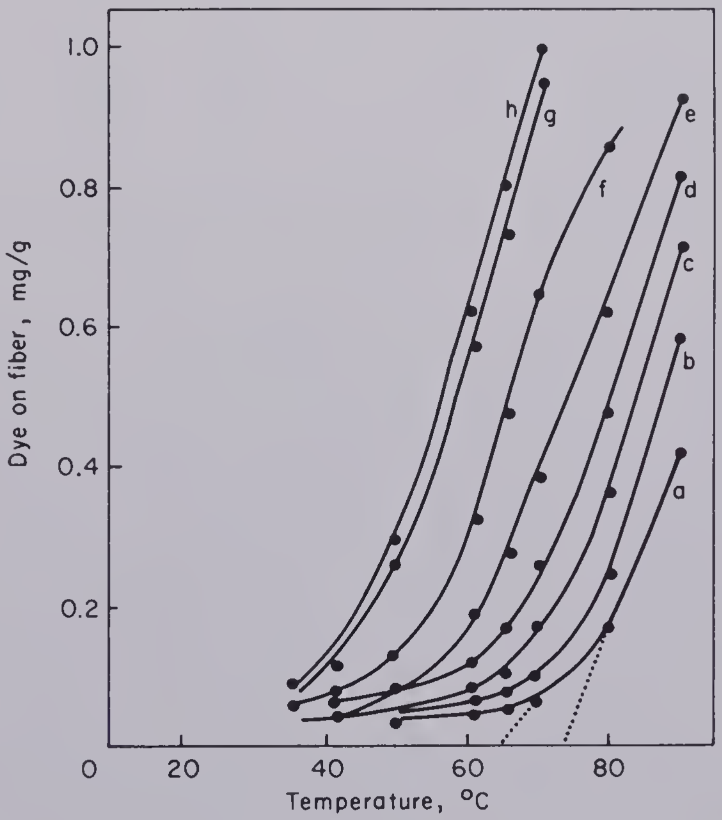

FIG. 10. Variation in uptake of CI Disperse Orange 3 by Acrilan filaments in presence of benzyl alcohol. (a) Water; (b) water + 0.05 mole/l benzyl alcohol; (c) water + 0.10 mole/l benzyl alcohol; (d) water + 0.15 mole/l benzyl alcohol; (e) water + 0.20 mole/l benzyl alcohol; (f) water + 0.30 mole/l benzyl alcohol; (g) water + 0.40 mole/l benzyl alcohol; and (h) water + 0.45 mole/l benzyl alcohol.[42]

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[81] K. Fujino, N. Fujimoto, and K. Eto, *Text. Mach. Soc. Jpn. Ed.* **14**, 449 (1961); K. Fujino, W. Kuroda, and F. Fujimoto, *J. Soc. Fiber Sci. Technol., Jpn.* **21**, 573 (1965).

[82] A. Takaoka and M. Aki, *Sen'i Gakkaishi* **21**, 425,427,452 (1965).

absorption after a short dyeing time is plotted against the dyeing temperature, a marked increase in the uptake occurs over a short temperature range. This may be seen for Acrilan filaments in the presence of varying quantities of plasticizer (benzyl alcohol) in Fig. 10.[42] These data show that the dye is more easily taken up by the fiber as the alcohol concentration is increased, and the shape of the curves are very similar to those observed for the increase in length given in Fig. 13. Since the dye increases are associated with the glass transition region, it seems logical to extrapolate the approximately linear portion to the ordinate to obtain a temperature that may be referred to as the dyeing transition T_d. In Fig. 11,[42] the T_g measured by the changes in length is plotted against T_d. Although the values of the T_d are approximately 12° higher than T_g, the linear correlation gives confidence to the suggestion that T_d may be taken as the relevant transition for dyeing. The increased value found for dyeing as compared with that from mechanical properties suggests that the cooperation of more chain segments is required to allow entry of dye.

The dyeing transition temperature, like the T_g deduced from the mechanical properties, gives linear relations with the carrier concentration. It can be used as a parameter for the fiber in the same way as T_g itself.[83] Although the glass transition temperature is the main

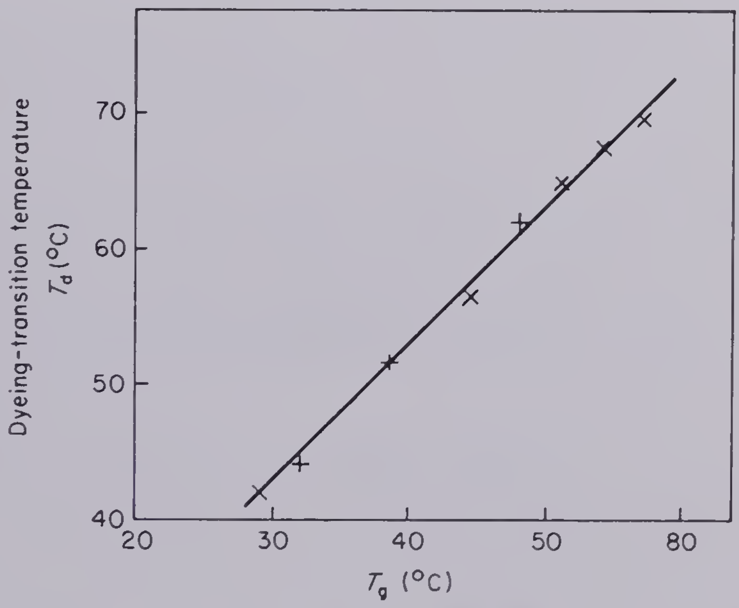

FIG. 11. Relationship between dyeing-transition temperature of Acrilan filament obtained using CI Disperse Orange 3 and glass-transition temperature obtained by physical measurement in presence of benzyl alcohol.[42]

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[83] W. Ingamells and K. V. Narasimham, *J. Appl. Polym. Sci.* **20** 2271 (1976).

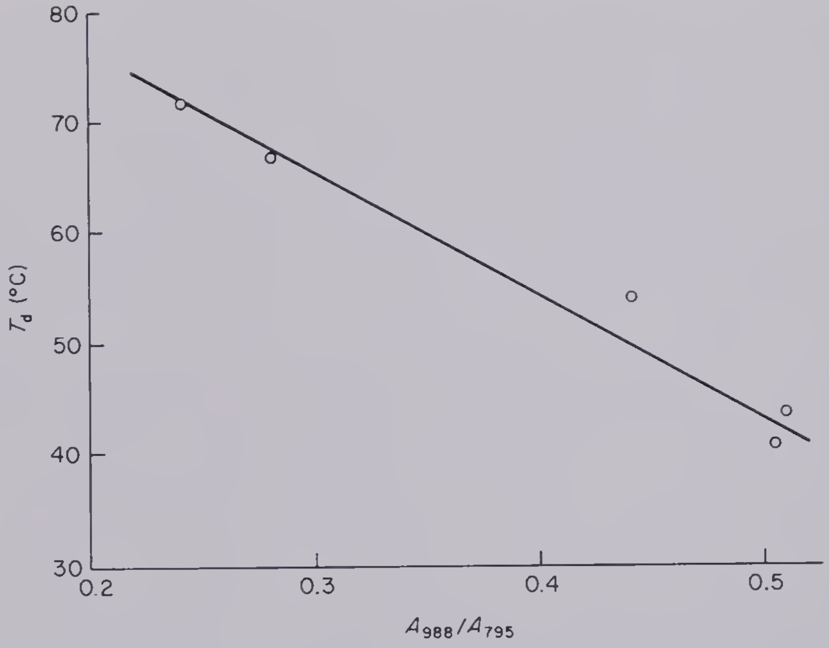

FIG. 12. Variation in the dyeing-transition-temperature (T_d) with the intensity of the Chain Fold Band.[83]

variable in determining the effect of fiber structure on dyeing rate, it must be noted that the physical and mechanical properties of a fiber are interrelated. As an example, with polyethylene terephthalate, carriers induce changes in the crystallinity. Some of the linear crystalline arrangements are transformed into folded forms; the number of chain folds are reflected by the increases in intensity of the fold band in the infrared spectrum. These changes in the crystalline arrangement are related to the dyeing properties, as shown by the relationship between the increase in the fold band and the dyeing transition temperature (Fig. 12).[83] Such changes in the fiber structure are irreversible, however, as demonstrated by examination of the fiber after removal of the carrier.[60,84–86]

vi. Measurement of the glass transition temperature. Measurements of the T_g must be made with the fiber in the dyebath itself. The simplest way is to measure the changes in length that occur as the temperature is raised. With the fibers supporting a small weight, it is found for a quasicrystalline fiber such as Acrilan that the length of the fiber extends

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[84] R. Rochas and M. Courmont, *Bull. Inst. Text. Fr.* 86, 15 (1960).

[85] E. Elöd, *Melliand Textilber.* 41, 718 (1960).

[86] P. Senner, V. Schwair, W. Morgenstern, and B. Sandner, *Melliand Textilber.* 48, 690,789 (1967).

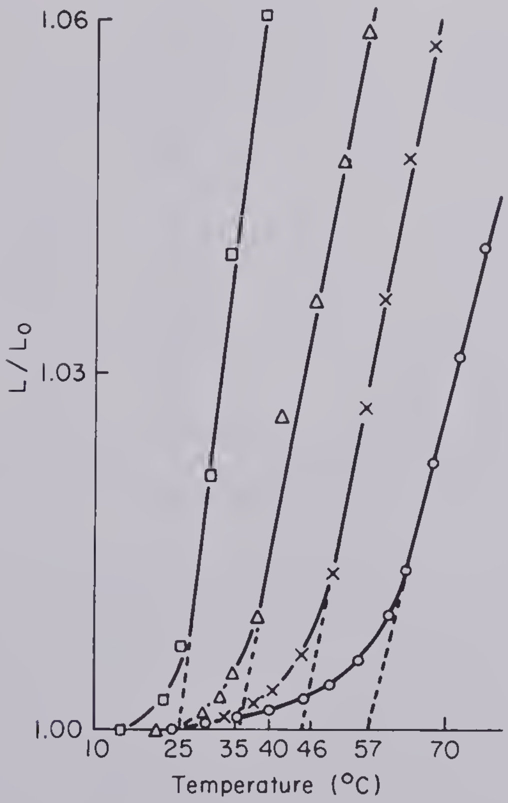

FIG. 13. The effect of temperature on the fractional increase in length of Acrilan filaments immersed in solutions of phenol. (○) Water; (×) 10 gm/liter phenol; (△) 20 gm/liter phenol; (□) 30 gm/liter phenol.[87]

significantly once the glass transition region is reached (Fig. 13). Extrapolation of the linear portion of the graph gives a good evaluation of the T_g. Some results obtained in this way are shown in Table VIII. In these experiments, the fiber was pretreated with the carrier; the decrease in T_g is considerable and dependent on the carrier concentration. The expected relationship is calculated, on the basis of free volume arguments, to be

$$T_g \sim T_{g_p} - (\alpha_c/\alpha_p)(T_{g_p} - T_{g_c})v_c$$

where T_{g_p} is the transition temperature of the polymer and T_{g_c} that of the carrier; α_c and α_p are the thermal expansion coefficients of the carrier and polymer; v_c is the volume fraction of carrier in the polymer, and since the quantities are small, may be replaced by concentration.

The reduction in T_g is a measure of increased segmental motion within the polymer chains and hence is a parameter reflecting the changes in mechanical and diffusion properties. For Acrilan, more

TABLE VIII

GLASS TRANSITION TEMPERATURES OF ACRILAN FILAMENTS WHEN EXTENDED IN DIFFERENT SOLUTIONS[a]

Solution	Concentration (gm/liter)	T_g (°C)
Water		57.0
Phenol	10	46.4
Phenol	20	35.0
Phenol	30	25.0
Toluidine	2.3	43.0
Nitrobenzene	1.0	52.5
Nitrobenzene	2.0	49.5
Dimethylformamide	10	53.0

[a] From W. Ingamells, R. H. Peters, and S. Thornton, *J. Appl. Polym. Sci.* **17**, 3733 (1973).

detailed changes in mechanical properties have been measured by the rate of increase in length of the fiber at each temperature when the latter carries a small weight. Since the extent of the creep is small, the system may be taken to be linearly viscoelastic, and hence the curves may be superimposed by a shift of the time scale. The data (Fig. 14) for Acrilan fibers and phenol at different concentrations confirm this point. The shift factors needed to produce such a master curve are related to the ratio of the internal viscosities of the treated fibers.

The internal viscosities are reciprocally related to the diffusion coefficients and hence both are related through the W. L. F. equation to

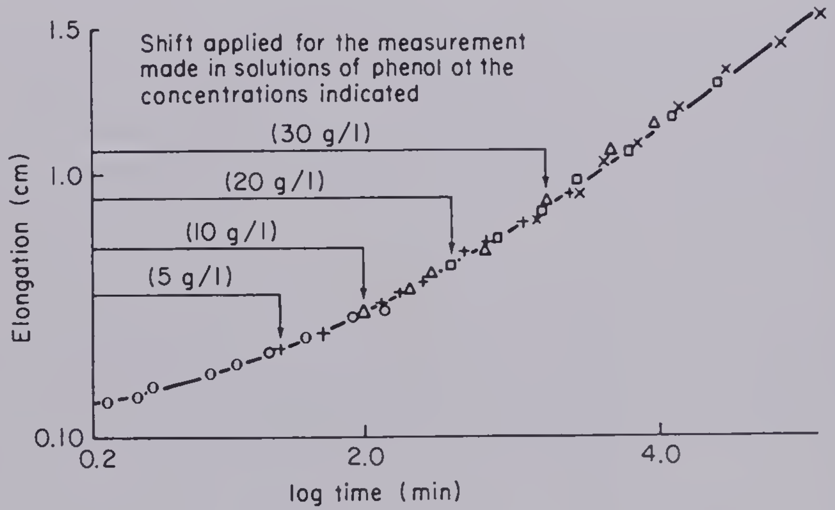

FIG. 14. Superimposition of the rate of elongation of Acrilan filaments made in phenol solutions of different concentration at 70°C. ○, Water; (+), 5 gm/liter phenol; (△), 10 gm/liter phenol; (□), 20 gm/liter phenol; (×), 30 gm/liter phenol.[87]

the factor $T - T_g$, where T is the temperature at which the measurements are carried out. The equation may be written as

$$B \ln \frac{\eta_g}{\eta_T} = \ln \frac{D_T}{D_g} = -\ln a_T = \frac{A(T - T_g)}{B + (T - T_g)}$$

where η_g and η_T are the internal viscosities of the fiber at the temperatures T_g and T, D_g and D_T are the corresponding diffusion coefficients, and A and B are constants. It may be noted that in the above equation values of T_g were taken as the reference temperature. The equation is equally valid, however, if T_g is replaced by another temperature, say T_0.

The equation states that the shift factors a_T and the diffusion coefficients of the dye are related through the same constants to $(T - T_g)$. This point is demonstrated by the results in Fig. 15. Similar results have been obtained using different carriers. With fibers such as polyethylene terephthalate, the simple extension method for the measurement of T_g is not feasible, since in the presence of the carrier, crystallization occurs causing some shrinkage. However, the similarity of behavior of this fiber to that of Acrilan has been shown by comparing the changes of the diffusion coefficients of two dyes; when log D_T was plotted against phenol concentration, the shapes of the curves for both dyes were similar to those obtained for Acrilan and by a simple shift of the ordinate could be superimposed.[87] Alternatively, the variations of

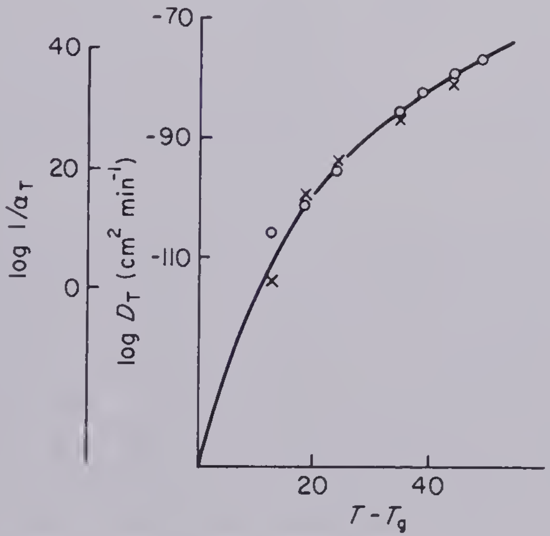

FIG. 15. Matching the diffusion data and the physical properties of Acrilan filaments to the WLF equation using $A = 10.8$ and $B = 28.5$. (○) Diffusion data for CI Disperse Red 1; (×) shift factors from Fig. 14.[87]

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[87] W. Ingamells, R. H. Peters, and S. Thornton, *J. Appl. Polym. Sci.* **17**, 3733 (1973).

diffusion due to changes in dyeing temperature for systems containing different amounts of carrier (phenol) were of the same form; plots of log D_T versus $1/T$ were also superimposable.[83] Hence, even though no direct measure of the T_g was possible for the polyester, the similarity of the dyeing behavior to that of Acrilan demonstrates the importance of T_g. In confirmation of this, it has more recently been shown that T_d may be used as an alternative to T_g.[83]

vii. Plasticization and Swelling. It has been postulated that these properties go hand in hand.[72,88] However, the mechanism of plasticization is one in which the interchain forces are reduced, and hence the T_g is lowered. The intensity of the attractions may be represented by the solubility parameter, a parameter that represents the energy required to separate the molecules by a distance large enough to eliminate the intermolecular attractions.

In a study of swelling and plasticization of Acrilan fibers, it was found that there was no correlation between the lowering of T_g and the swelling as determined by diameter increase (Table IX).[42] For example, *m*-toluidine and amyl alcohol reduced the T_g by 20° and 3° for the same degree of swelling, whereas benzyl alcohol and amylamine lowered the T_g by similar amounts (6.0° and 5.5°), but the swelling was 0.5% and 81.4%. More striking, perhaps, is the fact that some of the compounds examined cause significant swelling and actually raise the T_g. It is also interesting to note that the surface structure of the fibers is modified by the action of some of these solvents, developing fissures. Moreover, since the diffusion coefficient is dependent, as discussed earlier, on the value of $T - T_g$, those substances that actually increase the T_g will decrease the dye diffusion rate, as exemplified by ethyleneglycol (Table X).[42] As expected, the activation energy is increased as the T_g is raised.

The effect of a particular solution of a plasticizing agent will depend on the sorption characteristics, i.e., the partition coefficient of the material. These vary widely, e.g., from 2.37 at 70° for benzyl alcohol to 23.5 for *o*-ethylaniline.[89] It will also depend on the chemical nature of the plasticizing molecule. As indicated earlier, the reduction in T_g decreases linearly with plastizer concentration or volume fraction. From the slopes of these relationships, a plasticizer efficiency may be defined. They vary widely (Table XI). The decreases in T_g are plotted in Fig. 16[89] against the total solubility parameter δ and the association solubility parameter δ_a. Both plots show that as the solubility para-

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[88] E. Waters, *J. Soc. Dyers Colour.* **66**, 609 (1950).

[89] Z. Gur-Arieh, W. Ingamells, and R. H. Peters, *J. Appl. Polym. Sci.* **20**, 41 (1976).

meter approaches that of the fiber, the plasticizer efficiency improves. It must be noted, however, that the effects observed are the combination of water and the agent. An analogous plot of the diameter swelling does not give such a well-defined correlation, and indeed, the diameter swelling tends to decrease as the solubility parameters of the plasticizer and fiber get closer together.

viii. Dyeing from Benzyl Alcohol. Addition of small quantities of water to a solvent dyeing system is beneficial in improving exhaustion, one aspect of its mode of action being the reduction in solubility of the dye in the solvent phase. An additional mode of action is that the

TABLE IX

EFFECT OF AQUEOUS SOLUTIONS OF VARIOUS COMPOUNDS ON THE PHYSICAL PROPERTIES OF ACRILAN FILAMENTS[a]

Compound	*Solubility parameter* δ *($cal^{0.5}/cm^{1.5}$)*[b]	*Reduction*[c] *in T_g relative to T_g in water (°C)*	*Percentage increase in diameter relative to diameter in water*
m-Toluidine	10.7	20	10.3
o-Ethylaniline[d]	10.1	22	8.2
o-Ethylphenol[d]	11.0	18.5	9.9
m-Cresol	11.1	19.5	7.5
Aniline	11.0	12.5	2.6
Phenol	14.5	10.0	—
Benzyl alcohol	12.0	6.0	0.5
Amylamine	8.5	5.5	81.4
Amyl alcohol	10.6	3.0	10.0
Benzylamine	10.3	2.7	5.1
1,5-Diaminopentane	9.8	−1.5	56.3
Glycerol	21.1	−2.0	9.2
1,5-Pentanediol	11.9	−3.0	9.9
Digol	14.6	−4.0	9.7
Ethyleneglycol	16.3	−5.0	6.8
Ethylenediamine	11.4	−4.0	13.2

[a] Filaments were immersed in water containing 0.1 mole/liter of additive indicated. T_g of filaments in air = 90°C. T_g of filaments in water = 57°C. From Z. Gur-Arieh and W. Ingamells, *J. Soc. Dyers Colour.* **90**, 12 (1974).

[b] Values of solubility parameter for polyacrylonitrile are taken as 12.7 and 15.4 $cal^{0.5}/cm^{1.5}$.

[c] The reduction in T_g is expressed as (T_g of filament in water − T_g of filament in other solutions) and, therefore, a negative reduction indicates an increase in the value of T_g.

[d] Used at a concentration of 0.02 mole/liter.

TABLE X

EFFECT OF ETHYLENEGLYCOL ON DIFFUSION COEFFICIENT (D) OF CI DISPERSE ORANGE 3 INTO ACRILAN[a]

Parameter	*D (cm²/minute × 10^{10}) at ethyleneglycol conc. (mole/liter) of:* 0	0.1	0.2	0.3	0.4
Dyeing temperature					
90°	42.95	43.08	40.08	37.4	35.6
80°	3.782	3.618	3.157	2.592	2.375
T_g(°C)	57.0	62.0	62.5	63.0	67.0
Activation enthalpy (kcal/mole)	61.7	63.5	67.5	68.1	69.6

[a] From Z. Gur-Arieh and W. Ingamells, *J. Soc. Dyers Colour.* **90**, 12 (1974).

water may act as a plasticizer. This point has been examined using Acrilan and benzyl alcohol as solvent.[42] Measurements of T_g have shown that additions of the alcohol to a water system cause reductions in T_g of a similar magnitude to those caused by adding water to benzyl alcohol (Fig. 17). Unfortunately, it was found impracticable to deter-

TABLE XI

ORDER OF PLASTICIZING EFFICIENCY OF SOME AMINO AND HYDROXYL COMPOUNDS[a]

Plasticizer	*Reduction in T_g (°C) of Acrilan filaments with respect to their T_g in water caused by:* 1 mole of plasticizer/kg of fiber	*10×10^{-2} volume fraction of plasticizer in the fiber*	*Plasticizer*
Phenol	40.0	41.4	Phenol
Benzyl Alcohol	33.0	50.5	Benzyl Alcohol
m-Toluidine	19.2	19.2	*m*-Cresol
m-Cresol	18.2	18.5	*m*-Toluidine
2-Ethylphenol	16.6	17.5	Aniline
Benzylamine	14.4	16.4	2-Ethylphenol
Aniline	14.0	12.0	Benzylamine
o-Ethylaniline	10.2	11.1	*o*-Ethylaniline

[a] From Z. Gur-Arieh, W. Ingamells, and R. H. Peters, *J. Appl. Polym. Sci.* **20**, 41 (1976).

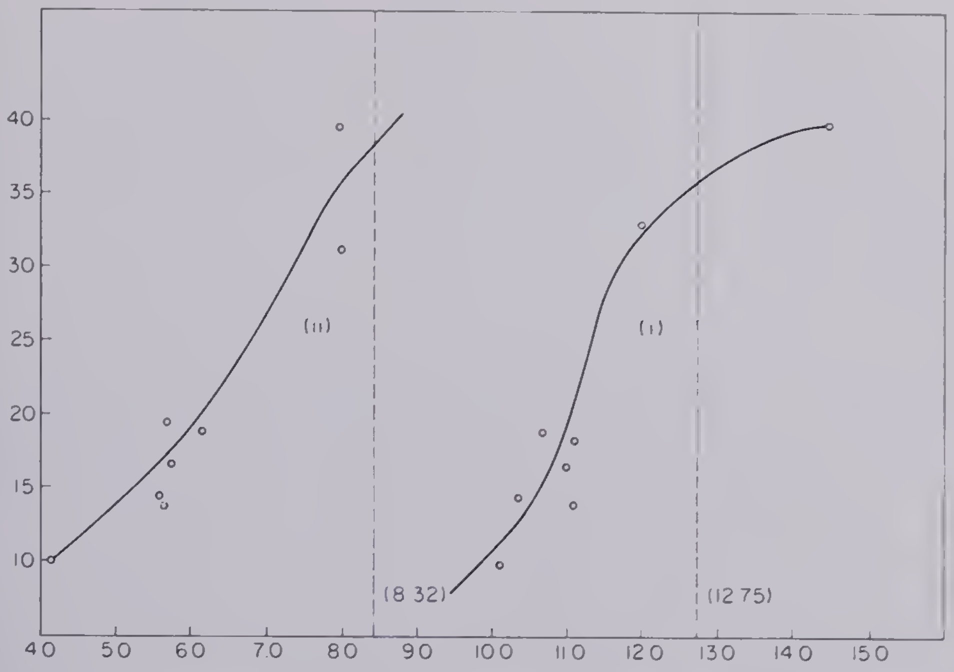

FIG. 16. The reduction in T_g ($\triangle T_g$) caused by equimolecular concentration of plasticizer in acrilan filaments related to (i) total solubility parameter δ; (ii) association solubility parameter δ; ordinate, plasticizing effect ($\triangle T_g$ in °C); abscissa, solubility parameter (cal$^{0.5}$/cm$^{1.5}$). Broken vertical lines represent the total solubility parameter (12.7 cal$^{0.5}$/cm$^{1.5}$) and the association solubility parameter (8.32) for polyacrylonitrile.

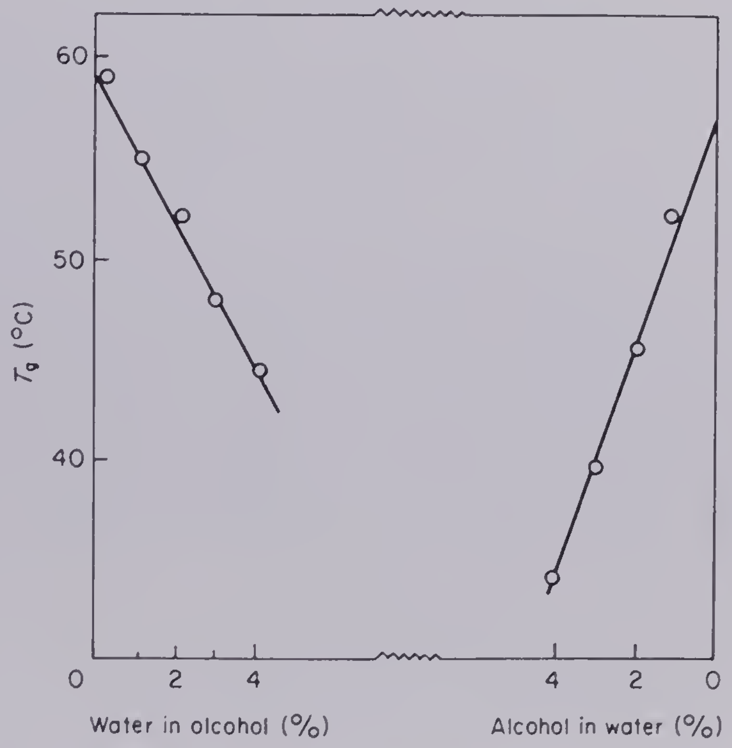

FIG. 17. Effect of benzyl alcohol and water on T_g of Acrilan.[42]

mine the diffusion coefficients because of the high solubility of the dyes in benzyl alcohol.

The action of water on the fiber, however, varies from that of a normal plasticizer. The decrease in T_g brought about by the addition of water is accompanied by a decrease in the slope of the extension versus temperature curve, suggesting a strengthening of the structure. This is reflected in the reduction in the diameter of the fiber,[89] whence it appears that water is acting as an antiplasticizing agent. Presumably, the water molecules are able to pack closely around and be bound to the strongly polar nitrile groups. Such a situation leads to a stiffening of the chains. Analogous effects have been observed in drawn nylon 6 fibers, where adsorption of water molecules increases the modulus below 20° and also the transition temperature normally observed at $-50°$. In this instance, it was suggested that water was bonded at the lower temperature to amide groups, but when the temperature was raised to 70°, the water dissociated, and hence this transition was unaffected. In the field of polyesters, it has also been shown for a series of aromatic carboxylic acids that they increase the density of the fiber, presumably because of strong dipolar interaction between the carboxyl, hydroxyl, or amino groups in the acid and the carbonyl groups in the fiber.[66]

II. New Fibers

In recent years, several new fibers have been manufactured for a variety of reasons. With the exception of polypropylene, which has achieved interest because of its low cost, the fibers are modifications of the three established types—polyamides, polyesters, and acrylic fibers.

A. POLYPROPYLENE

The interest in this fiber lies in the low cost of the monomer and the fact that it has good mechanical properties. In recent years, the production of polypropylene fibers has increased for use in upholstery and carpets as well as industrial uses.[90] The fiber is highly crystalline and very hydrophobic but has low affinity for normal disperse dyes,[91] presumably because of the paraffinic nature of the polymer and its lack of functional groups to act as sites. Although some of the more hydrophobic disperse dyes are able to build up into medium depths of shade, they were not in general satisfactory in practice because of their poor fastness to dry cleaning solvents.[29,92]

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[90] T. L. Dawson, *Rev. Prog. Color. Relat. Top.* **2**, 3 (1971).

[91] L. G. Maury, *Text. Chem. Color.* **4**, 143 (1972).

[92] AATCC, Metropolitan Section, *Am. Dyest. Rep.* **54**, 107 (1965).

TABLE XII

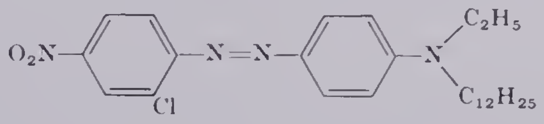
SORPTION OF DIMETHYL YELLOW IN POLYPROPYLENE[a]

Temperature (°C)	*Partition coefficient*	*Affinity (kcal/mole)*	*Heat of dyeing (kcal/mole)*	*Entropy (cal/mole/deg)*
80	455	−4.30	−11.8	−21.2
95	230	3.98	—	—

[a] From C. L. Bird and A. M. Patel, *J. Soc. Dyers Colour.* 84, 560 (1968).

In spite of this, polypropylene fibers are available that are capable of being dyed with selected disperse dyes, although the range is limited.[93] Polypropylene fibers suitable for disperse dyeing are said to contain additives such as 10–15% of an acrylic–styrene copolymer.[94]

A limited examination of the adsorption properties using Dimethyl Yellow has shown such a disperse dye to give the linear isotherms expected of a sorption process by a solution mechanism. The sorption data for this dye and the saturation values are shown in Tables XII[95] and XIII. Best results are obtained with oil-soluble dyes of a very strong hydrophobic character, e.g., (III), where a long aliphatic chain has been introduced.



(III)

TABLE XIII

SATURATION VALUES AT 80°[95]

Dye	*Saturation value (gm/100 gm)* *Film*	*Fiber*
Dimethyl Yellow	0.67	0.39
p-Aminoazobenzene → *o*-cresol	0.14	0.08[a]
1-Anilinoanthraquinone	0.32	0.19[a]

[a] Calculated.

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[93] J. G. Lee, *Polym. SPA Tech. Bull.* p. 3D (1968).

[94] J. G. Lee, *Int. Dyer, Text. Printer, Bleacher Finish.* **155**, 25 (1976).

[95] C. L. Bird and A. M. Patel, *J. Soc. Dyers Colour.* **84**, 560 (1968).

Pigment Coloration

Fibers that are difficult to dye can be colored by the introduction of pigments into the melt or solution prior to extrusion, and this method has been used to a substantial extent for polypropylene.[91] The method has limitations mainly in the lack of flexibility in production, but has the advantage that products of good fastness properties may be produced.[96] In general, pigment coloration leads to the production of large quantities of material with limited shade ranges. Moreover, only a few pigments readily dissolve or are uniformly dispersed in the polypropylene melt and at the same time are stable enough to resist decomposition at the high temperatures required in the melt (250°–300°).[97] In recent years, specially predispersed pigments have been developed consisting of fine pigment particles coated with or trapped in a compatible polymer such as polyethylene. These pigments have been carefully selected.

B. Modified Polypropylene

Because of the difficulties encountered in obtaining satisfactory dyeings with disperse dyes, many attempts have been made to modify the fiber either chemically or by adding additives so as to provide sites that would act as points of attachment for dyes.

1. *Additives*

a. Metals. The introduction of a small proportion of a metal-containing anion-exchange substance, such as an oxide, hydroxide, or salt of magnesium or calcium, yielded a fiber capable of being dyed with weakly acid dyes, which may form a salt or chelate compound with the metal.[98,99] The dyes contain carboxyl or hydroxyl groups and may be based on the structures of acid dyes containing special chelating systems, e.g., *o*-hydroxycarboxyl or aldehyde groups.

More satisfactory is to add metal salts capable of strongly chelating with dyes. The most satisfactory substances are the nickel salts of organic fatty acids or organonickel complexes, e.g., that of Bisphenol A.[100] The dye sites must be thermally stable, be readily dispersible, and not react with the UV and oxidation inhibitors. One product quoted is 2,2′-thiobis(*p*-*tert*-octylphenol)-*n*-butylamine nickel. Data from NMR

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[96] P. Ackroyd, *Rev. Prog. Color. Relat. Top.* **5**, 86 (1974).

[97] A. J. Hall, *Text. Rec.* **83**, 72 (1965).

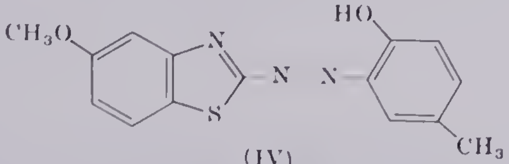
[98] ICI, *BP* 933,125.

[99] P. Arnaud, *Rev. Belge Matieres Plast.* **9**, 535 (1968).

[100] A. F. Turbak, *Text. Res. J.* **37**, 350 (1967).

measurements suggest that a 1:1 complex with the dye is formed yielding a product with an octahedral structure.[101]

The dye selection must be made with care, since a large number of hydroxy compounds are incapable of chelating within the fiber. Groupings that contain a large number of electron-donating groups [eg., (IV)] have been used. The important grouping for good chelation appears to be the iminoazo (—N=C—N=N—) together with a hydroxyl group in the ortho position.[100,101] Because of the fixation of these dyes by chelation, they do not migrate, and hence the fiber is more satisfactory for printing than for piece dyeing.



(IV)
Polypropylene Green BM

b. *Polymers.* An alternative approach is to blend a relatively small amount of polymer within the fiber. Little information is available as to the exact nature of the polymers used. Thus, disperse dyeing characteristics are imparted by blending a relatively inert polyester or vinyl polymer, e.g., polyethylene terephthalate or polyether esters. Other polymers used are polar and carry basic or acidic groups capable of acting as sites for ionic dyes. The introduction of the polymer modifies to some extent the crystallinity and orientation of the fiber, thereby making the polymer more accessible. The best results are obtained when the polymer forms a network of microfibrils passing through the interior and extending to the surface of the filament so that water-soluble dyes do not have to penetrate the impervious polypropylene matrix.[102]

Acid-dyeable fibers are commercially available, a wide variety of materials having been proposed for this purpose, e.g., polyamines, polyamides, and vinyl polymers carrying suitable side chains.[97,99,103–105] These fibers may be dyed with acid, chrome, premetallized, and reactive dyes.[93] One proprietary product, Meraklon DR, has been shown to sorb hydrochloric acid to an extent of 250 mEq/kg,[106] indicating that the fiber has an adequate capacity to sorb acid dyes. However, these fibers

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[101] R. R. Haynes, J. H. Mathews, and G. H. Heath, *Text. Chem. Color.* **1**, 74 (1969).

[102] J. Shore, *Rev. Prog. Color. Relat. Top.* **6**, 7 (1975).

[103] M. Levine and R. P. Weimer, *Text. Chem. Color.* **2**, 269 (1970).

[104] F. L. Sievenpiper, *Can. Text. J.* **31**, 37 (1966).

[105] *BP* 960,789.

[106] J. Cegarra and P. Puente, *Text. Res. J.* **39**, 611 (1969).

exhibit a high substantivity in practice, so that leveling is difficult and an anionic agent is recommended to assist.[93]

Little work has been carried out to elucidate the mechanism of dyeing. Kinetic data do not follow the normal diffusion equation,[107] and the quantity of dye on the fiber is proportional to $(\text{time})^{1/4}$. This presumably arises from the fact that the polymers are dispersed in the fiber and that some material carrying basic groups may be extracted during the dyeing.[108]

2. *Fiber Treatments*

Many attempts have been made to modify the fiber by chemical reaction. Thus, treatment with some common oxidizing agents (e.g., NaOCl or ClO_2) improves the ability of the fiber to accept basic and disperse dyes but, naturally, the oxidation of the fiber is accompanied by some degradation.[109] A more important treatment of the fiber is with chlorosulfonic acid, which causes acid groups to form within the fiber.[110] These groups are capable of acting as dye sites. Unfortunately, such treatments are costly and cause some fiber degradation. More recently,[111] it has been claimed that fibers modified by chlorination with chlorine, SO_2Cl_2, etc. possess reactive halogen atoms capable of reacting chemically with suitable groups in dyes.

The feasibility of forming basic sites attached to the polymer chain has been demonstrated.[112] Polypropylene was brominated and the bromine atoms replaced by amino groups by treatment with liquid ammonia. The resulting fiber was dyeable with acid and metal complex dyes, giving isotherms that were Langmuir in character. Almost complete replacement of the amino groups by hydroxyl brought about by treatment with sodium nitrite destroyed the acid-dyeing characteristics.

3. *Copolymers*

Although copolymers of polypropylene in which the comonomer contains phosphoric acid groups to impart basic dyeing properties have been patented,[113] in general, little progress has been made. This is primarily due to the ease with which the Ziegler catalyst used in the

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[107] J. Carbonell, *Textilis* **25**, 17 (1969).

[108] S. Intarachoti, M.Sc. Thesis, Manchester University (1974).

[109] I. Rusznák and J. Morgós, *Period. Polytech., Chem. Eng.* **15**, 65 (1971).

[110] S. Harda, O. Ishizuka, and K. Sakaka, *Text. Cell. Ind. Jpn.* **18**, 511 (1962).

[111] A. Agster, *Melliand Textilber.* **56**, 470 (1975).

[112] B. G. Ferrini and H. Zollinger, *Helv. Chim. Acta* **50**, 897 (1967).

[113] Montecatini-Edison Ltd., *BP* 1,293,861.

formation of polypropylene is poisoned by polar monomers. Attention has therefore been paid to the idea of forming graft copolymers. Attachment of grafts may be carried out by a free-radical process using traditional initiators, e.g., peroxides in the presence of a suitable vinyl compound (e.g., acrylic acid, vinyl pyridines, vinyl acetate).[99] By such means, dye sites that are permanently attached and molecularly dispersed may be introduced. Again, however, little or no commercial development has occurred.

C. POLYAMIDES

In recent years, new varieties of polyamides have been developed; these have been produced because of their silklike properties (Qiana) or their novel dyeing properties. The interest in the latter products arose from the desire to produce fabrics or carpets in many colors. By using fibers of different dyeing properties, the storage and rewinding of dyed yarns may be avoided. Various patterns can be produced by weaving, knitting, or tufting undyed yarns and the material stored white until required to be dyed in the desired colorations. Differential-dyeing synthetic fibers have been used commercially to a substantial extent for tufted carpets with the major type being the nylons.[114–117]

1. *Qiana*

This fiber is notable for its silklike appearance, its trilobal cross section producing highlights by internal reflection. The polymer is a polycondensate of diaminodiphenylmethane and decane dicarboxylic acid.[118] The fiber has a crystallinity similar in magnitude to that of polyesters and is set at 125° in steam or 190° when dry.[119] It has a relatively low moisture regain ($\sim 2\%$ at 65% relative humidity).

Qiana is processed in much the same way as polyester fibers and must be dyed with disperse dyes at the boil in the presence of a carrier (e.g., butyl benzoate, methyl salicylate) or at a high temperature (125°–130°) in the absence of a carrier. It will accept acid and metal complex acid dyes.[120] Disperse dyes have affinities for this fiber that are similar to those for polyester. Acid dyes are more difficult, and a

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[114] H. Stern and L. E. Kaiser, *J. Soc. Dyers. Colour.* **85**, 653 (1969).

[115] H. Egli, *Textilveredlung* **2**, 856 (1967).

[116] G. M. O'Mahony, *Am. Dyest. Rep.* **57**, 853 (1968).

[117] H. Egli, *Am. Dyest. Rep.* **57**, 1099 (1968).

[118] A. Liddiard, *Rev. Prog. Color. Relat. Top.* **1**, 64 (1969).

[119] Du Pont Bulletin N506 (1971).

[120] Du Pont Bulletin Q500 (1975).

temperature of 130° is recommended, with the addition of a carrier such as butyl benzoate.[121] Monosulfonated dyes have the highest affinity, but some polysulfonated and 1:2 metal complex acid dyes may be applied.

2. *Nomex*

This fiber is of particular interest because of its resistance to high temperatures; when heated it does not melt, but it chars at around 420°. Moreover, at temperatures at which the normal nylons melt, Nomex retains its physical properties to an extent of about half the values at room temperatures. It finds outlets in protective clothing, in the aircraft industry, etc.[122]

Nomex is formed from an aramid polymer, which is prepared by the condensation of *m*-phenylenediamine and isophthalic acid. The exact composition of this fiber has not been revealed, but the types available (T450, T454, or E8) may be dyed with selected basic dyes.[123] The fiber has a very high glass transition temperature (275°), above which crystallization occurs readily[124]; dyeing must therefore be carried out under more vigorous conditions than for most fibers, namely, under pressure at a temperature of approximately 120°–125° in the presence of large quantities of a carrier. The carriers commonly used for polyester and other fibers (e.g., diphenyl or methyl salicylate) are not very effective; two carriers recommended for this fiber are benzaldehyde[122] and acetophenone,[125] although proprietary brands are available. For dyeing, the fiber is treated with the carrier at 40° for 5 minutes, after which the dye is added; 5 minutes later, sodium nitrate is added to exhaust the carrier onto the fiber surface. The carrier takes the dye with it, the latter moving from the carrier to the fiber as dyeing proceeds at a temperature of about 120° for up to 2 hours. The fabric is then scoured.

More fundamental studies of dye adsorption by Nomex have been restricted because of the difficulties of obtaining equilibrium data without dye destruction. To avoid the long times necessary to obtain equilibrium, an expanded form of the polymer has been used.[124] This form was obtained by adding a dilute solution of the polymer in dimethylacetamide to water to yield an amorphous powder of particle size that after sieving was not greater than 150 μm and contained about two to three times its weight of water. The powder was used in an

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[121] Du Pont Bulletin Q1 (1975).

[122] R. W. Schumm and C. J. Cruz, *Text. Chem. Color.* 1, 388 (1969).

[123] B. A. Evans and R. W. Schumm, *Text. Chem. Color.* 2, 262 (1970).

[124] H. E. Ulery, *J. Soc. Dyers Colour.* **90**, 401 (1974).

[125] Du Pont Bulletin N249 (1971).

undried state and in this form was readily dyeable, equilibrium being reached within a few hours.

The isotherms so obtained gave linear plots on a Freundlich basis, i.e., plots of the logarithm of the concentration of dye on the fiber (C_F) versus the logarithm of that in solution (C_B). Langmuir type plots ($1/C_F$ versus $1/C_B$) gave straight lines only at the lower concentrations; these linear portions on extrapolation gave an intercept that yielded a saturation value of 60 – 100 mEq/kg, a value close to that of the number of carboxyl groups in the fibre (80 mEq/kg).

Desorption experiments using dilute formic acid at different pH values showed increasing quantities of the dyes removed as the pH increases, suggesting that there exists competition between the hydrogen and dye ions for the negatively charged carboxyl groups in the fiber. However, the situation is different when the desorption behavior in the presence of strong bases, acids, or salts is examined when the uptake is in general increased by the addition of the electrolyte. Unfortunately, it is difficult to obtain a clear picture of the mechanism, since the dyes are likely to aggregate in the presence of electrolytes and the polymer may change its structure due to the electrolyte present. There are also some results that suggest that an electrolyte such as sodium chloride is adsorbed. The picture is therefore complicated by the apparently specific action of the various ions.

3. *Polyamides with Modified Dyeing Properties*

These fibers are available in three forms, namely, regular, deep dye, and basic dyeable.[117,126–129] The disperse dyes have approximately equal substantivity for all three fibers. The basic dyeable yarns are reserved by selected acid dyes, but readily dyed with cationic dyes. The first two forms are dyed with acid (or metal complex) dyes to the normal depths (regular) and to substantially deeper shades.

The polymers used are chemical modifications of the normal nylon 6 or 66 structure. The deep-dye polymer is obtained by increasing the number of amine ends. An increase in amine ends may be obtained by forming the polymer in the presence of an excess of hexamethylenediamine or other amines.[130,131] Unfortunately, polymers produced in

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[126] M. D. Chantler, G. A. Patlett, and J. A. B. Whiteside, *J. Soc. Dyers Colour.* **85**, 621 (1969).

[127] R. Vincent, *Teintex.* **37**, 329 (1972).

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

[129] C. Schork, *Text.-Prax.* **22**, 725 (1967).

[130] E. Lux, *Text.-Prax.* **22**, 650 (1967).

[131] B. C. M. Dorset, *Text. Manuf.* **92**, 370 (1966).

this way tend to yellow; amines of greater thermal stability have been examined but have not apparently been developed commercially.[132] The approach most studied is to protect the free amine during polymerization with different additives such as boron- or phosphorus-containing compounds. Examples of such additives are phosphinic, boric, and phenylboric acids. After polymerization, the additives can be washed out in boiling water.

The amine end group content of a set of regular, deep-dye and ultra-deep-dye nylons has been shown from their uptake of hydrochloric acid to be 41, 89, and 95 mEq/kg. The adsorption characteristics of these fibers using (a) a monosulfonated acid dye, (b) a milling dye and (c) a chrome dye, are shown in Fig. 18.[133] The curves show that the deep-dye types adsorb more dye than regular nylon and are not so dependent on pH. Moreover, the dyes with the high affinities (the milling and chrome dyes) show sorption in excess of the amine ends as would be predicted from the analysis of dye adsorption made by McGregor and Harris.[134] It is difficult, however, from the rather scant data to assess whether the dyes possess different affinities on the different fibers, although from the practical point of view the substantivities are clearly different.

As the difference between deep-dye and regular nylon is chemical, the greatest difference in the amount of dye adsorbed by these yarns when dyed together occurs with dyes that are most sensitive to chemical

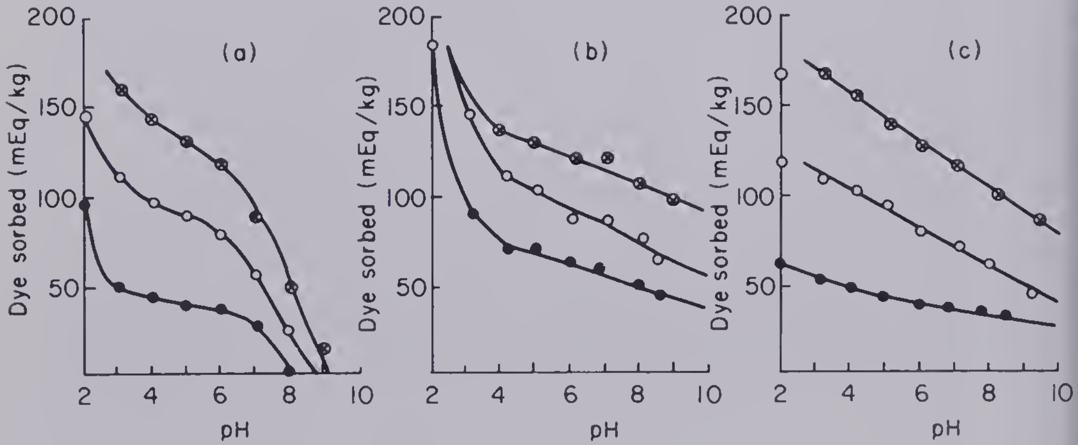

FIG. 18. Sorption of acid dyes by nylon; (a) CI Acid Yellow 29, (b) CI Acid Blue 113, (c) CI Acid Red 216; (⊗) ultra deep dye; (○) deep dye; (●) regular.[133]

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[132] W. de Winter and D. Decorte, *Text. Res. J.* **41**, 726 (1971).

[133] H. Ekli, *Am. Dyest. Rep.* **57**, 1099 (1968); *Text. Chim.* **25**, 145 (1969).

[134] R. McGregor and P. W. Harris, *J. Appl. Polym. Sci.* **14**, 513 (1970).

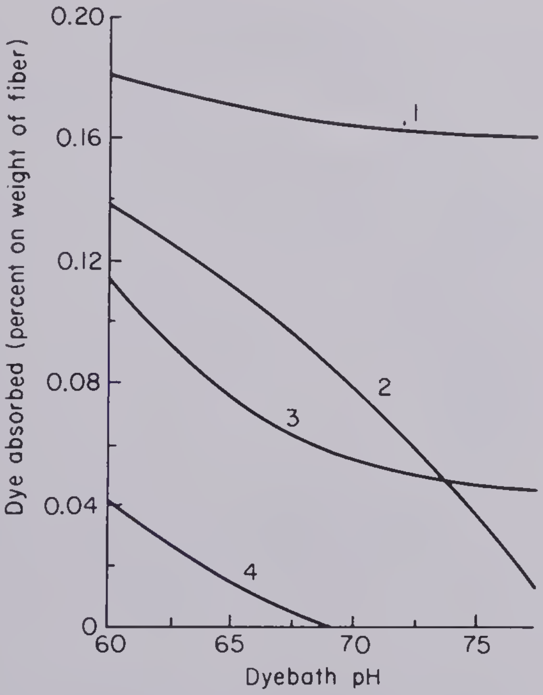

FIG. 19. Effect of pH on dye uptake for mono- and trisulfonated dyes on deep-dyeing and regular nylon; (1) Monosulfonated deep-dyeing nylon; (2) trisulphonated deep-dyeing nylon; (3) monosulphonated regular nylon; (4) trisulfonated regular nylon.[126]

variations in nylon. This is exemplified in Fig. 19, where the sorption of the trisulfonated dye falls off very steeply as the pH is increased compared with the monosulfonated dye.[126] For example, at pH 7.0, the concentration of dye on the regular yarn is zero for the trisulphonated dye, whereas that on the deep dye yarn will be substantial. It is clear from the diagram that two-tone effects may be obtained when the fibers are dyed in the same bath at the appropriate pH.

Basic dyeable fibers are formed by the addition of sulfocarboxylic acids (e.g., sulfonated isophthalic acid) in the polymerization stage[130,135]; the fibers so produced have virtually no substantivity for anionic dyes but can be dyed with basic and of course disperse dyes. The adsorption of the basic dye is significant over the pH range but increases with pH (Fig. 20). This effect is the converse of the behavior of acid-dyeable material whose sorption increases with decreasing pH. In practice, therefore, when dyeing mixtures of these fibers, a compromise pH is required. It is possible to dye these fibers in a single bath, provided an antiprecipitant is added. These are surfactants that hold in dispersion the complexes formed from the acid and basic dyes.

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[135] H. Beutler, *Melliand Textilber.* **51**, 1189 (1970).

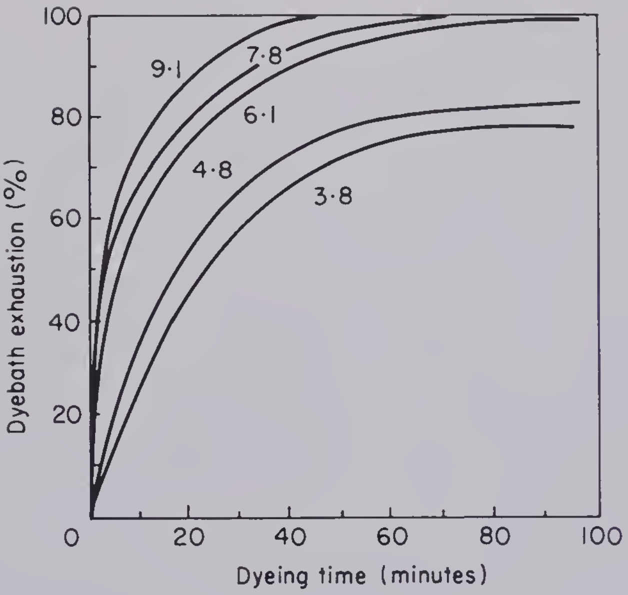

FIG. 20. Effect of dyebath pH on the exhaustion of CI Basic Red 25 (the pH is given on each curve).[126]

These modified fibers enable a variety of colored effects to be produced in a single-bath dyeing process by combining a selection of the fibers in the undyed article. The degree of contrast obtained can be varied by careful choice of dyes and conditions.[118] Thus, for carpets, maximum contrast can be achieved with the basic and deep-dye fibers or, for two colors and a white, an acid dye may be selected that strikes on the ultradeep dye nylon together with a basic dye for the basic dyeable fiber, both reserving the regular nylon.[116] It must be admitted that color effects may be obtained with blends of different fibers,[129,136] e.g., by mixtures of polyamides with polyesters or acrylic fibers, but these systems may be a little more difficult in practice because of the different dyeing temperatures required and the different mechanical properties of fibers of very diverse types.

D. POLYESTERS

These fibers are available apart from the regular type as basic or deep-dyeable. A satisfactory acid-dyeable fiber has proved very difficult to achieve.

1. *Deep-Dyeable Fibers*

Modified fibers have been made from copolyesters in which either the acid or glycol component in polyethylene terephthalate is replaced.

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[136] J. R. Stewart, *Can. Text. J.* **85**, 37 (1968).

By so doing, fibers of a more open structure are produced. Such fibers are not as strong as the regular type and in general shrink to a greater extent.[137] They are of interest because of their better pilling properties, easier stain removal, and their greater acceptability for dyes.[138] The introduction of the comonomer lowers the melting point, the glass transition, and the resistance to hydrolysis. A wide variety of comonomers have been examined, e.g., isophthalic acid, aliphatic dicarboxylic acid, and various aliphatic glycols.[139] In practice a compromise is chosen between the technological and dyeing properties, and it seems that for the lower-molecular-weight aliphatic diacids 5–8 mole % is desirable, whereas with isophthalic acid or *p*-hydroxybenzoic acid 10–15% is desirable.[139,140] Although the composition of particular fibers has not been disclosed, it seems likely that commercial products contain sebacic, suberic, or isophthalic acid.[135]

Little information on the fundamental dyeing properties of these fibers is available. They may however be dyed under milder conditions than the regular product, with additions of sodium sulfate to minimize fiber hydrolysis.[141] Other commercial fibers that are dyeable at the boil without carrier, but have a lower melting point (226°) and density (1.32), are produced from polytetramethylene terephthalate (4GT).[142–144]

2. *Basic-Dyeable Fibers*

Even though regular polyethylene terephthalate fibers contain at their chain ends carboxyl groups to the extent of 25–60 mEq/kg, the fiber is not dyeable with basic dyes. Presumably this is due to the inability of these groups to ionize in the hydrophobic environment of the fiber.[139] To confer basic-dyeing properties, it appears that strongly acidic groups must be introduced into the fiber. This is achieved by the introduction of a small percentage of dicarboxylic acid or glycol, that carry sulfonic acid groups. Of the possible choices of comonomer, 5-sulfoisophthalic acid has been used commercially, the fiber containing about 3 mole %.

Basic-dyeable polyester fibers are therefore copolymers and hence possess a lower tensile strength and improved pilling properties when

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[137] J. K. Thimm, *Text. Chem. Color.* **2**, 69 (1970).

[138] E. V. Burnthall and J. Lomartire, *Text. Chem. Color.* **2**, 218 (1970).

[139] F. Jakob, *Chemiefasern* **5**, 388 (1972).

[140] S. Morimoto, *in* "Man-Made Fibres" (H. Mark, ed.), p. 21. Wiley (Interscience), New York, 1967.

[141] N. D. Steward, *Int. Dyer, Text. Printer Bleacher Finish.* **147**, 524 (1972).

[142] J. K. Thimm, *Chemiefasern* [N.S.] **23**, 811 (1973).

[143] W. E. Welge and H. Zimmermann, *Chemiefasern* [N.S.] **25**, 843 (1975).

[144] P. Grosjean, *Teintex* **40**, 333 (1975).

compared with the regular yarn. The modification of the mechanical properties is also helpful, because when used in blends with cotton, the abrasion of both fibers is more even than when the regular fiber is used.

These fibers, being copolymers, have a more open structure and hence are more easily dyed with disperse dyes and may be dyed with these dyes in blend with the regular yarns to yield tone-in-tone effects.[118,145–147] The fiber by virtue of the sulfonic acid groups is readily dyed with basic dyes,[135] but care must be taken to use the correct pH, since the fiber is susceptible to hydrolysis under acid and alkaline conditions. The fiber should not be dyed at a temperature greater than 120°; additions of sodium sulfate are made to protect the fiber. Because of the lower temperatures recommended, dyeing is best achieved with additions of carriers.[148]

Some analysis of the adsorption isotherms for a basic dye, CI Basic Blue 3, have been carried out using Dacron T64C and D65.[146,149,150] It is suggested that the equilibria between the fiber and bath may, as for acrylic fibers, be treated as an exchange of ions between the strong acid group in the fiber and the external solution. If F represents the fiber, D^+ the dye cation, and X^+ the hydrogen or sodium ions, the reaction may be represented by the equation

$$\mathrm{FSO_3^-X^+} + \mathrm{D^+} \rightleftharpoons \mathrm{FSO_3^-D^+} + \mathrm{X^+}$$

The equilibrium may be written in terms of the ion exchange constants and saturation values as

$$\frac{[\mathrm{D}]_\mathrm{F}}{[\mathrm{S}] - [\mathrm{H}]_\mathrm{F} - [\mathrm{D}]_\mathrm{F}} = K^{\mathrm{D}}_{\mathrm{Na}}[\mathrm{D}]_\mathrm{S}$$

and

$$\frac{[\mathrm{D}]_\mathrm{F}}{[\mathrm{S}] - [\mathrm{Na}]_\mathrm{F} - [\mathrm{D}]_\mathrm{F}} = \frac{K^{\mathrm{D}}_{\mathrm{H}}}{[\mathrm{H}]_\mathrm{S}}[\mathrm{D}]_\mathrm{S}$$

where $[\mathrm{H}]_\mathrm{F}$, $[\mathrm{Na}]_\mathrm{F}$, and $[\mathrm{D}]_\mathrm{F}$ refer to the concentration of these ions in the fiber and $[\mathrm{H}]_\mathrm{S}$, $[\mathrm{Na}]_\mathrm{S}$ and $[\mathrm{D}]_\mathrm{S}$ to those in solution.

This leads to a Langmuir equation, which may be written as

$$\frac{[\mathrm{S}] - [\mathrm{D}]_\mathrm{F}}{[\mathrm{D}]_\mathrm{F}} = \frac{1}{[D]_\mathrm{S}}(K^{\mathrm{Na}}_{\mathrm{D}}[\mathrm{Na}]_\mathrm{S} + K^{\mathrm{D}}_{\mathrm{H}}[\mathrm{H}]_\mathrm{S})$$

[145] C. Renard, *Teintex* **36**, 845 (1971).

[146] J. Park and W. S. Davies, *J. Soc. Dyers Colour.* **89**, 37 (1973).

[147] E. Siepmann, *Melliand Textilber.* **49**, 577 (1968).

[148] W. Beckmann, *Farben Rev.*, (*USA*) **22**, 22 (1972).

[149] V. Rossbach, H. Müller, and D. Nissen, *Textilveredlung* **9**, 339 (1974).

[150] W. Beckmann, *Chemiefasern* [N.S.] **23**, 436 (1973).

TABLE XIV

Acid Groups in Basic-Dyeable Polyester Fibers

	pH 1.8; *sulfonic acid content (mEq/kg)*		pH 4.5; *acid end group content (mEq/kg)*	
Fiber	*By chemical means*	*From isotherm 100°C*	*By chemical means* [a]	*From isotherm*
Dacron T64C	86	88	107	109
Dacron T65	94	92	129	123

[a] The acid end group content comprises the sulfonic acid groups together with the carboxyl groups.

The fibers were dyed at different temperatures at pH 1.8 and 4.5, and the saturation values were determined from Langmuir plots. Table XIV shows acid group contents determined directly and as dyestuff saturation equivalents.

The data are notable for the fact that at pH 1.8 only the sulfonic acid groups are acting as sites, whereas at 4.5 both these and the carboxyl groups are active. The situation is complicated, however, since the saturation values decrease as the temperature is reduced and are modified by the presence of carrier. It may be that when lower saturation values are observed, the fiber is not uniformly dyed.[150]

The kinetic behavior is similar to that of polyacrylonitrile fibers in that the surface of the fiber is rapidly saturated so that the rate of dyeing in the initial stages is independent of the concentration of dye in the bath. Because of the rapid strike and the relatively low number of groups in the fiber available, incompatibility of dyes in admixture can occur. Careful selection of dyes in a similar way to that proposed for basic dyes on acrylic fibers is recommended.[148] Carriers may be recommended to insure that complete dye penetration is achieved.[147]

E. Acrylic and Modacrylic Fibers

Acrylic fibers, i.e., those containing at least 85% by weight of acrylonitrile, contain a comonomer such as vinyl acetate or methyl methacrylate. These comonomers are introduced to modify the structure, to enhance the solubility of the polymer, and to make the structure of the resulting fiber more accessible to dyes. In addition to these comonomers, others are used to modify the dyeability, namely, (1) acidic monomers, e.g., sulfonic, phosphonic, or carboxylic acids, which enhance substantivity for basic dyes; (2) basic monomers (e.g., compounds containing amino or pyridine groups) conferring substantivity to acid dyes; (3) polar nonionizable monomers (e.g., alcohols, ethers, ketones) containing functional groups capable of forming complexes with dyes; (4) monomers that contain no reactive groups but alter the physical structure of the fiber.

In order to obtain a range of fibers with different dyeing properties, chemical modifications have been made in order to confer substantivity for acid dyes. Mixtures of the various types are used for color effects or different basic dyeable types to give tone-in-tone effects.[128,151] There are (1) regular-dyeable types, which have some substantivity for disperse dyes and different abilities to absorb basic dyes; (2) acid-dyeable with a similar substantivity for disperse dyes and no substantivity for basic dyes; (3) modacrylic types with varying substantivity for basic and disperse dyes but not for acid dyes. These last fibers are of interest because they possess nonflamable characteristics due to the introduction of significant amounts of comonomers such as vinyl bromide or vinylidine chloride.[152] Combinations of regular dyeable and modacrylic fibers enable tone-in-tone effects to be obtained.[118]

Disperse dyes have similar substantivities for all three types of fiber, but owing to the more open structure of the acid-dyeable and modacrylics, saturation levels tend to be higher, and hence darker colors are obtained.[153] If regular and modacrylic fibers are dyed with basic dyes in one bath under neutral conditions, the regular dyeable fiber is darker owing to its greater substantivity. If dyeing is carried out under strongly acid conditions, the modacrylic may be almost reserved.[118] Acid-dyeable fibers are dyed at pH 2.0–2.5 to achieve complete penetration and optimum light fastness.[154]

F. Biconstituent Fibers

In recent years, a new type of fiber has been produced in which two polymers are used together. Three combinations are available: (1) by extrusion of the polymers side by side to give a bilateral arrangement, (2) by making the core of the fiber different from the skin, or (3) by extrusion of a blend so that one polymer is dispersed in a matrix. In preparing bilateral or skin–core fibers, the polymers must be carefully chosen so that the two halves of the fiber have good adhesion, e.g., nylon 66 may be coextruded with nylon 6 or comonomers of nylon 6 and 66 or two kinds of acrylonitrile polymer may be used.[155] Bilateral

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[151] W. Pedrick, *Mod. Text. Mag.* **50**, 60 (1969).

[152] Monsanto, *BP* 1,089,740; 1,099,845 (1965).

[153] A. Würz and H. J. Ulrich, *Z. Ges Textil Ind.* **67**, 285 (1965).

[154] A. M. Jowett and A. S. Cobb, *Rev. Prog. Col.* Relat. Top. **3**, 81 (1972).

[155] E. M. Hicks, E. A. Tippetts, J. V. Hewett, and R. H. Brand, *in* "Man-Made Fibres" (H. Mark. ed.), p. 375. Wiley (Interscience), New York, 1967.

fibers are of interest because of their ability to crimp arising from the different properties of the two polymers and hence are used for high-bulk articles.[154]

Skin–core fibers are of particular importance, since adjacent fibers within a web may be fused together under heat, because the polymer forming the skin has a lower melting point than the core, the latter being unaffected. Such materials are of value in the nonwoven and needle-punched carpet fields.

The third variety possesses useful mechanical properties, since the dispersed phase can act as a reinforcement for the matrix. Thus, in the fiber Source, polyethylene terephthalate is dispersed in a nylon matrix, the amine end of the latter being blocked with a carboxylic acid to avoid reaction with the polyester.[156] After drawing, the polyester is in the form of fine needle-shaped fibrils about 100–200 μm long.[157,158] The wide variety of types of biconstituent fibers is listed elsewhere.[159] In general, dyeing these fibers causes little problem, since the individual components can be dyed in the conventional way.

III. Disperse Dyes for Cellulose

A solvent-dyeing system of a novel type has been developed to obtain fast coloration of cellulosic fibers with selected disperse dyes. The principal application is in the printing of polyester–cellulose blend fabrics under the trade name Dybln (Du Pont).[160]

Water-insoluble dyes of the vat and sulfur classes can of course be temporarily solubilized by reduction and, after diffusion into the fibers, reconverted to the insoluble form. The Dybln system also uses temporary solubilization, but by the physical increase of solubility in a solvent, at temperatures above 150°.

Application, by padding or printing, of dye dispersed in a 10% aqueous solution of a high-boiling point, hydrophilic solvent, is followed by drying and thermofixation. The solvent enters the water-swollen fiber and, because of its low volatility, remains primarily within the fiber after drying. At temperatures of 150°–180° for cellulosic fabrics or 180°–220° for polyester–cellulose blend fabrics, the dye dissolves in solvent at the fiber surface, and diffusion into the fibers is substantially complete within 20 seconds to 2 minutes. A washing-off treatment is

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[156] B. T. Hayes, *Chem. Eng. Prog.* **65**, 50 (1969).

[157] P. V. Papers, E. Kuber, and L. Rolden, *Text. Res. J.* **37**, 823 (1967).

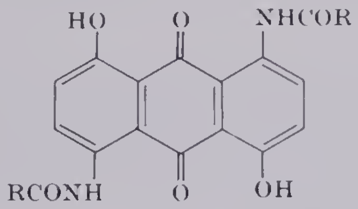
[158] *Mod. Text. Mag.* **49**, 48 (1968).

[159] P. A. Koch, *Textilveredlung* **5**, 312 (1970).

[160] *BP* 1,249,896 (1971).

TABLE XV

SOLUBILITY, FIXATION, AND FASTNESS OF SELECTED DYES[161]



R	Solubility		Dye fixed (%) (cotton)	Fastness[c]
CH_3CH_2—	8.3[a]	5.1[b]	13	2–3
$CH_3(CH_2)_2$—	1.0	20	42	3–4
$CH_3(CH_2)_6$—	0.25	45	79	4–5

[a] Relative optical densities of saturated solutions in 0.1 M Na_2CO_3 at 100°.

[b] Relative optical densities of saturated solutions in perchloroethylene at 50°.

[c] Shade change after AATCC wash test 3A.

required to remove solvent and surface dye. Suitable solvents are glycol ethers and esters with boiling points in the range 230°–290°, including diethyleneglycol *n*-butyl ether, and diethyleneglycol diacetate.

Fastness to washing has been correlated with solubility of dye in a boiling solution of sodium carbonate, which is inversely related to solubility in perchloroethylene and in the preferred solvents,[161] as shown in Table XV. Most disperse dyes have too high solubility in water, but a satisfactory range of dyes of very low solubility, which also have the required volatility for vapour-phase transfer to polyester, is available. Suitable dyes include CI Pigments Yellow 1 and Orange 6, Vat Oranges 5 and 7, and Vat Reds 10 and 40. Because the preferred dyes have very low water solubility, they are not suitable for exhaustion dyeing on polyester, and therefore, staining of unprinted ground areas during the washing off of prints is not a problem, as it is with conventional disperse dyes on polyester–cotton. Distribution of dye between polyester and cellulosic fibers can be varied by adjustment of the amount of solvent used and the conditions of thermofixation. Prints show better wet-rubbing and abrasion fastness and softer handle than typical pigment prints.

IV. Microfoams for Dye Distribution

One interesting result of work on the solvent dyeing of nylon with ionic dyes using small amounts of water emulsified in perchloroethylene

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[161] R. F. Sklar, Du Pont Bull. No. 204 (1975).

was the realization that the solvent was acting primarily as an inert extender of the dyebath volume. Dyeing was occurring from a very small volume of water, but uniform distribution could only be obtained from the larger total volume. A cheaper alternative is to use a foam, in which air is the extender rather than the solvent.[162] Suitable surface-active agents were found to produce stable foams of high volume within the fabric structure, and this resulted in the rapid attainment of a uniform distribution of dye dissolved in only about 1.5 parts of water (on weight of fiber). This system was given the commercial name Sancowad and has been applied primarily in the garment-dyeing field.

Dry garments are loaded into a rotary perforated drum machine, and dye solution containing the required Sancowad agent is sprayed onto the material. Tumbling for 15 minutes at room temperature generates the microfoam and produces the desired uniformity, which would be impossible without the foam. The introduction of steam, with precautions to avoid unevenness due to water condensation, initiates the fixation stage. Steaming for 15–30 minutes was found to be adequate for a wide range of dye–fiber systems. Cooling, high-speed rotation (centrifuging), and rinsing complete the process. Rinsing is also at low liquor ratio, so that total volumes of water and effluent are reduced substantially, as are steam consumption and dyeing times.

The process is comparable to the pad-roll dyeing of piece goods, and low substantivity conditions are equally desirable at the impregnation stage. With dyes of high substantivity, electrolyte concentration, pH, and retarding agents should be chosen so as to reduce the initial strike. The system is especially valuable for dyeing nylon, wool, and wool–nylon half-hose with acid or reactive dyes and for cellulosic knit wear with reactive dyes, but it is by no means restricted to these examples. Sancowad foaming agents are available for all classes of dye and may be nonionic, anionic, or cationic in character. Examples of surfactants that have suitable properties are (1) the condensation product of octylphenol and 10 moles of ethylene oxide, (2) lauryldihydroxyethyl sulfate, and (3) the condensation product of 3-stearylaminopropylamine and 90 moles of ethylene oxide. For polyester fiber, additions of benzyl alcohol as a carrier are recommended in preference to the usual ones, as it has a smaller adverse effect on the generation of foam. Suitable rotary drum machines are manufactured by Samuel Pegg & Son Ltd., they have provision for garment drying to follow the dyeing process, thereby reducing the handling costs.

Although tumbling in a rotary drum is a convenient method of generating foam, the concept is not limited to garment dyeing. A

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[162] S, *BP* 1,371,781 (1970); G. H. Lister, *J. Soc. Dyers Colour.* 88, 9 (1972).

winch-dyeing machine with the Roto-stream-type rotating cage (see Section IV) could be adapted for the Sancowad system, for example.

V. Jet Dyeing

Many fabrics are easily stretched and flattened in the hot, wet state, and therefore appropriate mechanical handling must be provided for dyeing. Mechanical stresses must be limited, especially for fabrics made of wool and of acrylic fibers, for knitted structures, and when maximum softness and fullness of handle are required. The traditional winch machine, or beck, in which the fabric is sewn end to end and dyed in rope form, has been used for such fabrics for a very long time without essential change in design. In winch dyeing, fiber and fabric relaxation are assisted by the frequent flexing of the fabric, but extension, creasing, and rub marking are regular hazards.

The limitations of the winch became more apparent with the introduction and importance of bulked-filament polyester yarns, especially in weft-knit constructions. Extension and creasing during dyeing were difficult to avoid, even after a presetting treatment. The use of pressurized, high-temperature winches did not reduce the difficulties. The solution to the problem, which has been widely adopted, was to circulate the dye–liquor and use the liquor flow to move the fabric.[163] In the true jet-dyeing machines, the venturi principle is employed to

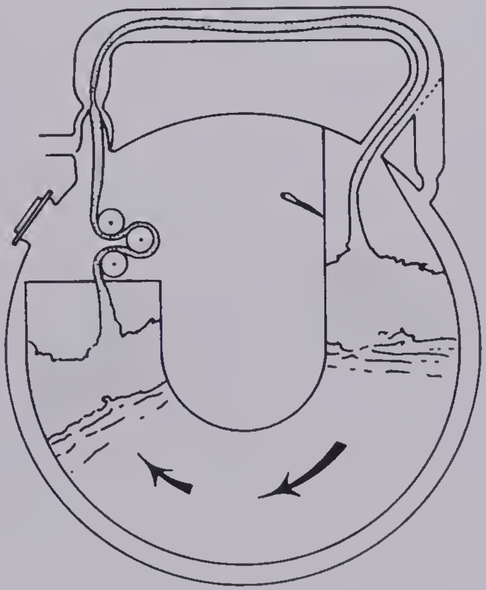

FIG. 21. Typical early jet-dyeing machine.[164]

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[163] Burlington Industries, *USP* 2,978,291 (1958).

suck the fabric into the jet and project it into a storage chamber (Fig. 21). The diameter of the jet tube must be such that the fabric rope nearly fills the jet but is not rubbed because of the liquor flow around it. With the high liquor velocities used, the fabric speed through the jet is often around 150 m/minute. This has the advantage of allowing rapid loading and unloading and also longer ropes than on winches. Fabric circulation times of up to 3 minutes are practicable in many machines.

A major, additional advantage of high-velocity circulation of the liquor is that temperature uniformity is substantially improved, and increased rates of temperature rise are possible. Dyeing times can therefore be reduced. Because the introduction of jet machines coincided with widespread use of programmed dye cycle control, spectacular increases in rate of rise were shown to be practicable. On winches, 1°/minute was often considered satisfactory, but rates of 10°/minute for heating and cooling have been reported for some polyester fabrics.[164] When high temperatures are employed, this can effect a large reduction in dyeing time, but it also leads to high temporary steam demands. The use of computer control may be necessary to ensure that staggering of the peak demands of neighboring machines occurs to avoid exceeding the maximum steam supply rate.

A bewildering variety of machine designs has been marketed.[165] In early machines, the fabric was not fully submerged below the liquor, and the jet sucking in air created excessive foaming unless all auxiliaries were selected with care.[166] Completely filled machines were therefore built, and the liquor ratio was kept at an acceptable level by constructing them entirely of stainless steel tube of relatively small diameter (Fig. 22).

An alternative approach,[167] which has proved to be as successful as its design is logical, employs a simple cylindrical vessel with internal underwater jet and fabric passage channel (Fig. 23). The latter is of changing cross section to encourage rearrangement of the cloth folds, and the size and inclination of the main chamber allow free floating and opening of the rope. A free-running roller changes the fabric direction and provides a valuable indication of cloth speed. Some of the circulating liquid is diverted to counterjets, which control the fabric approach to the roller and jet. This type of design appears to provide

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[164] H. Bellis and F. Birtwistle, *J. Soc. Dyers Colour.* **88**, 321 (1972).

[165] M. Patterson, *Rev. Prog. Color. Relat. Top.* **4**, 80 (1973).

[166] A. N. Derbyshire and A. T. Leaver, *J. Soc. Dyers Colour.* **91**, 253 (1975).

[167] K. Limbert, *J. Soc. Dyers Colour.* **88**, 385 (1972).

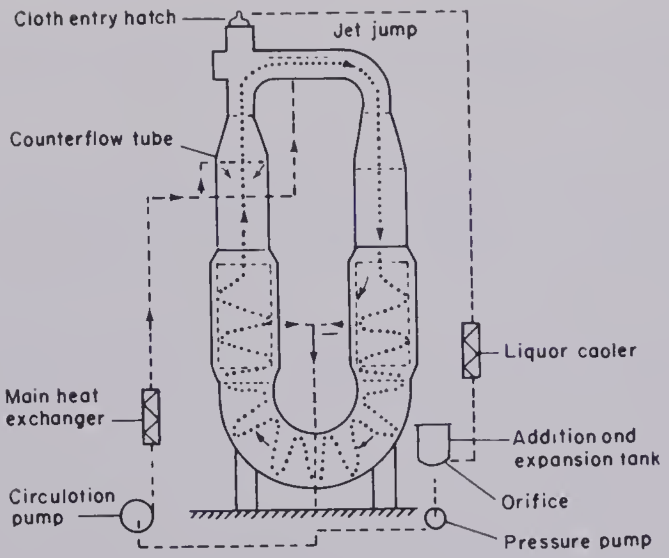

Fig. 22. Thies "jet-stream" dyeing machine.[164]

the maximum flexibility for varying fabric types. Although weft-knitted fabrics still form a large fraction of the fabrics dyed on jet machines, the machines have also been used for a very wide range of woven and knitted fabrics.

For the most delicate fabrics, lower velocities are found to be desirable to avoid surface distortion. Machines have been designed specifically for this purpose described as soft-flow machines. They generally

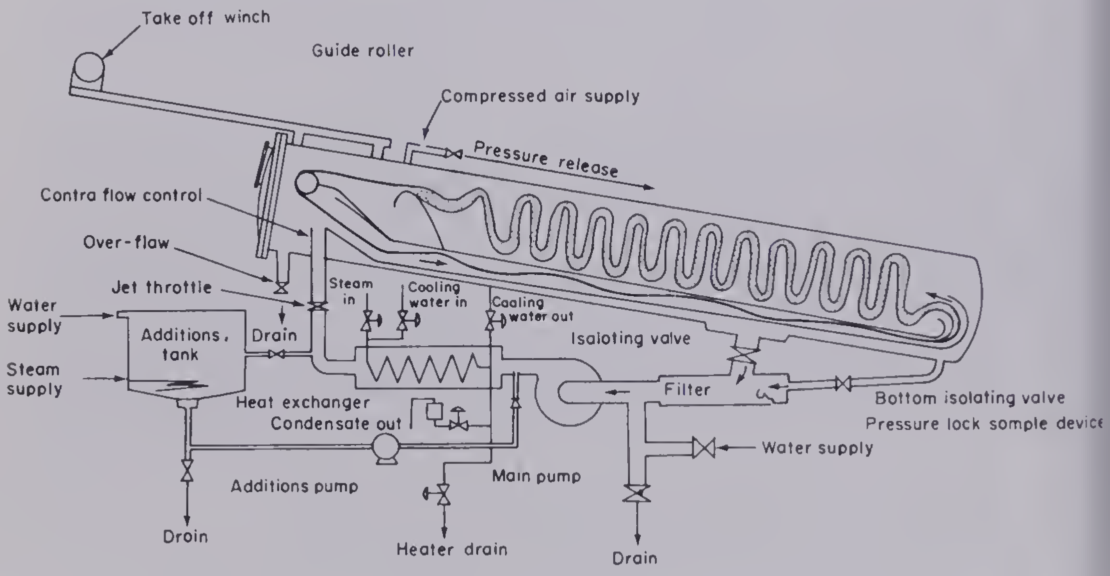

Fig. 23. Ventura jet-dyeing machine.[167]

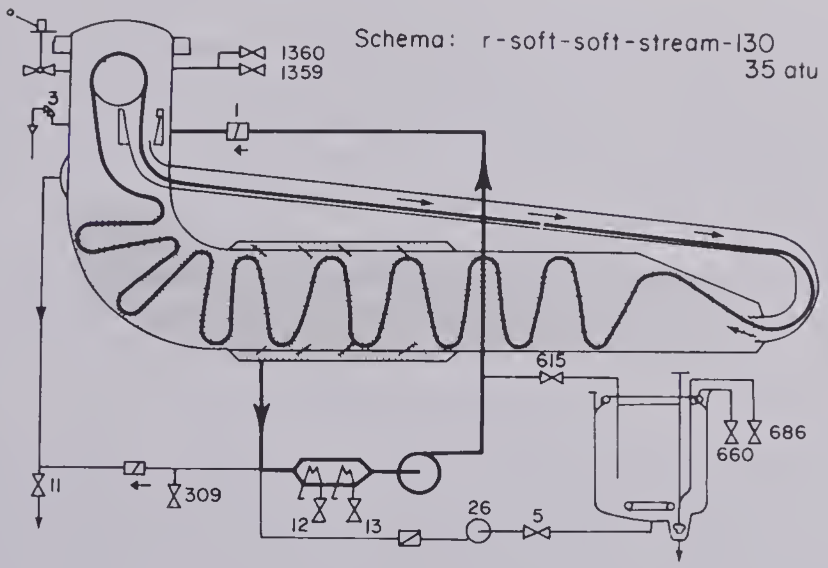

FIG. 24. Soft-stream dyeing machine (Thies AG).

use winches to lift the fabric over the minimum distance, but provide a liquor stream to return the rope along a tube to the entry end of a storage chamber (Fig. 24).

A recent development allows the reduction of operating liquor ratios to the very low level of about 2:1 by feeding the fabric from the jet into a suspended cage, which rotates to bring the rope to the jet entry once more. Friction between fabric and storage chamber is therefore avoided, but no opening of the rope can occur within the cage. The risk of permanent creasing must therefore be increased.

The development of jet dyeing has occurred quickly and with considerable success. It is now possible to handle many fabrics with reasonable confidence so that creasing and other undesirable distortions can be avoided and excellent levelness attained. The dyer must still, however, acquire a considerable amount of know-how to decide which machine and conditions will be suitable.

VI. Continuous Exhaustion Dyeing

Continuous dyeing processes are usually made up of three unit operations—impregnation, mangling, and fixation. Inevitably there are limitations to the perfection of each operation in practical situations. Ideally, no strike should occur at the impregnation stage; therefore, this is usually at room temperature, which is convenient but slow and often requires high concentrations of wetting agents. Mangling should leave a constant weight of dye in each part of the material, which, however, is impossible for loose fiber or any material of nonuniform thickness. Very wide and tubular fabrics are particularly difficult to squeeze uniformly, and for pile fabrics mangling is undesirable. During fixation the distribution of dye should not become less uniform. Migration in drying and frosting in steaming processes are constant hazards, however.

Therefore, the alternative, single-unit operation of continuous exhaustion dyeing should be considered. Early use of Williams units and liquid boosters in the continuous application of vat dyes was abandoned for sound reasons, but the approach may be more useful in new circumstances.

The British Cotton and Wool Dyers' Association has developed a system of dyeing loose fiber or sliver in a U-tube that provides 8 minutes' exhaustion at temperatures up to 106° in the long horizontal section of the tube.[168] Fiber is automatically weighed into the machine, and a difference in height between the entrance and exit legs of the U-tube and the delivery of a controlled volume of dye liquor to the entry leg cause a flow through the tube, which conveys the material along with it. Exhausted dye liquor is replenished with dye and additives and recirculated. Fast but controlled dye sorption is obviously required. Comparison with the Standfast molten metal dyeing machine,[169] which provided only 3–10 seconds at 95° for exhaustion, shows that 8 minutes will be long enough for some dye–fiber systems.

Artos has adopted the same approach with the Fluid-O-Therm machine, which is designed for dyeing 5 m wide carpet.[170] The carpet is preheated in steam, then entered, face down, into the dye liquor at 98°–100° in an 18 m long shallow trough. Carpet and dye liquor are moved slowly through the machine to give 3 minutes' exhaustion time for nylon and 6 minutes for wool or acrylic fiber carpets. Pumped circulation of the dye liquor is necessary to maintain side to middle uniformity. Selection of suitable acid dyes, pH, and auxiliaries has given excellent results, showing advantage over other continuous methods in the contrast obtained with differential dyeing fibers. Relatively high liquor ratios of about 15:1 are not a disadvantage if liquor recirculation is used.

Clearly, the success of both systems depends on the movement of substrate and dye liquor through the exhaustion unit at the same speed.

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[168] *BP* 1,067,736; K. Limbert, *J. Soc. Dyers Colour.* **89**, 7 (1973).

[169] J. Ardron, M. R. Fox, and R. W. Speke, *J. Soc. Dyers Colour.* **68**, 249 (1952).

[170] H. Putze, *Chemiefasern* **3**, 230 (1973).

Constant concentrations at all points along the length of the machine can then be maintained and tailing can be avoided. Provided this can be achieved, there must be a potential advantage in a continuous exhaustion system for any material that has not been dyed by continuous methods because of difficulties in application of the pad-fixation approach. Weft-knitted polyester fabrics would be an obvious target, but polyester cannot be dyed rapidly without the use of carriers, high pressures, or nonaqueous solvents. The last, perhaps, offer the best prospect.

VII. Vacuum Impregnation

Rapid wetting of fiber assemblies is recognized as a significant advantage of dyeing with liquid ammonia or a halogenated hydrocarbon solvent. Slower and incomplete wetting is characteristic of aqueous systems. It has been demonstrated that preevacuation to remove occluded air can give useful improvements in degree and uniformity of wetting and, therefore, more uniform dyeings.[171]

Machinery for vacuum padding is available from at least two manufacturers and has shown particular advantage for dark colors on densely constructed cellulosic fabrics in the scoured or gray state. The vacuum should be maintained at a maximum pressure of 100 Torr. In Fig. 25, the fabric (1) is shown passing between an open-ended rotary screen (3) and a flexible endless belt (2). Within the screen are the vacuum (4) and impregnation (8) chambers, and either the volume of liquor supplied is accurately controlled or a mangle would follow the impregnator.

Excellent results have been obtained with vacuum padding in the application of vat and reactive dyes by pad-jig, pad-batch, and pad-dry-stream processes. Desizing before padding is recommended to avoid the loss of depth due to removal of dyed size at the washing-off stage. The vacuum padding of tubular knitted fabrics has the advantage of eliminating the wet edges obtained in conventional padding at the edge folds.

Penetration can also be improved, to a lesser extent, by preheating the fabric to temperatures of about 150° immediately before impregnation. The explanation is presumed also to be the production of a vacuum within the fabric structure because of the expansion of air and generation of steam within the fabric and subsequent condensation in the cooler pad liquor.

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[171] M. R. Fox and B. N. Parson, *J. Soc. Dyers Colour.* 89, 46 and 474 (1973); ICI, *BP* 1,158,284 (1966).

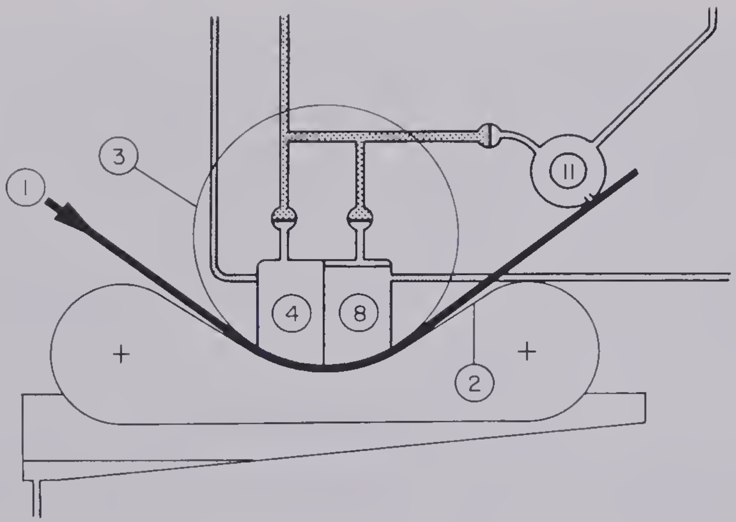

FIG. 25. Vacuum impregnator (Sir James Farmer Norton & Co., Ltd.). 1 = fabric; 2 = sealing blanket; 3 = rotary mash screen; 4 = vacuum chamber; 8 = dye liquor chamber; 11 = suction slot.

The application of preevacuation to package dyeing machines for yarn has also been exploited by Thies and Gaston County for rapid-dyeing processes.[172]

VIII. Space Dyeing

This term was introduced to provide a generic description for a variety of processes used for both random and patterned coloration of yarn, most of which was used for producing tufted carpets. The processes vary from simple to sophisticated,[173] some of the latter being described as warp printing. With the emergence of a continuing demand for multicolored carpets and fabrics, the extension of space dyeing to fabric was logical, because the delays and costs of colored yarn stocks could be avoided.

The most widely used approach has been the ICI Polychromatic dyeing system, being applied to flat and tubular fabrics, carpet, and warp beams.[174] Controlled volumes of a number of streams of dye solutions are fed on to the substrate shortly before it enters a mangle nip (Fig. 26). The colors already applied are little affected by the mixed dye solution, which is spread over colored and uncolored areas at the nip. The jets that control the flow volume and direction are

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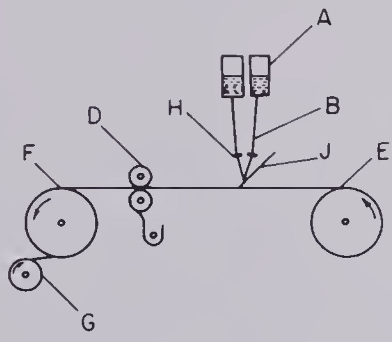
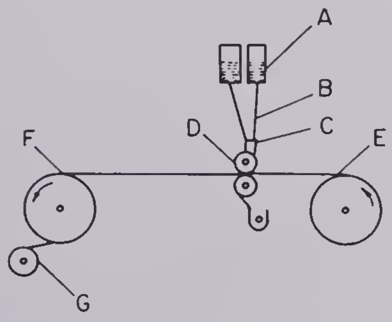
[172] Burlington Industries, *BP* 1,246,806–7 (1967).

[173] L. W. C. Miles, *Rev. Prog. Color. Relat. Top.* 4, 45 (1973).

[174] *BP* 1,243,403–4; M. R. Fox, *J. Soc. Dyers Colour.* 89, 17 (1973).



(a) Dye-weave system



(b) Flow-form or Dye-transfer system

FIG. 26. Polychromatic dyeing process (ICI Technical Information D1140). *Key:* A = individual dye-liquor tanks, B = flexible feed pipes, C and H = dye liquor jets, D = pad-mangle, E and F = feed and take-up rolls, G = polythene interlining feed (if impregnate–batch process being used), J = inclined plane.

mounted on bars that can be stationary or reciprocated to give sine-wave patterns. The jets may feed onto the mangle bowl or onto an inclined plane to obtain a wide variety of effects. The inclined plane may be smooth or grooved, in contact with or above the fabric to give continuous or interrupted patterns. By precise control of all the variable factors, remarkably good reproducibility of pattern is achieved. Fixation follows by standard techniques.

Precisely patterned carpets are now being produced by the projection of jets of dye solution directly onto the carpet. This is done by the Millitron machine, developed in the United States by Deering Milliken.[175] Dye solution is pumped through rows of needle jets, 10 per inch width, the pattern on a magnetic disk providing the activating impulse for control of individual jets.

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[175] D. Ward, *Text. Month March*, p. 40 (1975).

CHAPTER V

TRANSFER PRINTING

C. E. Vellins

L. B. HOLLIDAY & CO. LTD., HUDDERSFIELD, YORKSHIRE, ENGLAND

I. General Introduction

Transfer printing involves the transfer of color from one surface to another surface, generally from paper to a textile material. The actual transfer can be brought about by a number of different techniques, and each technique has its own particular physical and dyestuff requirements. There are three commercial processes of transfer printing in current use:

1. Physical or melt transfer, which involves the printing of dyes or pigments together with a thermoplastic binder on paper and then transferring the complete plastic film onto any textile substrate under pressure and heat.

2. Migration printing uses water soluble dyes, which are printed on paper together with the chemicals necessary to give fixation on the appropriate textile material. The transfer can be facilitated by application of heat and pressure as well as by the use of a radiofrequency treatment. It is essentially a method of printing using a short liquor ratio.

3. Vapor phase printing uses disperse dyes which are printed on paper and applied to textile materials at temperatures between 180–220° for approximately 30 secs. This process has been called the Sublistatic-, sublimation-, dry heat- and the thermoprinting process, but is now more loosely referred to as "Transfer Printing."

Within the last few years there has been a considerable overlap between these three processes. Modern transfer printing as we know it today was commercially developed by Sublistatic in 1968, and since then there has been a dramatic and almost universal interest in this process. New industries have been, and are still being, created in an attempt to keep abreast of modern developments. Transfer printing is a living technology in which enormous changes can happen, virtually overnight.

Never before has there been such a need for cooperation between industries with such a wide variation in job requirements. Transfer printing owes its success to a liaison between (1) the dyestuff manufacturer who provides dyestuffs with the requisite physical, chemical, and textile properties; (2) the ink maker who can manufacture gravure, flexographic, screen printing, lithographic and letterpress inks; (3) the paper manufacturer who has to provide the correct paper suitable for the different methods of printing; (4) the manufacturer of various printing presses, together with their ancillary trades who provide printing rollers, stereos, screens, plates, etc; (5) the textile designer who has to understand the advantages and limitations of transfer printing; (6) the manufacturer of the heat-printing machines that transfer the design from the paper to the textile material; (7) the producer of textile materials who must present the material in a suitable form and condition to be printed; and (8) the purchaser of the transfer printed material who has to be sure that the fastness properties are suitable for the end use of that material.

The growth of transfer printing is real. From 1968 to 1975 there has been a growth from virtually nothing to approximately 600 million/m^2 and this is expected to rise to 2500 million/m^2 by 1980.[1,2]

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[1] H. Schaub, *Stork Symp. Leicester, 1976.*

[2] *Am. Dyest. Rep.* **64** (7), 54 (1975).

II. History

The transfer of patterns from paper to textiles and ceramics has been known for some time. At least a century ago, embroidery patterns were applied to linen from a paper print containing a mixture of ultramarine with shellac by means of a hot iron. In 1925, Morse patented transfer sheets printed with a medium consisting of paraffin, resin, cocoa butter, mutton tallow, and a mineral coloring matter; the transfer from the paper to the textile fabric was obtained by the application of heat.[3] The transfer printing of cellulose esters or ethers from paper was described in 1929 by British Celanese, who also applied dyes in the vapor phase to the same materials.[4] Suitable dyes were found to be 4-nitrobenzeneazo-*p*-xylidine (orange), 2-nitro-4-chloro-4′-methyldiphenylamine (golden yellow), 4-nitro-2-methoxybenzeneazodimethylaniline (red), and 4-nitro-2-methoxybenzeneazodiethylaniline (red). Denglar described the heat transfer of dyes on to mordanted material.[5] Lawrence differentiated between decalomania prints, in which the transfer is effected by moistening the back of the printed paper, and heat transfer which is effected by the use of a hot iron.[6] Kaumagraph Transfers claimed an improvement for indelible transfers and for a transfer printing method for dyeing fibers.[7] Star Stampa improved the existing transfer techniques by using organic dyes in the intaglio printing of paper.[8] The print was transferred from the paper to the fabric by passing between two pressure rollers at a variable pressure and temperature according to the fabric to be printed. Levy described one of the first machines specifically designed for transfer printing.[9] The use of high vacuum in transfer printing was patented by Kunsch, who vaporized dyes such as Heliogen Blue G and Celliton Fast Blue B onto nylon in a vacuum chamber.[10] However, the first patent for transfer printing as we know it today was applied for in October 1958 by Filatures Prouvost[11] and published in June 1960. The dyestuffs suitable for the process were found to be disperse or plastosoluble dyestuffs belonging to one of the three classes: (a) nitroarylamine; (b) azo; (c) anthraquinone.

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[3] T. W. Morse, *BP* 252,402.

[4] BrC, *BP* 293,022; 349,683.

[5] A. Denglar, *BP* 337,877.

[6] W. Lawrence, *BP* 421,372.

[7] British Kaumagraphic, *BP* 559,878–9.

[8] Star-Stampa, *BP* 754,233.

[9] Levy-Knitella, *BP* 771,375.

[10] Kunsch, *BP* 830,348.

[11] Filatures Provoust, *FP* 1,223,330.

In general, the preferred dyes contained an amino group that could be substituted, but they did not contain sulfonic acid groups. The selected dyestuffs, which must vaporise without decomposition, were made into a paste with locust gum and impregnated on filter paper. The printed paper was dried and brought into contact with materials, in particular of synthetic origin, and heated at temperatures from 120° to 200° from $\frac{1}{2}$ minute to 2 minutes. No aftertreatment was necessary to fix the dye on the textile material that had been printed through the vapor phase. Thus, the invention was completely different from all other existing dyeing and printing processes. The idea of using sublimable dyes for a variety of different end uses was at first slowly taken up before developing into a major race to exploit the numerous facets of this new industry. Agfa used dyes having a melting or sublimation point of between 80° and 220° incorporated in a binding agent to make a copy paper that could be used as a printing forme to give a hundred reproductions by the application of heat.[12] ICI described the preparation of a printing paste utilizing Disperse Blue 35, which was screen printed on paper and transferred to cellulose triacetate, polyester, and nylon at temperatures between 170° and 220°; this patent was not sealed.[13] The transfer printing of anodized aluminium with certain anthraquinone dyes, azo dyes having a hydroxyl group ortho to the azo group, and dyes containing the 1,3-indandione group was patented by Martin Marietta.[14] Cassella described the transfer printing under high vacuum of polyester, acrylics, nylon, triacetate, polypropylene, and polyvinyl chloride using water-insoluble dyes with a molecular weight less than 800.[15] Ciba achieved transfer printing without paper by the direct printing of a material made of or containing a synthetic product with a solution of resin containing a disperse dye that sublimes at 140°–230°; the printed area is then heated to sublimation temperature.[16]

Nine years after filing their first, and at that time still the only, major patent on transfer printing,[11] Filatures Prouvost took out a further patent that was to become one of the major patents concerned with the gravure printing of transfer printing paper.[17] It was filed on the same day (July 24, 1967) as patents from Ciba[18] and Trentesaux-

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[12] AGFA, *BP* 951,987.

[13] ICI, *BP* 959,315.

[14] Martin Marietta, *BP* 1,052,625.

[15] CFM, *BP* 1,105,734.

[16] CIBA, *BP* 1,221,149.

[17] Filatures Provoust, *BP* 1,189,026.

[18] CIBA, *BP* 1,221,126.

Toulemonde.[19] The first[17] covered a process for dyeing synthetic textile materials with at least one disperse dye which vaporized in the range of 160°–230°, whereby the support was printed with an ink consisting of the dye and an organic solvent substantially free of water, then bringing this printed support in contact with a textile and heating to a temperature above the vaporization temperature of the dye for a sufficient time to permit vaporization of the dye and penetration onto the textile material and then terminating the heating and separating the dyed textile from the support. The second[18] claims dyestuff preparations containing at least one dyestuff and/or fluorescent brightening agent that transfers at 100°–300° and at least one resin soluble in organic solvents that serves as the dye carrier with a 1:4 ratio of dyestuff to resin. The third patent[19] claims a printed support carrying at least one of the following dyes: 1,4-dimethylaminoanthraquinone, 1-hydroxy-3-phenoxy-4-aminoanthraquinone, 4-(4′-methyl-2′-nitrophenylazo)-3-methyl-5-pyrazalone, hydroxyquinophthalone, and the butyl or propyl ester of 1,4-diaminoanthraquinone 2-carboxylic acid, together with at least one binder that is soluble in an organic solvent and is heat stable so that it does not become sticky below 250°. These three patents are fundamental in transfer printing, since they give the ink formulation recipes, some of the dyes being used, and the possible conditions and variations. It is of interest to note that the above three patents were published in 1970–1971 showing how relatively recent is the modern concept of transfer printing.

III. Developments since 1970–1971

Water-soluble dyes, both reactive and nonreactive, have been used for the migration printing of materials containing natural fibers such as wool and cotton. Ciba[20] keeps the wet textile material in contact with the printing paper, which is heated to at least 100° for 20–220 seconds. Dawson Holdings[21] pads the textile material or material made of animal fibers with a print paste and then heats in contact with the transfer paper at 80°–120° up to a pressure of 10 lb/in^2 and for a period not exceeding 10 minutes; the printed material is then washed and dried. This is the basis of the Fastran process, which is further extended by winding the pasted fabric together with the paper around a roller so as to produce a pressure of 10 lb/in^2 and leaving it at room temperature for 36 hours.[21] Ciba has devised a process whereby the

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[19] Trentesaux Toulemonde, *BP* 1,190,889.

[20] CGY, *BP* 1,227,271.

[21] Dawson Holdings, *BP* 1,284,824; 1,388,200.

printed support is applied to the article to be decorated and then treated at an elevated temperature under pressure and in humid conditions, whereby the transfer is effected without the aid of a binder.[22] The transfer printing of a metal complex-forming dye onto a material that has been pretreated with the appropriate metal compound has been investigated by several companies. Thus, Ciba transfers chelatable dyes onto materials containing different metals, such as nickel-modified polypropylene and wool impregnated with a chromium compound.[23] Precision Processes does likewise, but transfers onto keratinous fibers pretreated with a polyvalent metal compound, followed by a water or steam treatment, so as to effect the complex formation.[24] Sublistatic claims a process for transfer printing a vinyl chloride homopolymer or copolymer, whereby the transfer paper is held in contact with the polymer between 70° and 140° until at least 50% of the disperse dye(s) used has migrated into the polymer.[25] There has been a considerable number of improvements in the transfer of a film to leather or a leather substitute,[26] or textiles, together with optical brightening agents,[27] in the use of a polyurethane film by laminating on to a cotton tricot fabric, and in the transfer of a vinyl resin onto an alkyd melamine resin surface.[28] The use of polythene and polyamide resin films,[29] a mixture of nitrocellulose and an aminoplast,[30] and the production of a three-layer laminate by the lithographic offset print process[31] have been claimed. There is also a process for the application of a hydroslidable transfer, together with a description of the apparatus necessary to facilitate this transfer.[32] A random transfer print effect can be obtained by scattering small pieces of transfer-printed paper onto the textile material prior to heating.[33] The use of a pressure-sensitive technique in transfer printing has been described.[34,35] Ciba claims the use of reactive disperse dyes for the transfer printing of natural or synthetic polyamide materials at a temperature below

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[22] CGY, *BP* 1,243,223.

[23] CGY, *BP* 1,320,819.

[24] Precision Processes, *BP* 1,395,881.

[25] Sublistatic, *BP* 1,342,021.

[26] CGY, *BP* 1,331,145.

[27] R. V. Carter, *BP* 1,221,649.

[28] CGY, *BP* 1,331,135; 1,343,978.

[29] Letraset, *BP* 1,320,842.

[30] Trentesaux Toulemonde, *BP* 1,320,400.

[31] Tugwell, *BP* 1,393,922.

[32] Deorlitalia, *BP* 1,380,222.

[33] CGY, *BP* 1,294,158; 1,294,599.

[34] Adhesive Materials, *BP* 1,329,089.

[35] Res. Lab. of Australia, *BP* 1,320,526.

240°; other synthetic materials are also claimed, and the transfer can also take place in a vacuum; a typical dye and recipe used in this process are: 6 parts of 1-(2-chloro-4-nitrophenylazo)4-*N*-ethyl-*N*-chloroacetoxyethylaminobenzene are dispersed with 6 parts of triacetylcellulose in 89 parts of a solvent mixture containing mainly methylene chloride and isopropyl or ethyl alcohol; 1-hydroxy-4γ-chlor-β-hydroxypropylaminoanthraquinone is also used as a reactive anthraquinone dye.[36] Bright yellow prints on acrylic and polyester fibers can be obtained by the use of styryl dyes.[36] Ciba has described the use of anthraquinone dyes for blue prints on synthetic textile materials, and in particular on polyamide materials, which can be obtained by the use of 1-amino-2-cyano-4-anilinoanthraquinone, 1-amino-2-cyano-4-cyclohexylaminoanthraquinone, 1,4-bisisobutylaminoanthraquinone, 1,4-bis-isopropylaminoanthraquinone, and 1-amino-2-bromo-4-iso-propylaminoanthraquinone.[36] LBH describes the use of blue anthraquinone dyes based on a cyanated 1-amino-4-alkylaminoanthraquinone for transfer printing with high light fastness on polyester.[37]

Mono- or dichlorinated or a mixed chlorinated or brominated 1:5-dihydroxy-4,8-diaminoanthraquinones are blue dyes suitable for transfer printing.[38] An application of an isocyanate or a masked isocyanate is claimed to improve the wet fastness properties of transfer printing dyes containing a mercapto, hydroxyl, and/or an amino group, both on textile and nontextile materials. The isocyanate can be applied to the material either simultaneously with the dye or after printing.[38]

ICI has considered both the Thermosol and transfer printing processes under a vacuum of 0.1 to 100 Torr at temperatures of 110°–240°; they also claim an apparatus suitable for transfer printing under vacuum with or without paper.[39]

Among the large number of anthraquinone dyes suitable for transfer printing, the following dyes are claimed to be of particular interest: 1-isopropylamino-4-anilino-5-hydroxyanthraquinone, 1-isopropylamino-4-amino-5-hydroxyanthraquinone, 1-isopropylamino-5-methoxyanthraquinone, 1-isopropylamino-5,8-dihydroxyanthraquinone, 1-isopropylamino-4-amino-5,8-dihydroxyanthraquinone, 1-isopropylamino-4-amino-8-hydroxyanthraquinone, and 1-isopropylamino-8-methoxyanthraquinone. In addition, the preparation of a large number of greenish yellow methine dyes suitable for transfer printing have been described.[40]

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[36] CGY, *BP* 1,254,021; 1,259,206; 1,334,114.
[37] LBH, *BP* 1,390,864.
[38] CGY, *BP* 1,344,353; 1,395,188.
[39] ICI, *BP* 1,271,372; 1,363,852; 1,423,358.
[40] FBy, *BP* 1,404,179; 1,404,180; 1,404,441.

Glover has developed a method of printing a colored pattern on open-mesh canvas, as well as a machine for the vacuum transfer printing of carpet tiles.[41] Wax crayons suitable for transfer printing have been prepared by mixing 3–10% dispersed dye with paraffin wax, stearine, and an extender.[42] Transfer printing can be carried out on the exposed surface of a pleated fabric.[43] A heat-stable printed sheet with volatile dyes for use in the making of permanent color prints comprises a backing of a dye-receptive polymeric coating containing as a dye fixative a nickel, cobalt, or copper salt together with an organic acid in an amount by weight of at least $\frac{1}{4}$ part for each 10 parts of the polymer.[44] A warp of yarns can be transfer printed prior to conversion into a fabric.[45]

Printing ink formulations such as the following have been described: solvent ink,[46] lithographic ink,[47] inks containing two or more sublimable disperse dyes, that have a similar shade but a different degree of volatility.[48] YC claim the use of anthraquinone dyes containing a group —NH—COR (R = alkyl of one to four carbons).[49] The anthraquinone nucleus can be further substituted; they also claim anthraquinone dyes substituted in the 2-position by a nitro or cyano group and in which the 1- and 4-positions can be substituted by a hydroxy, amino, or alkylamino group: the remaining ring in the anthraquinone nucleus can be optionally substituted by a halogen atom.[49]

Inclusion of a carrier, such as a polyglycol or an ester or ether, in the printing ink facilitates the transfer of the dyes to the textile substrate.[50] Sublistatic includes the use of an optical brightening agent and describes a process for obtaining level monochrome dyeings by the transfer printing method.[51] A method has also been developed to overcome the possibility of spoiling the transfer print paper by handling and to inhibit deterioration of the printed paper on long storage by printing at least one layer comprising polyvinyl alcohol or a cellulosic binder in contact with the color print, or with a coating of protein material such as gelatin.[51] Ciba claims a process for the photoelectro-

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[41] R. Glover, *BP* 1,312,070; 1,376,108.
[42] Binney & Smith, *BP* 1,420,070.
[43] Sketchley, *BP* 1,400,968.
[44] Minnesota Mining and Mfg. Co., *BP* 1,275,067.
[45] Courtaulds, *BP* 1,403,887.
[46] CGY, *BP* 1,415,081.
[47] YDC, *BP* 1,295,634.
[48] ICI, *BP* 1,408,273.
[49] YDC, *BP* 1,403,619; 1,424,203.
[50] S, *BP* 1,410,703.
[51] Sublistatic, *BP* 1,243,219; 1,342,304; 1,391,012; 1,392,390.

phoretic reproduction of an image by placing at least one volatile disperse dye in a non conductive liquid between two electrodes and causing the dye particles to migrate to one of the electrodes by application of an electric field with simultaneous irradiation of the suspension, at least one of the electrodes being at least partially transparent to the radiation.[52]

Anthraquinone dyes can be based on 1-hydroxy-4-anilinoanthraquinone in which the phenyl group can be further substituted by a methyl or ethyl group as well as a methoxy group and a fluorine or chlorine atom; the anthraquinone nucleus can also be substituted in the 5-position by another hydroxyl group.[53]

A basic dye, which has poor heat transfer-printing properties, can be printed together with an oxidizing agent capable of increasing the heat transfer-printing properties of the basic dye when subjected to heating during the contact with the material on which the pattern is to be transfer printed so that only the basic dye is transferred; the materials printed can be selected from wool, silk, acetate, polyamide, acrylic, and polyvinyl chloride.[54] A cellulosic material may be pretreated with a swelling agent before being transfer printed with a sublimable disperse dye.[55] The material is optionally washed and dried.

The designs of a number of transfer printing machines have been patented.[56–65] ICI has adapted the polychromatic printing technique to prepare transfer printing papers; several streams of dyes are applied to the paper, thus obtaining an irregular pattern without the use of engraved rollers, screens or plates.[66]

LBH claims a method for the transfer printing of textile fabrics composed of a natural or a synthetic cellulosic material, either alone or in a blend with a synthetic material such as polyester cotton,

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[52] CGY, *BP* 1,381,225.

[53] Toppan Printing Co., *BP* 1,425,098.

[54] Dainippon Printing Co., *BP* 1,414,096.

[55] Toyobo Co., *BP* 1,403,119.

[56] Hunt & Moscrop, *BP* 1,227,681.

[57] Kannegeisser, *BP* 1,257,109; 1,312,529; *USP* 3,707,345; 3,874,846; *DBP* 2,005,186.

[58] Bentley Machine, *BP* 1,287,847; 1,298,849.

[59] J. Farmer Norton, *BP* 1,344,701.

[60] Fuji Photo, *BP* 1,360,682.

[61] Wira, *BP* 1,430,381.

[62] ICI, *BP* 1,405,457; *FP* 2,194,838.

[63] Lemaire, *FP* 1,574,675; 2,176,318; 2,180,260; *DBP* 1,961,444.

[64] Toppan, *DBP* 2,135,760.

[65] CGY, *DBP* 2,263,140.

[66] ICI, *BP* 1,407,261.

whereby the fabric is pretreated with curable resin containing hydroxymethyl or alkoxymethyl groups, which are capable of reacting with specific groups in the dye, and is then transfer printed in the uncured or precured state.[67] Other claims concern the transfer printing of cellulose-containing materials in which the curing is facilitated only during the transfer print process.[68,69] By the incorporation of a nonvolatile dye or optical brightening agent into the tack layer, a visual inspection can be carried out under ultraviolet light.[70]

IV. Basic Work on Transfer Printing

In one of the first investigations of vapor-phase dyeing, Kartaschoff in 1925 studied the absorption of compounds such as 1-amino-4-hydroxyanthraquinone and 1-aminoanthraquinone by secondary cellulose acetate.[71] Majury[72] studied the absorption from the vapor phase of five model dyes on cellulose acetate and determined the vapor pressure of the dyes over a range of temperatures by manometric and also by Knudsen's effusion method. The vapor pressure data and the Clausius–Clapeyron equation were used to evaluate the heat of sublimation of the dyes. The experimental results showed that in general Henry's law was obeyed, which led Majury to consider a solvent–solute relationship in which bonds are continuously broken and reformed as a result of the thermal motion of both components rather than of specific absorption sites as obtained in normal dyeing. Jones[73] investigated the kinetics of the absorption of saturated azobenzene vapor on cellulose acetate and also determined the absorption isotherms of a number of disperse dye vapors on cellulose acetate, and they were found to have a linear relationship. The vapor phase dyeing of polyester fibers in the form of small packages at 180°–220° showed that this method could have a technical significance, and a laboratory machine for this purpose was devised. The dyeings on polyester were level, and no ring dyeing was observed; there was no apparent change in the

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[67] LBH, *DBP* 2,453,362.

[68] Sublistatic, *DBP* 2,458,660.

[69] Heberlein, *DBP* 2,436,783.

[70] ICI, *BP* 1,393,258.

[71] V. Kartaschoff, *Helv. Chim. Acta* 8, 928 (1925).

[72] T. G. Majury, *J. Soc. Dyers Colour.* 72, 41 (1956).

[73] F. Jones, *J. Soc. Dyers Colour.* 77, 57 (1961); F. Jones and J. Kraska, *ibid.* 82, 333 (1966).

tensile strength of the polyester yarn. A review on heat transfer printing by Moore[74] has collectively shown that the vapor-phase dyeing of synthetic materials takes place by initial condensation of the disperse dye vapor on the fiber surface to form a polymer–dye solution boundary layer followed by diffusion into the fiber according to Fick's law, and that this occurs at a temperature between the glass transition temperature and the melting point, i.e., during the semiamorphous state when the dye mobility is increased. Bent *et al.*[75] studied the dyeing mechanism involved in the Thermosol process, which is brought about by impregnating a polyester–cotton blend with an aqueous suspension of a disperse dye followed by a high-temperature fixation treatment. During this heat treatment, the dye transfers from the cellulosic portion to the polyester, and it was shown conclusively that the transfer occurred solely in the vapor phase and not by physical contact. In many respects, transfer printing from paper to a textile material is very similar to the Thermosol process, where the printed paper is behaving similarly to the dye-impregnated cotton portion of the polyester–cotton blend. Gerber[76] impregnated a cotton fabric with a disperse dye and heated it in direct contact with a polyester fabric. Measurements were then carried out to show that the rate of dyestuff transfer was more dependant on the diffusion of the dye into the polyester than the transport of the dye through the vapor phase. Datye *et al.* investigated a number of parameters involved in the transfer process, such as the vaporization, adsorbtion onto the fiber, diffusion into the fiber, equilibrium, and saturation of the material with the dye; they studied several dyes under a variety of conditions of fiber, concentration, distance, time, and temperature.[77] The mechanism of the process was shown to be a rapid condensation of the dye from its sublimed vapor phase, followed by a slow diffusion into the fiber phase in a Fickian way. The kinetic and thermodynamic factors of the transfer process were found to be similar to the Thermosol process. In a comprehensive review of transfer printing on a number of synthetic fibers made by Courtaulds, it was shown that the uptake of dyes on Terylene > Tricel > Celon > Dicel > Courtelle occurred in this order.[78] A number of basic dyes were transfer printed from paper containing 0.5% sodium hydroxide to convert the dyes to the free base;

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[74] N. L. Moore, *J. Soc. Dyers Colour.* **90**, 318 (1974).

[75] C. J. Bent, T. D. Flynn, and H. H. Sumner, *J. Soc. Dyers Colour.* **85**, 606 (1969).

[76] H. Gerber, *Textilveredlung* 8, 449 (1973).

[77] K. V. Datye, S. C. Pitkar, and U. M. Purao, *Textilveredlung* 8, 262 (1973).

[78] G. Holland and A. Litherland, *J. Soc. Dyers Colour.* 87, 488 (1971).

the washfastness was good, but poor lightfastness was obtained with the red and blue shades.

The use of differential thermal analysis (DTA) as a means of selecting dyes for transfer printing is being studied by Nishida *et al.*[79] Preliminary results showed that the geometry and polarity of the dye molecule was important; e.g., a small low-molecular-weight dye was thought to pass through the fabric near the vaporization temperature without dyeing the cloth, while a reactive disperse dye showed no significant vaporization under the experimental conditions used. DTA was further studied under reduced pressure, and these results indicated that a vacuum transfer print machine produces better prints than a conventional transfer print machine.[79] The kinetics and thermodynamics of the heat transfer printing process under a variety of conditions have been studied, and the results applied to commercial dyes used in the process[80]; in the deep-shade dyeings, significant savings in cost could be achieved by knowledge of the color transfer versus the ink concentration relationship. Jones and Leung[81] consider some fundamental aspects of transfer printing and describe a technique based on the Daynes time-lag method, which allows the steady-state diffusion coefficients of disperse dyes to be determined under conditions involved in transfer printing. In the transfer process there is a high initial concentration of dye just within the fiber surface, which is rapidly achieved due to the large number of dye molecules striking the surface in unit time combined with a high partition coefficient in favor of the polymer. The degree of penetration is also dependent on the mean free path length of the dye molecules in the vapor, and by creating a vacuum, there is a resultant increase in the mean free path length, which results in an improved penetration. The properties of Disperse Yellow 3, Red 9, and Blue 14 are also discussed.[81]

V. Selection of Dyes for Transfer Printing

Transfer printing is a relatively new commercial process, and consequently there was no initial disclosure of the structures of the dyes in use. The matter is further complicated by the fact that there are several industries involved between the selection of the appropriate dye(s) and the coloration of the textile material, so that the requisite

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[79] K. Nishida, T. Katoh, Y. Takahashi, and K. Minekawa, *Am. Dyest. Rep.* **63** (2), 36 (1974); and K. Nishida, T. Ohtsu, H. Iwamoto, H. Toda and K. Minekawa, *Am. Dyest. Rep.* **65** (2), 62 (1976).

[80] R. A. Fenoglio and E. J. Gorondy, *Am. Text. Chem. & Colour.* **7**, 84 (1975).

[81] F. Jones and T. S. M. Leung, *J. Soc. Dyers Colour.* **90**, 286 (1974).

shade could be produced by use of a mixture, but without obtaining the required fastness properties.

After the ITMA Exhibition in Paris in 1971, transfer paper and prints became more available, and it was found that the lightfastness of the blue component on polyester was about 3. Furthermore, at that time in 1971, the only fiber being considered for transfer printing was polyester, and the process appeared to be passing through a twilight period, during which time various groups and companies were formed. Ciba supplied dyestuffs to Sublistatic, YC to Transprints (a joint company of English Calico, Storey Bros., and YC), and ICI to Inprint; Lowe & Carr and Bemrose were independent. There was a heavy veil of secrecy drawn down on anything to do with dye selection for transfer printing, although excellent lectures on transfer printing were given by Burtonshaw and Consterdine.[82–84]

In September 1971, LBH entered the field of transfer printing by introducing their Sublaprint range of twenty-four colors especially prepared for this process,[85] and they gave specific dye recommendations for polyester, nylon, polyester/cotton 67/33 blend, acrylics, Qiana, di- and triacetate, and various elastomeric materials.[84,86] These Sublaprint dyes were the results of an intensive research programme assessing the effect of molecular weight and polarity on the sublimation properties of the dyes. One particular series that could easily be prepared and investigated was obtained using coupling components containing an R_1—N—R_2 group, where R_1 and R_2 could represent H, Me, Et, CH_2CH_2OH, CH_2CH_2CN, or CH_2CH_2Cl. The azobenzene residue could also be further substituted. This work established that it was possible to get quick- or slow-subliming dyes and to classify them into groups designated A, B, C, and D, where A represented a very fast transferring dye, B normal, C slow, and D slower. The A dyes were recommended for good penetration or for heat-sensitive fabrics or thicker than normal materials such as carpets.[84] In addition LBH was the first company to manufacture new dyes specifically for transfer printing and in particular to develop a new high lightfast blue transfer color for polyester.[37,84]

In general, the most suitable dyes for transfer printing have a molecular weight between 240 and 340. For example, Disperse Yellow 3 (269), Disperse Red 4 (269), and Disperse Blue 14 (266) are three dyes

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[82] D. Burtonshaw, *Dyer* **145**, 335 (1971).

[83] K. Consterdine, *Coventry Text. Soc. 1971.*

[84] E. Dempsey and C. E. Vellins, ed., "Heat Transfer Printing" (1975).

[85] *Dyer* **147**, 258 (1972).

[86] C. E. Vellins, *Br. Knitting Ind.* April, **45**, 65 (1972); Jan. **46**, 45 (1973).

that have very different chemical constitution but possess virtually identical molecular weights and can successfully be used together in mixture shades.

Holland and Litherland[78] evaluated the transfer properties of 139 dyes at 200° on polyester, triacetate, nylon 6, diacetate, and Courtelle (acrylic). These comprised 2 acid, 91 disperse, 2 mordant, 9 solvent, 1 vat, and 34 basic dyes; of these 39 were considered worthy of further evaluation. The presence of a highly polar group such as a sulfonic acid group excluded the possibility of sublimation. The amount of dye transferred to the fabric was estimated by extraction and was expressed as optical density per unit area; graphs were drawn using the results obtained from CI Disperse Red 83 and Disperse Blue 24 for concentrations at 1–6%. Of the different fibers investigated, Terylene (ICI) was shown to have the highest substantivity and S-finished Tricel (Courtaulds) had the lowest. An examination of cross-sections of the printed fibers showed that the penetration of the dye into polyester and nylon was progressive into the whole body of the filament; for Dicel and Tricel, only the surface skin was colored, and for Courtelle, scarcely any dye was taken up. An after-steam treatment of the Dicel prints allowed migration of the dye into the interior, and a completely colored cross-section was obtained.

Fenoglio and Gorondy[80] critically examined the transfer print process from both the theoretical and practical point of view. They evaluated a large number of dyes and came to the conclusion that the three workhorse colors for transfer printing were Disperse Yellow 54, Disperse Red 60, and Disperse Blue 56.

Aihara *et al.* give an excellent review of CI dyes suitable for heat transfer printing[87]; these are (a) *Yellow:* Disperse Yellows 1, 3, 8, 9, 13, 16, 23, 33, 36 (=23), 39, 41 (=59), 42, 49, 51, 54, 59, 60, 61, 64, 116, Solvent Yellows 18, 30. (b) *Orange:* Disperse Orange 1, 3, 7, 15, 25; Solvent Orange 7. (c) *Red:* Disperse Red 1, 4, 9, 11, 13, 15, 17, 22, 41, 55, 59, 60, 65, 73, 83; Solvent Red 23, 24, 25. (d) *Violet:* Disperse Violet 1, 4, 6, 8, 12, 18 (=28), 23, 26, 27, 28, 33; Solvent Violet 13. (e) *Blue:* Disperse Blue 3, 5, 14, 19, 24, 26, 35, 56, 58, 60, 62, 63, 64, 71 (=56), 72. (f) *Brown:* Disperse Brown 2.

Nishida *et al.* have examined the relationship of the DTA of Disperse Yellow 7, 33, 42; Disperse Blue 1, 3; and Disperse Red 1, 17 and 60 with the dyeing behavior on a piece of multifiber cloth consisting of nylon, acrylic, secondary cellulose acetate, polyester, and polyvinyl alcohol

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[87] J. Aihara, K. Nishida, and U. Miyataka, *Am. Dyest. Rep.* **63** (7), 20 (1974); J. Aihara **64** (2), 46 (1975).

fibers.[79] The dye transferability was visually assessed, and in general, the results obtained fitted the expected facts, supporting the idea that DTA could be a useful tool for the future investigation of dye selectivity for heat-transfer printing.

In a review on dyestuffs suitable for transfer printing inks, Wich[88] lists the dyestuffs being used in the United States: Disperse Yellow 3, 23, 42, 49, 50, 54, 60; Disperse Orange 20, 25; Disperse Red 4, 11, 13, 50, 55, 59, 60, 65, 73; Disperse Violet 1, 4, 23; Disperse Blue 3, 14, 19, 24, 26, 58, 64, 72.

Griffiths[89] has evaluated the transfer printing of nylon and polyester with a number of dyestuffs containing the azide group. The sulfonyl azides were more difficult to sublime than the aryl azides, but possessed good washfastness properties, although it was difficult to prepare blue and red dyestuffs with this grouping. However, a full color range was prepared containing the aryl azide group, which had good volatility and was converted during the heat process to the less volatile amino group.

Although a number of articles by Vellins[84,86,90,91] were written from a combined theoretical, practical, and commercial point of view, recommendations were made for 23 different materials, both textile and nontextile, that could be transfer printed (see Table I). In particular, recommendations were given for dyestuffs suitable for (1) nylon furnishings and carpets with a minimum light fastness of 5, nylon swimwear with good fastness to seawater and light; (2) polyester materials with very high color value, good washfastness, and a minimum lightfastness of 5; (3) acrylic materials for furnishings with a minimum lightfastness of 5–6; (4) acrylic materials for dress goods with good color value, fast to washing; (5) Tricel materials with good color value with good washfastness and a minimum lightfastness of 5; (6) Dicel materials with a minimum lightfastness of 5; (7) blends of materials such as polyester–wool, polyester–cotton, and blends containing elastomeric fibers; (8) Koratron-treated polyester–cotton; (9) faster than normal transferring dyes that give good level penetration, and consequently can be used for self shades or for heat-sensitive materials or for thicker than normal materials such as carpets; (10) a range of high lightfast dyes for Aluminum; (11) dyes of high lightfastness for PVC floor covering; and (12) dyes suitable for full chrome polyurethane leather. Specific problems have been considered in dye selection for the

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[88] E. A. Wich, *Am. Inkmaker* (1974).

[89] J. Griffiths, *Dyer* **151**, 346 (1974).

[90] C. E. Vellins, *Am. Dyest. Rep.* **63** (2), 18; (7), 38; (10), 54 (1974); **64** (2), 41; (7), 29 (1975).

[91] C. E. Vellins and H. Broadbent, *Am. Dyest. Rep.* **65** (2), 68 (1976).

TABLE I

TEMPERATURE AND TIME REQUIRED FOR TRANSFER PRINTING OF VARIOUS MATERIALS[a]

Material	*Temperature (degrees)*	*Time (seconds)*
Dicel (Courtaulds)	185	15
Tricel (Courtaulds)	195	25
Tricelon (Courtaulds)	195	20
Courtelle standard (Courtaulds)	185	20 (yellows)
Courtelle HR	195	20
Acrilan (Monsanto)	205	20
Orlon 42 (DUP)	205	20
Nomex (DUP)	250	30 (weak)
Polyester (ICI)	210	20
Polyester/cotton 70/30 and 80/20	210	20
Lirelle (Courtaulds—Polyester)	210	20
Spectran (Monsanto—polyester)	210	20
Polyester/Lycra (DUP)	195–200	5
Celon (Courtaulds—nylon 6)	200	20
Ultron (Monsanto—nylon)	200	20
Qiana (DUP)	200	20
Nylon 6.6/Lycra (DUP)	190	5–10
Dacron/wool (DUP)	200	25
Polyester/Cotton Koratron sensitized	200	20
Self-extinguishing fiber (S.E.F.) (Monsanto)	175	25
Basic dyeable Dacron Type 65 (DUP)	205	20
Teklan (Courtaulds)	140	40
Aluminum (anodized)	220	20–60

[a] From Vellins.[84,86,90,91]

transfer printing of acrylics,[90] as well as their suitability for use in screen printing[90,92] and lithographic printing.[91]

A comprehensive list of dyes being considered in the United States is available.[93] The following is a list of trade names of dyes used for transfer printing: Amasolve (Am. Color and Chem. Corp.), Atlantic Transfer (ATL), Lurafix & Palacet (BASF), Teraprint (CGY), Intratherm (Crompton and Knowles), Latyl (DUP), Eastman & Eastone (ECP), Celutate (HSH), Sublaprint (LBH), Dispersol TP (ICI), Orcocilacron & Orcocil (ORC), Transforon (S), Resiren (VC).

From a practical point of view, all the aspects of a transfer-printing dye should be considered, because a poor dye for one material may be

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[92] R. M. Jacobs, *Am. Dyest. Rep.* **63** (7), 25 (1974).

[93] *Am. Dyest. Rep.* **64** (2), 34; (7), 52 (1975); **65** (2), 48 (1976).

excellent for a different material or end use. The compatability of mixture shades in black, green, and brown is important, as different operators use different conditions of time, temperature, pressure, and machinery to effect the actual transfer from paper to the textile material, and an unbalanced mixture will give poor results. In addition, the normal textile fastness properties of satisfactory wash-, perspiration-, light-, rub-, and gas-fume-fading-fastness, as well as fastness to dry cleaning, should be observed. The selected dye(s) should have a good transfer color yield of above 80% and should be able to give a good depth of shade and fastness on the different types of materials on which it is to be used. The use of polynitrated dyes should be avoided to avoid fire and explosion hazards. One major difficulty that presents itself immediately to the dye manufacturer is the lack of control in choosing a depth of shade for evaluation of fastness properties. Different strengths of the same dye can give different fastness results, and the potential catalytic effect of one dye on another is unpredictable.

Another difficulty concerns the textile material in views of the large number of trade names: polyamide 6 (244 names), polyamide 6.6. (175), polyester (244), polyacrylonitrile (172), modacrylics (30), triacetate (29). These have been collected on a world basis. In the United Kingdom, the trade names given in H.M. Customs and Excise Tariff for 1970 are: polyamides (47 names), polyester (25), polyacrylonitrile (30), modacrylics (5).

The combinations possible with a blend of two components can run into thousands. In fact, in many cases it is extremely difficult even for a competent technical expert to determine the fiber used in a textile product by touch and sight alone. Another problem encountered with transfer printing depends upon the actual construction of the material, whether it is a double or single jersey; a piqué, crepe, or twill; an open or closely woven construction; a needlefelt; tufted; or a stitchbonded material. In addition, the history and preparation of the material are important. It is possible to get an 8% shrinkage on transfer printing texturized polyester.

Occasionally, the material contains a relatively high proportion of an optical brightening agent that may decompose at the transfer temperature. This happens particularly with nylon, and a drop in lightfastness can result. The presence of lubricating oils or other additives can also produce undesirable effects.

In practice, the actual mechanics of the heat transfer of the design to the textile substrate can vary from factory to factory. If the machine is run at too high a temperature, a glazed look is obtained and the handle can be spoiled. Different operators can, and do, run the process at different temperatures and speeds, and it is not unusual to find differences of up to 20° and 15 seconds in the industry. Quite often, an operator finds the best setting for his machine and sticks to it irrespective of the paper or textile material.

A comprehensive review of many of the aspects involved in transfer printing in Germany is given by Bobek.[94]

VI. Transfer-Printed Carpets

The first transfer-printed carpets were introduced by the Armstrong Cork Co. Ltd. at the 1972 Northern Floor Coverings Exhibition at Harrogate, using a Spooner vacuum transfer printing machine capable of printing carpet tiles a half meter square.

The Spooner machine was based on RGS and ICI patents. It was found that vacuum assisted transfer enabled a deeper penetration into the tufted carpet tile. The process involves placing the carpet tile on the mesh of a vacuum chamber and then covering it with the transfer-printing sheet so that the pattern side is in contact with the pile. The heated platten is then positioned and the chamber is raised to create an air tight seal and then evacuated to a predesignated reading. The dye then transfers from the paper to the carpet, and depending on the dyes used, it is possible to obtain a good penetration into the carpet pile. Normally, the platten is heated at 220°, and the time of printing can be up to 60 seconds, depending on the carpet construction being printed; it is also important to have an even contact pressure to prevent a variation in the amount of color transferred across the face of the carpet tile. For a deep penetration, it is also important to have a good reservoir of dye on the paper, which can be obtained by printing with highly concentrated screen or gravure inks. It is better to use a heavier weight of paper than that used for high fashion garments to prevent any curling during the process, and a minimum weight of 80 gm/m^2 is recommended.

At first, and even now, the carpet industry has not taken kindly to this new process; but since the carpet industry devotes a considerable amount of money and time in the drying of a normally dyed or printed carpet. this completely dry process is being further evaluated by a number of companies. The main immediate objections to the transfer printing of carpets are (a) the available paper width is limited; (b) the penetration of the dye into the fabric is limited; (c) there is an inadequate dye selection to give accepted light- and washfastness properties; (d) pile deformation can occur in the thermoplastic state.

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[94] E. Bobek, *Melliand Textilber.* **10**, 834; **11**, 909; **12**, 998 (1975).

It was found that the carpet construction is also an important feature to be considered; e.g., needlefelt gives a better result than a tufted carpet, which gives a better result than a shag carpet. Ward,[95] Dawson,[96] and Savage[84,97] have reviewed the transfer printing of carpets, and Vellins[86,90] has suggested a suitable dye selection with adequate penetration for certain types of carpets. As yet, no one has succeeded in the continuous transfer printing of a "modestly tufted full width carpet."

VII. Selection of the Paper or Other Materials for Transfer Printing

The selection of a suitable carrier to be printed with the appropriate dyestuffs necessary for the heat transfer process depends upon several factors: (1) cost, (2) availability, (3) flexibility, and (4) technical performance. Any material that has little or no substantivity for disperse dyes can be used as a support in the transfer process. The materials that have been considered are paper, aluminum, and stainless steel.

Paper is relatively cheap and readily available in suitable widths in most countries. The technical performance can be achieved by appropriate selection or by a pre- or aftertreatment of the print.[51] But for the future, and particularly for a continuous in-line process, the use of a recoverable or reusable substrate is being considered. In general the correct selection, storing, handling and movement of paper before and after printing are of paramount importance to the success of the process. There are many factors to consider—the nature of the printing surface, the density, porosity, permeability, moisture content (before and after printing and moisture regain on storing), the pH, edge-to-edge variation, pinholing, thermal conductivity, cockling, distortion, stretching, strength, as well as the loading of the paper with inorganic pigments such as china clay, titanium dioxide or coating with a polyvinyl alcohol or a cellulose binder such as ethyl or hydroxypropylcellulose.[51] The actual choice of paper also depends on the method of printing and the nature of the ink being used in the process, e.g., gravure, flexographic, screen printing, lithographic, and letterpress. The critical factor governing the choice is whether the ink is aqueous or nonaqueous. An aqueous ink requires a paper with a higher porosity than a purely solvent ink and a 55 gm/m^2 machine-glazed bleached kraft is widely used with flexographic inks. However, a solvent ink

[95] D. Ward, *Can. Text. J.* **91**, 58 (1974).

[96] T. L. Dawson, *Text. Manuf.* **102**, 42 (1975).

[97] J. Savage, *Dyer* **152**, 457 (1974).

rapidly goes through to the back of many papers. and it is advisable to use a coated paper so that the ink stays and dries rapidly on the surface.

The physical properties of paper associated with transfer printing that can be specified are surface absorbency as measured by the Cobb test in gm water/minute/m^2, the porosity measured by the Bendtsen air porosity meter in ml/minute, and the pH. In addition. it is important to have a paper that gives a good dye release, good strength on heating (particularly if the paper is to be used a second time, which is not recommended, but is practiced commercially), and a low permeability to the dye vapor to ensure that little or no vapor sublimes backward through the paper during the heat transfer from paper to textile. Inman gives a comparative description of a number of different types of paper found to be suitable for transfer printing.[98] Henry Cooke Ltd. describe the development of a machine-glazed bleached paper suitable for transfer printing.[99] Other companies recommending paper are Bowaters, Reeds, Van Gelder, and Fletchers; an American list of paper suppliers is given in ref. 100.

VIII. Transfer-Printing Inks

The actual formulation of transfer-printing inks being used commercially are trade secrets, although several recipes have been disclosed in patents.[18,46,47] All types of inks can be used for the preparation of heat-transfer papers. These are gravure. flexographic, lithographic, letterpress, and screen-printing inks. In all cases the requirements are

1. dye(s) chosen to give the required shade and fastness properties, prepared in the appropriate physical form.
2. medium—the ink medium or vehicle, such as water, methylated spirits, toluene, white spirit, isopropanol, or linseed oil.
3. resin binder or thickener to give the right viscosity, e.g., ethylcellulose, polyvinyl acetate, acrylic resin, alkyd resin.

In practice other additives may be included (a) to give hot adhesive properties (tack) to prevent paper flutter during a sheet-fed operation; (b) to prevent froth formation in the ink duct; (c) to improve the rub resistance to prevent set-off in the paper reel; (d) to facilitate flow properties; (e) to inhibit corrosion with aqueous inks. The transfer-printing inks are prepared on normal ink-making machinery, as a ball

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[98] W. J. Inman, for a summary, see *Dyer* **152**, 445 (1974).
[99] *Dyer* **152**, 455 (1974).
[100] *Am. Dyest. Rep.* **65** (2), 22 (1976).

mill, an attritor, or a triple-roll mill, and are usually kept in the form of a concentrated ink that can be diluted with ink medium depending on the depth of shade required.

IX. Methods Used for Printing the Paper

Transfer-printing papers are being produced by all the methods of printing used in the paper industry, as well as those used in the textile industry. The choice of the machine to be used depends on economics, availability, width and quantity of paper required, need for half tone, register of design, number of colors in the design, line work, special effects, the back up and availability of ancillary equipment, etc. The printing methods used are (1) gravure,[101–107] (2) flexographic,[99–109] (3) lithographic and letterpress,[106,107] (4) screen (both rotary and flatbed screen printing).[1,90,92,105–107,109–112]

A. Gravure Printing

At present, the major proportion of transfer papers are printed by the gravure technique. In this process, the design is engraved into a smooth deposit of copper on the surface of a steel cylinder and then chromed to give hardness. A separate cylinder is engraved for each color in the design. Each cylinder is fed with the appropriate color of ink, and the excess ink is removed from the surface of the printing cylinder with a steel doctor blade. The ink from the engraved areas is applied directly to the paper, and the impression is dried between each color application. Speeds of about 300 feet/minute are normally achieved, using quick drying solvent inks. The advantages of gravure printing are that it gives photographic reproduction and that fine line work and half tones are possible, but the actual engraving and storing of the cylinders is expensive.

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[101] Y. Mahé, *Am. Dyest. Rep.* **63** (7), 30 (1974).

[102] B. Hunt, *Br. Printer* Sept. p. 61 (1972).

[103] M. Ehrwein, *Text. Mon. July*, p. 48 (1972).

[104] R. Wood, *Pap., Film Foil Converter*, Feb. p. 62 (1976).

[105] *Text. Mon.* Nov. p. 84 (1974).

[106] J. Aihara, *Jpn. Text. News* **243**, 60 (1975).

[107] I. J. Gorondi and O. S. Larson, *Am. Dyest. Rep.* **64** (2), 53 (1975).

[108] M. Ball, *Am. Dyest. Rep.* **64** (7), 32 (1975).

[109] G. A. Winterburn, *Am. Dyest. Rep.* **63** (2), 31 (1974).

[110] G. Cailliez, *Br. Knitting Ind.* June, **47**, 49 (1974).

[111] F. Buser, *Dyer* July, **152**, 79 (1974).

[112] J. Zimmer, *Dyer* Feb, **151**, 128 (1974); *Text Manuf.* June, **101**, 33 (1974).

B. FLEXOGRAPHIC PRINTING

Flexographic printing uses a roller fitted with a molded rubber stereo carrying the design as a raised image. The ink is taken up from a trough by a rubber inking roller and transferred to the Anilox roller, which meters the correct amount of ink to the rubber stereo, which then prints the design on the paper. The advantages of flexographic printing are lower costs for origination and for the preparation and storage of the stereos and rollers, but there are some design limitations.

C. LITHOGRAPHIC PRINTING

Lithographic printing is a noncontinuous method of printing and consequently is used for individual sheets or panels. The process depends on an oil–water partition, the image is oil accepting, so that the ink adheres to the image and is then transferred to the paper via an intermediate roller or blanket. The advantages of lithographic printing are low investment costs in equipment and plates, and it is ideally suited for engineered designs with high-quality reproduction, but the method can only produce sheets of paper.

D. LETTERPRESS PRINTING

This is also a noncontinuous printing method using a raised image on a metal or plastic plate to produce sheets of printed paper.

E. ROTARY SCREEN PRINTING

The conventional continuous rotary screen printing machine has been modified to print paper by use of tension control units on and off the machine. Print speeds of up to 80 meters/minute can be achieved, and the use of an 80 mesh screen is recommended. The printing of paper wet on wet without intermediate drying has been successfully accomplished by Stork, who introduced their RD III and more recently the RD IV to give repeats in design of up to 2 yards. The cylinder engraving costs are lower than for flexographic and gravure rollers, but the production of fine line work is limited.

F. FLAT-BED SCREEN PRINTING

This is the usual type of squeegee machine and is being used with either solvent inks or emulsion inks to give transfer papers mainly for rugs and carpet tiles.

X. Heat-Transfer Print Machines

There are fundamentally three types of machine suitable for heat-transfer printing. These can be for a batchwise or a continuous process using papers containing disperse dyes or by a migration process using water-soluble dyes. In general, the batchwise machines print individual garments, and if they are operated under vacuum, they can be used for printing carpet tiles or rugs. The continuous machine is normally operated for widths of material from 20 to 120 inches. The pioneers in this field were Lemaire, France[110,113]; Kannegiesser, Germany[84,114–116]; Hunt & Moscrop, England[84,117–119]; and Gessner, United States.[120]

Since their inception, there are as many as thirty manufacturers of such machinery.[121] In addition, Stork has introduced a continuous machine that can be operated under vacuum.[122] The machine suitable for wet processes is the Dewprint Machine, which has been developed by the Dinting Engineering Co. based on the Fastran process of Dawson Holdings.[21,123] Another model of the wet-transfer printing system based on the development of the Star Stampa Printing process is being marketed in Japan under the name Max Spelio.[87] There are a number of patents describing the production of transfer print machines.[9,39,56–65]

A. Flat-Bed Presses for Batchwise Operation

These machines are used to print fashion garments from sheet transfers and may be fitted with a conveyor.[118] Either the top or both plates of the press can be heated by electricity, steam, or oil, which would allow for the possibility of printing both sides of the garment simultaneously.[124–127] At present there are two companies manufacturing commercial flat-bed vacuum machines—Spooner[96,128,129] and Naomoto Kogyo.[87] The advantages of printing under vacuum are (a) no flattening of the fabric, thus allowing pile fabrics to be printed; (b) minimum changes in fabric feel or luster; and (c) better penetration into the fiber.

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[113] Lemaire, *Textilbetrieb* (*Wuerzburg, Ger.*) Sept, p. 21 (1972).

[114] Kannegeisser, *Br. Knitting Ind.* June, **47, 41** (1974).

[115] *Dyer* **154**, 522 (1975).

[116] *Dyer* **152**, 148 (1974).

[117] Hunt & Moscrop, *Text. Mon.* Jan, p. 55 (1971).

[118] *Dyer* **154**, 13 (1975).

[119] W. J. Mount, *Text. Inst. Ind.* **13, 73** (1975).

[120] *Text. Mon.* July p. 57 (1972).

[121] *Am. Dyest. Rep.* **63** (2), 15 (1974); **64** (2), 23; (7), 42 (1975).

[122] *Am. Dyest. Rep.* **65** (2), 30 (1976).

[123] *BP* Appl. 53,605/74.

[124] Haigh, *Hosiery Trade J.* p. 95 (1970).

[125] *Br. Knitting Ind.* July, **45**, 87 (1973).

[126] *Dyer* **145**, 223 (1971); **147**, 640 (1972).

[127] *Jpn. Text. News* **225**, 28 (1973).

[128] *Burns Text. Mon.* Feb., p. 69 (1973).

[129] *Text. Mon.* July, p. 28 (1971).

B. CONTINUOUS TRANSFER-PRINTING MACHINES

The most popular type of continuous machine is where the paper and the fabric pass face to face round a heated cylinder, the diameter of which determines the speed of production, while contact is maintained by use of a Nomex endless blanket. In certain cases, a backing paper or edge strips are used to minimize contamination of the blanket. The uniform temperature of the cylinder is important, and it can be heated by means of hot oil or electricity. A uniform pressure between the paper and the textile is important so that there is no slip, and the sublimed dyes are rapidly deposited to give a sharp print. Typical machines are made by Hunt & Moscrop, Lemaire, Kleinwefers,[130,131] Gessner, and Bates and Pla-Ma. Another kind of continuous machine is the Kannegeisser, which utilizes a perforated steel drum, which is evacuated so that the paper and textile passing over the surface are held in intimate contact by the vacuum action. The heat is supplied by infrared heaters, and the flow of air through the paper–textile sandwich helps to transfer the sublimed dye. One of the limitations of the continuous machines is the tendency to flatten a pile fabric during the printing operation.

Recently, Stork introduced a new continuous transfer-printing vacuum calender, the TC 451. The unit has a print width of 78 inches and can operate at a temperature of 180°, which is about 30° lower than most other calenders. The lower temperature gives an improved handle on the fabric, and a better dye penetration is also achieved. Alternatively, a higher speed of printing can be achieved using a higher temperature, e.g., 40 meters/minute at 210°.

The DewPrint machine has been developed to operate by means of a wet process and consists essentially of an impregnation mangle, a transfer calender operating in the range of 100°–120° by use of low pressure steam, followed by an afterprint washing unit and a dryer. The operation speed varies from 5 yards/minute to 15 yards/minute, depending on the drum diameter of the calender, and allows for the wet processing of nylon, acrylics, and natural fibers.

XI. Japanese Patent Situation

A review of the transfer printing situation in Japan is given by Aihara.[87] Dainippon[132] considers the transfer printing of glass fiber

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[130] *Dyer* **154**, 30 (1975) and **153**, 205 (1975).

[131] *Text. Mon.* Jan, p. 55 (1971).

[132] Dainippon, *JP* 23,679/72; *CA* 78, 44983; *P* 51,365/74; *CA* 81, 122093.

fabrics with cellulose acetate inks at 170°, and also of paper coated with inks containing a photo-resist material, which is used to copy originals by an infrared treatment.[133] The transfer printing of polyester with disperse dyes, followed by steaming at 140°, is described by the same company, which also claims to be able to sprinkle flock material on an adhesive-coated release paper that can then be impregnated with ink and used for transfer printing.[134,135] Toyo[136] claims the printing of polymers pretreated with metal components such as aluminum stearate and also describes the transfer printing of polyester on a machine with an endless belt[137]; an improvement in the rub- and lightfastness of acrylic transfer prints is obtained by steaming.[138]

Chlorinated rubber is included in a transfer-printing ink used for the printing of plastic moldings with nonflat surfaces.[139] Toyo also claims the transfer printing of textiles using papers coated with a water-soluble protective coating of polyamide,[140] the transfer printing of polyester–cotton in which the cotton is preacetylated,[141] and an increased fastness when the fabric is treated with benzyl chloride prior to transfer printing.[142]

Sumitomo transfer prints acrylics with basic dyes and hydrophobic fabrics with anthraquinone dyes[143]; transfer printing is facilitated by using an infrared source when the opposite side of the printed paper is coated with an infrared absorber.[144] Sumitomo further claims the continuous printing of textiles with inks containing an oil vehicle and an organic solvent[145] and the transfer printing of polyester–cellulose with anthraquinone dyes containing reactive groups such as vinylsulfone.[146]

Mitsubishi Rayon sandwiches transfer-printing paper inside an aluminum sheet and passes an electric discharge to give multicolored

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[133] Dainippon, *JP* 85,152/73; *CA* **80**, 102346.

[134] Dainippon, *JP* 57, 190–1/74; *CA* **81**, 154467–8.

[135] Dainippon, *JP* 52,361/75; *CA* **83**, 133263.

[136] Toyo Ink Mfg. Co., *JP* 42,964/72; *CA* **78**, 137441.

[137] Toyo Ink Mfg. Co., *JP* 33,184/75; *CA* **79**, 80242.

[138] Toyo Ink Mfg. Co., *JP* 82,175/73; *CA* **80**, 97250.

[139] Toyo Ink Mfg. Co., *JP* 41,689/74; *CA* **81**, 121913.

[140] Toyo Ink Mfg. Co., *JP* 83,508/74; *CA* **82**, 74359.

[141] Toyo Ink Mfg. Co., *JP* 35,476/75; *CA* **83**, 81122.

[142] Toyo Ink Mfg. Co., *JP* 116,778/75; *CA* **84**, 45947.

[143] Sumitomo Chemical Co., *JP* 42,278/73; *CA* **81**, 122644; *JP* 06,884/75; *CA* **83**, 44624 ; *JP* 111,382–3/75; *CA* **84**, 32494; *JP* 110,985/74; *CA* **83**, 12059.

[144] Sumitomo Chemical Co., *JP* 00,187/75; *CA* **82**, 172518.

[145] Sumitomo Chemical Co., *JP* 14,879/75; *CA* **83**, 61490.

[146] Sumitomo Chemical Co., *JP* 14,887/75; *CA* **83**, 44628.

sheets, which are then used to transfer-print polyester.[147] They also carry out discharge printing by dry heat treatment,[148] saponify acetate textile material prior to transfer printing,[149] and transfer print using basic dyes applied from inks containing inorganic salts.[150]

A salt-and-pepper effect can be obtained on synthetics and semisynthetics,[151] and the replacement of transfer paper by a cotton cloth is considered for the transfer printing of polyester with disperse dyes.[152]

Mitsubishi also claims that a sandwich of heat resistant material with a cut-out pattern in the shape of a design can be placed between the paper and material.[153] The inclusion of an ultraviolet absorber in the transfer printing ink is claimed to give prints of better lightfastness.[154]

Transfer printing paper is coated with a zinc oxide ink and then an electric discharge is passed through it to give a multicolored pattern.[155] Better color yields are obtained by either printing with an ink containing an epoxyhalide copolymer and a fatty acid polyalkylene–polyamine condensate[156] or by impregnating the textile materials with a polyamine type of polymer.[157] The fastness properties of the transfer prints can be improved by the addition of stearic acid to the printing ink.[158]

Kanebo[159] irradiates a mixture containing an electrostatic material and sublimation dyes and prints on nylon, acrylics, and other textile materials.[160] Osaka Printing Ink claims the transfer printing of damp wool or cotton with papers printed with water-decomposable complexes of dyes.[161] Muneharu Ushida claims the transfer printing of padded wool at 120°–140° for 10–30 seconds.[162]

Toppan uses basic dyes to transfer print acrylics,[163] describes a

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[147] Mitsubishi Rayon Co., *JP* 29,891/75; *CA* **83**, 81119.

[146] Mitsubishi Rayon Co., *JP* 68,889/73; *CA* **80**, 4832.

[149] Mitsubishi Rayon Co., *JP* 68,884/73; *CA* **80**, 4830.

[150] Mitsubishi Rayon Co., *JP* 12,292/74; *CA* **83**, 61477.

[151] Mitsubishi Rayon Co., *JP* 47,430/74; *CA* **83**, 61497.

[152] Mitsubishi Rayon Co., *JP* 118,982/74; *CA* **82**, 113117.

[153] Mitsubishi Rayon Co., *JP* 29,895/75; *CA* **83**, 81120.

[154] Mitsubishi Rayon Co., *JP* 76,392/75; *CA* **83**, 165700.

[155] Mitsubishi Rayon Co., *JP* 100,390/75; *CA* **84**, 32492.

[156] Mitsubishi Rayon Co., *JP* 101,117/75; *CA* **83**, 207498.

[157] Mitsubishi Rayon Co., *JP* 101,678/75; *CA* **83**, 195106.

[156] Mitsubishi Rayon Co., *JP* 127,716/75; *CA* **84**, 45957.

[159] Kanebo, *JP* 41,085/73; *CA* **79**, 67753; *JP* 41,088/73; *CA* **79**, 67755.

[160] Kanebo, *JP* 56,712/74; *CA* **81**, 154474.

[161] Osaka Printing Ink Chubu Sales Co., *JP* 42,277/73; *CA* **81**, 27124.

[162] Muneharu Ushida, *JP* 44,584/73; *CA* **79**, 116316.

[163] Toppan, *JP* 82,182/73; *CA* **80**, 97249; 40,878/75; *CA* **83**, 99076.

method for printing water-repellant treated textiles,[164] transfer print with reactive dyes followed by steaming and base treatment,[165] and transfers print cotton.[166] Steaming at 120° for 20 minutes is used in the transfer printing of thick fabrics having a 50% pick-up of water, and a further wet-transfer-printing process is also described.[167] A polyvinyl alcohol layer is placed between the paper and the textile material prior to steaming.[168] The transfer printing of textile materials with anthraquinone dyes[169] and cutting transfer paper into arbitrary shapes are described.[170] An improved handle is achieved in the transfer printing of cotton textiles by impregnation with polyethyleneglycol and leaving overnight prior to transfer printing.[171] The cotton can be padded with a water-soluble resin, dried, and then transfer printed with disperse dyes,[172] or it can be impregnated with polypropyleneglycol prior to transfer printing.[173]

Ohmori discuss heat transfer printing sheets,[174] and Matsui the transfer of films containing pigments from a release paper.[175] Kobayashi claim transfer printing inks containing thermoplastic particles,[176] and Masahiro also claim ink compositions suitable for transfer printing.[177] Akaza discuss a film transfer onto cotton and synthetic fibers.[178]

Transfer onto padded wool and leather[179] and transfer printing of wet padded textiles have been claimed.[180] Treatment of polyester with polyisocyanates gives fast prints.[181] Diazo thermoprinting[182] and the use of water-soluble transfer printing inks have been described.[183,184]

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[164] Toppan, *JP* 42,989/74; *CA* **81**, 107289.
[165] Toppan, *JP* 57,188/74; *CA* **81**, 154469.
[166] Toppan, *JP* 57,884/74; *CA* **81**, 154469.
[167] Toppan, *JP* 94,982/74; *CA* **82**, 87573; *JP* 118,984/74; *CA* **82**, 99955.
[168] Toppan, *JP* 85,886/73; *CA* **80**, 97229.
[169] Toppan, *JP* 120,967/74; *CA* **82**, 141539.
[170] Toppan, *JP* 14,888/75; *CA* **83**, 29764.
[171] Toppan, *JP* 35,481/75; *CA* **83**, 81123.
[172] Toppan, *JP* 58,384/75; *CA* **83**, 165689.
[173] Toppan, *JP* 69,382/75; *CA* **83**, 165701.
[174] Ohmori Mfg. Co., *JP* 91,386/73; *CA* **80**, 109761.
[175] Matsui Shikiso Kagaku Kogyosho Co., *JP* 92,677/73; *CA* **80**, 122309.
[176] K. Sakaoka, *JP* 09,303/74; *CA* **81**, 14631.
[177] M. Nishizawa, *JP* 13,489/74; *CA* **81**, 65110.
[178] Akaza Textile Industry Co., *JP* 14,419/74; *CA* **82**, 74349.
[179] Omi Kenshi Spinning Co., *JP* 30,671/74; *CA* **81**, 38842.
[180] Miwa Fumio, *JP* 31,989/74; *CA* **81**, 107283.
[181] Nippon Kagaku Co., *JP* 30,685/74; *CA* **81**, 65114.
[182] Mita Industrial Co., *JP* 45,174/74; *CA* **81**, 144234.
[183] Naigai Ink Mfg. Co., *JP* 51,007/74; *CA* **81**, 137519.
[184] Janome Sewing Machine Co., *JP* 77,711/74; *CA* **82**, 32389.

Hagashi transfer prints damp wool or silk with acid dyes.[185] Osaka Ozakiori claims the film transfer printing of polypropylene.[186] Nippon Gakki claim the transfer printing of resin-impregnated wood.[187]

Cotton can be transfer printed using direct dyes and polyethyleneglycol by treatment at 120°, followed by steaming.[188] Maruichi also claims vapor-phase dyeing.[189] Rotationally molded polyolefins can be transfer printed with pigments.[190,191] Kunitoshi describes the transfer printing of fabrics with milling colors whereby the paper is coated with a water-soluble unsaturated carboxylic acid–vinyl copolymer that sticks to the fiber. The system is steamed for 30 minutes.[192] Sei Ohkawa claims to improve the fastness to sublimation of transfer prints by pretreating with a catalyst or thermally active resin.[193] Transfer-printing inks may contain microencapsulated organic solvents or swelling agents.[194] A number of different auxiliaries can be added to the transfer-printing inks, e.g., urea for nylon dyes and sodium bicarbonate for cotton dyes.[195]

Selected anthraquinone dyes are used for the transfer printing of polyester.[196] A paper carrier is coated in succession with a water-insoluble hydrophilic layer, a water-soluble paste, and the dyestuff paste; the paper is used to print cotton.[197] Resist transfer printing agents[198] and the impregnation of the textile material with an organic solvent before transfer printing with a finishing agent are claimed.[199] Matsui Shikiso transfer print textiles with a film transfer containing resin and pigments, and also introduce a coagulating agent into the ink to give a speckled effect.[200] Polyester transfer printed with disperse dyes is submitted to an after-steaming process.[201] A system of transfer

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[185] Hagashi Kagaku Kogyo Co., *JP* 55,983/74; *CA* **81**, 107299.

[186] Osaka Ozakiori Mark, K. K., *JP* 57,911/74; *CA* **82**, 32640.

[187] Nippon Gakki Co., *JP* 86,509/74; *CA* **82**, 60362.

[188] Y. Toyota, *JP* 87,879/74; *CA* **82**, 74357.

[189] Maruichi Seni K.K., *JP* 100,383/74; *CA* **80**, 141540.

[190] Silver Jushi Kogyo K.K., *JP* 112,967/74; *CA* **82**, 112842.

[191] Sekisui Jushi K.K., *JP* 121,869/74; *CA* **82**, 112843.

[192] K. Mishima and N. Makino, *JP* 117,789/74; *CA* **82**, 141532.

[193] S. Ohkawa, *JP* 118,976/74; *CA* **82**, 113118.

[194] Seiren Co., *JP* 133,682/74; *CA* **82**, 157740.

[195] Fuji Wool Textile Co., *JP* 00,186/75; *CA* **82**, 157702.

[196] Nippon Kagaku Co., *JP* 17,481/75; *CA* **83**, 81110.

[197] Haidoron Kagaku K.K., Sanei Chemical Industries, *JP* 24,588/75; *CA* **83**, 99056; *JP* 64,592/75; *CA* **83**, 165697.

[198] Nihon Sashin Insatsu K.K., *JP* 55,412/75; *CA* **83**, 116807.

[199] Omi Kenshi Spinning Co., *JP* 70,691/75; *CA* **83**, 195192.

[200] Matsui, *JP* 63,290/75; *CA* **83**, 165691; *JP* 108,012/75; *CA* **84**, 45930.

[201] Daido-Manita Finishing Co., *JP* 111,381/75; *CA* **84**, 19088.

printing to give a network pattern consists of floating kerosine on an aqueous ink, contacting the polyester with the interface, drying, and then following with a hot press.[202] Toray adds carbon black to the transfer-printing ink containing disperse dyes, and irradiates with an infrared lamp.[203]

Toyobo claim the transfer printing of cellulose with sublimable reactive dyes, azo dyes, and anthraquinone dyes[204]; cotton is treated with diethyleneglycol prior to transfer printing and then treated with a finishing agent such as dimethyloldihydroxyethylene urea; the paper can contain the dye and the swelling agent and can be used on polyester cotton; or the cellulose can be pretreated with a swelling agent prior to a damp printing with disperse dyes.[205] Toyobo claims the film transfer printing of polyester, and of polyester or nylon from silicone-coated paper,[206] the use of basic dyes (such as Rhodamine B) on acrylics by treatment at 110° for 30 minutes,[207] and the use of water-soluble transfer printing inks containing polymeric binders.[208] Toyobo also claims the transfer printing of cotton or wool fabrics with disperse reactive dyes after pretreatment of the fabric with a swelling agent and leaving damp for printing; a good handle and luster can be obtained by transfer printing at 120° followed by a 30 minutes steaming and a wash with a reducing agent; nylon and acrylics can also be transfer printed with a good handle.[209] Finally, Toyobo describes a method for the continuous transfer printing of polyester textiles whereby ink is put onto a moving belt which is brought into contact with the fabric and pressed with heat.[210]

Nippon Kayaku have developed a method of chemically treating the paper prior to printing.[211]

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[202] Nippon Kayaku Co., *JP* 112,576/75; *CA* **84**, 45938.

[203] Toray Industries, *JP* 132,277/75; *CA* **84**, 45966.

[204] Toyobo, *JP* 91.387/73; *CA* **80**, 109762; *JP* 12,386/75; *CA* **83**, 12072; *JP* 12,388/75; *CA* **83**. 12074; *JP* 18,782/75; *CA* **83**, 44631.

[205] Toyobo, *JP* 30.686/74; *CA* **81**, 65115; *JP* 36,987/74; *CA* **81**, 107285; *JP* 13,685/75; *CA* **83**, 61492.

[206] Toyobo, *JP* 36,986/74; *CA* **81**, 122652; *JP* 54,692/74; *CA* **81**, 171210; *JP* 61,489/74; *CA* **82**, 5313.

[207] Toyobo. *JP* 54,689/74; *CA* **81**, 154459.

[208] Toyobo, *JP* 94,985/74; *CA* **82**, 113103.

[209] Toyobo. *JP* 20,085/75; *CA* **83**, 29769; *JP* 24,589/75; *CA* **83**, 44437; *JP* 25,881/75: *CA* **83**, 8115; *JP* 29,892/75; *CA* **83**, 99059; *JP* 35,482/75; *CA* **83**, 99061; *JP* 83,578/75; *CA* **83**, 207495.

[210] Toyobo. *JP* 35,484/75; *CA* **83**. 99062.

[211] Nippon Kayaku, Co., *JP* 65,677/75; *CA* **83**, 195073.

XII. Advantages and Disadvantages of Transfer Printing

Transfer printing has the following advantages: (a) it is simple; (b) it is a dry heat process and requires no aftertreatment; (c) it is a clean and effluent-free process with no pollution problems; (d) there are no drainage or water considerations; (e) a wide range of synthetic materials can be printed; (f) virtually any intricate design can be reproduced with outstanding definition; (g) semiskilled labor can be rapidly trained to use the machine; (h) there is no time delay in changing a color scheme or change of pattern; (i) the process can be carried out continuously or with individual garments; (j) there are no delay or problems with color matching; (k) space requirements are low compared to conventional printing; (l) capital cost of equipment and installations are low; (m) waste and reject factor is low; (n) it is possible to overprint on predyed cloth or garments to give interesting effects; (o) it is possible to produce a reversible print with either a plain shade or an alternative design; (p) it is possible to carry out a simultaneous lamination process; (q) the coverage of poor-quality and irregular material is excellent; (r) the process is now applicable for the printing of certain types of carpets.

The disadvantages are the following: (1) no completely dry process (as yet) for cotton or wool; (2) the wetfastness properties on nylon require to be improved; (3) there is a distortion of some fabric constructions and loss of fiber properties; (4) the printed material should not be used for pleating, since the fastness to sublimation is inadequate.

Chapter VI

STRUCTURAL FACTORS AFFECTING THE LIGHTFASTNESS OF DYED FIBERS

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I. Introduction

A. Scope of this Chapter

Fastness to light is one of the most important properties a dyed fiber needs in order to fulfil its function over a period of time. The effects of solar radiation falling on a dyed textile are manifested in two principal ways: (a) a change in the shade and/or depth of shade of the coloration, and (b) the physical degradation of the substrate fiber as evidenced by changes in tensile strength, abrasion resistance, etc. However the changes in the dye component usually occur in a much shorter time, and therefore, the problem of dye fading is of greater significance than fiber degradation in textiles exposed to sunlight.

The fastness to light of a dyed fiber depends on many factors (summarized in Section I,C), the most important of which are the inherent photostability of the dye chromophore and the way in which this stability is affected by the chemical nature of the substrate. Within any one class of dye, structural modifications may lead to an increase or decrease in the lightfastness on a particular substrate, while with any one dye, the lightfastness may be dependent on the physicochemical interaction occurring with various substrates and on the physical state the dye adopts within the fiber. This chapter aims to bring together information relevant to the relationship between lightfastness of a dyed fiber and the chemical structure of the dye molecule and also on how the nature of the fiber can affect this relationship.

Most of the lightfastness data have been taken from CI unless otherwise cited and from publications that appeared in the chemical and textile literature up to December 1975. In view of the quantity of data available in this field, this review must necessarily be selective and reflects to some extent the personal interests of the authors.

B. Some Principles of Photochemistry

The chemical changes that molecules undergo following absorption of visible or ultraviolet light is a relatively new field of interest to organic chemists. The past twenty years have seen many advances in the understanding of photochemical mechanisms,[1–5] and the photochemistry of dyes, both in solution and on textile and other substrates, has been actively studied.[6–11]

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[1] N. J. Turro, "Molecular Photochemistry." Benjamin, New York, 1965.

[2] D. C. Neckers, "Mechanistic Organic Photochemistry." Van Nostrand-Reinhold, Princeton, New Jersey, 1967.

[3] J. G. Calvert and J. N. Pitts, "Photochemistry." Wiley, New York, 1966.

[4] P. Suppan, "Principles of Photochemistry." Chem. Soc., London, 1973.

[5] D. R. Arnold, N. D. Baird, J. R. Bolton, J. C. D. Brand, P. W. W. Jacobs, P. de Mayo, and W. R. Ware, "Photochemistry—An Introduction." Academic Press, New York, 1974.

[6] J. F. McKellar, *Radiat. Res. Rev.* **3**, 141 (1971).

[7] C. H. Giles and R. B. McKay, *Text. Res. J.* **33**, 527 (1963).

[8] K. McLaren, *J. Soc. Cosmet. Chem.* **18**, 245 (1967).

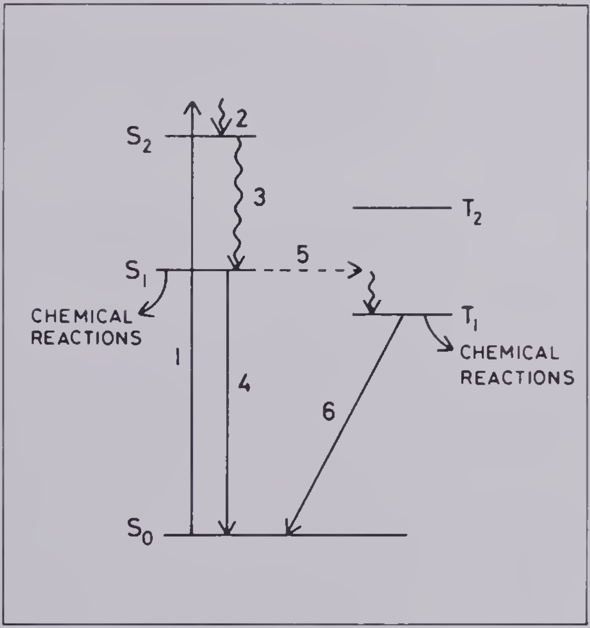

FIG. 1. Typical energy-level diagram for an aromatic compound.

The sequence of events that may occur during a photochemical reaction is now well understood and may be summarized, with reference to Fig. 1, as follows:

1. Absorption of a photon by the molecule resulting in its excitation to some vibrational level in an excited singlet state S_1, S_2, or higher. The time required for this process is approximately 10^{-15} seconds.

2. Loss of excess vibrational energy through a fast (10^{-11}–10^{-13} second) vibrational cascade to reach the lowest vibrational level of the excited state.

3. If the molecule has been excited to the S_2 level, internal conversion to the lowest excited singlet level S_1 occurs rapidly. This S_1 state is one of the important reactive species in photochemical reactions and has a lifetime usually in the range 10^{-5}–10^{-9} second.

4. Emission of radiation (fluorescence) or further internal conversion to return the molecule to its ground state.

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[9] G. S. Egerton and A. G. Morgan, *J. Soc. Dyers Colour.* **86**, 79, 242 (1970); **87**, 223 and 268 (1971).

[10] H. Meier, *CSD IV*, p. 389.

[11] P. Bentley, J. F. McKellar, and G. O. Phillips, *Rev. Prog. Color. Relat. Top.* **5**, 33 (1974).

5. Intersystem crossing (ISC) from the S_1 state to the lowest excited triplet state T_1. This route is the principal pathway by which excited triplet states are generated. The T_1 state is relatively long lived (10^{-4}–10^{2} second), and many photochemical reactions occur while the molecule is in this state.

6. The T_1 state may decay to the ground state by emission of a photon (phosphorescence) or by ISC or collisional deactivation.

The lightfastness of a dye on a fiber will usually be dependent on (a) the relative rates by which the two states S_1 and T_1 are populated; (b) the relative rates by which they react either unimolecularly or with other molecules such as the dye in the ground state, oxygen, water, or the fiber; and (c) the relative rates by which the two states collapse to the ground state via the nondestructive pathways outlined above. Accordingly, the variations in lightfastness of a particular dye on different fiber substrates may be understood in terms of the behavior of the S_1 and T_1 states in the differing environments imposed by the chemical and physical nature of the fiber. Thus, chemical reactions or deactivation steps may be promoted or suppressed.

C. Factors Affecting Fading of Dyed Textiles

The change in hue or depth of color that is observed upon exposure of a dyed fiber depends on many factors,[7,8,10] which may be summarized as follows:

1. The photostability of the dye molecule as determined by the reactivities of the excited states S_1 and T_1 (discussed in Section I,B). In general, the chromophore nucleus is most important in determining the lightfastness of a dye, but nuclear substituents may substantially alter the fastness one way or the other.

2. The dye concentration. The lightfastness of a dyed fiber usually increases with increasing dye concentration. In many cases, this increase in fastness is caused by aggregation of dye molecules within the fiber.

3. The wavelength distribution of the incident radiation.[12–14] Not all absorbed wavelengths in the visible and ultraviolet are equally effective in initiating a fading process. McLaren[12] has shown that fugitive dyes are faded mainly by visible radiation, while dyes of high lightfastness are faded mainly by violet and ultraviolet radiation.

4. The nature of the fiber. Three kinds of effects appear to be important: (a) the reactivity of a dye in an excited state with certain chemical groups within the fiber, as exemplified by the phototendering

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[12] K. McLaren, *J. Soc. Dyers Colour.* **72**, 86 (1956).

[13] R. E. Bedford, *J. Soc. Dyers Colour.* **75**, 37 (1959).

[14] S. B. Maerov and H. Kobsa, *Text. Res. J.* **31**, 697 (1961).

of cotton by some vat dyes[6]; (b) the stabilization of a dye by the quenching of the excited state through the agency of some group within the fiber; and (c) the permeability of the fiber to various components of the atmosphere that are capable of reaction with the dye in its excited state.

5. Composition of the atmosphere. The moisture content of the atmosphere is known to have a pronounced effect on the fading rates of certain dyes; for example, dyed wool fades faster in atmospheres of high humidity.[15] Atmospheric contaminants, such as sulfur dioxide, oxides of nitrogen (gas-fume fading), and ozone, are known to react with dyes in the absence of light. However, it seems possible that such reactions are accelerated when the dye is in an electronically excited state.

The environmental factors 3 and 5, which were important considerations when lightfastness test methods were being devised, need to be controlled if reproducible test data are to be obtained.

D. Lightfastness Test Methods

The development of test methods for the assessment of lightfastness of dyed fabrics has a long history, which has been covered by several reviews.[7,16–19] The most commonly used method, ISO (International Organization for Standardization), requires the test sample to be exposed to sunlight or a xenon lamp alongside a set of selected blue dyes on wool, rated 1 to 8. The faded test sample is visually matched with the standard that is judged to have faded at the same rate. The standard blue dyes were selected on the basis that each dye fades at approximately twice the rate of the dye that is one number higher in the set. Hence, a dyed fabric with a lightfastness of 2 fades at twice the rate of a sample of fastness 3.

The AATCC method uses a set of graded standards that are prepared by dyeing wool with varying proportions of a fugitive dye and a fast dye.

Care must be taken when comparing lightfastness values obtained from different sources of illumination such as high intensity lamps used in accelerated fading[18] and sunlight exposures.[20] Some of these methods

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[15] J. J. Hedges, *J. Soc. Dyers Colour.* **43**, 261 (1927).

[16] S. Burgess, *J. Soc. Dyers Colour.* **65**, 732 (1949).

[17] K. McLaren, *Can. Text. J.* **76**, 71 (1959).

[18] W. R. Hindson and G. Southwell, *J. Soc. Dyers Colour.* **89**, 254 (1973).

[19] J. Park, *Rev. Prog. Color. Relat. Top.* **6**, 71 (1975).

[20] K. G. Roessler, W. Ackerman, C. H. Bayley, P. W. Benn, G. R. Boule, C. F. Fitton, D. Heggie, J. H. Lowe, A. G. Plumb, A. J. Straw, and C. R. Teichgraber, *Text. Chem. Color.* **1**, 252 (1969).

can yield anomalous results, and therefore, a comparison of lightfastness properties within a group of dyeings should be based on a uniform set of test conditions. The lightfastness data quoted in this chapter are all based on the ISO method unless otherwise stated.

II. Azo Dyes

Azo dyes form the largest group (approximately one-half of the structures disclosed in CI) of all the synthetic colorants. Their color range spans the entire visible spectrum, and they can be structurally modified to make them substantive to all types of fiber.

A. ACID DYES

Water-soluble azo dyes of the type A—N=N—B, where A is derived from a substituted aniline and B is either a pyrazolone, naphthol, naphthylamine, or aminonaphthol (the solubilizing sulfonate group may be attached to A or B or both), can vary in color from yellow to violet (depending on the choice of A and B[21]) and constitute a very important class of dyes for wool. Although the lightfastness ratings in CI vary over a span of five units, it is not possible to identify any structural features that are universal in their influence on lightfastness. The problem is made more acute by the great variety of structural variation within the components A and B used in commercial azo dyes.

The early attempts to identify structural substituents which influence the rate at which an azo dye fades in light have been reviewed by Venkataraman[22,23] and Egerton and Morgan.[9] Some workers suggested that substituents situated ortho and para to the azo link had the greatest control over the fastness, while others claimed that hydroxyl and amino groups were responsible for low lightfastness. The first systematic study[24] aimed at elucidating the effect of substituents on the fading rate of azo dyes used a Hammett analysis that clearly showed that the fading process on wool and gelatin substrates was reductive. The study also showed that the photochemical stability of a series of dyes (substituted aniline $\longrightarrow$ R-salt) was largely controlled by the ortho substituent; carboxyl and sulfonate groups conferred high lightfastness, and nitro and chloro substituents low fastness.

The effects of para substituents in the diazo component have been examined for a range of dyes (para-substituted aniline $\rightarrow$ γ-acid,

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[21] *CSD III*, p. 249.

[22] *CSD I*, p. 468.

[23] *CSD II*, p. 1220.

[24] R. H. Kienle, E. I. Stearns, and P. A. van der Meulen, *J. Phys. Chem.* **50**, 363 (1946).

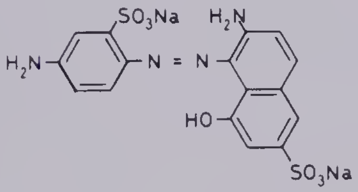
TABLE 1

LIGHTFASTNESS OF DYES (PARA-SUBSTITUTED ANILINE → γ-ACID) ON WOOL[25]

	Lightfastness	
Substituent	*Alkaline coupled*	*Acid coupled*
H	6	5–6
SO_3Na	6	6
SO_2NH_2	6	5–6
CO_2H	5–6	5–6
CO_2Et	5–6	5–6
Cl	5–6	6
Me	6	6
OMe	5–6	5–6
OEt	4	4
NO_2	6	6
NH_2	4	2–3
NHCOMe	5–6	4
NHPh	4	3–4

acid or alkaline coupled)[25] (Table I). It was found that ethoxy, amino, and anilino groups lowered the lightfastness, while no group was found to increase the fastness above that shown by the unsubstituted dye. Acetylation of the amino group increased the photostability of the dye on wool; a similar observation was made over forty years ago (reviewed in Egerton and Morgan[9]).

A further example of the decrease in photostability imparted by an amino function is given by the dye (I), which has a reported lightfastness of 2–3 on wool,[26] compared with 5–6 for the corresponding *N*-acetyl dye. A somewhat disconcerting aspect of such a general conclusion is that structure (I) is that disclosed for CI Acid Red 34 (CI 17030), for which a lightfastness of 6–7 is listed. This is a very large discrepancy and needs to be resolved.



(I)

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[25] M. Sekido and T. Iijima, *Sen'i Gakkaishi* **15**, 214 (1959); *CA* **53**, 9673 (1959).

[26] I. Okubo and T. Kitagawa, *J. Chem. Soc. Jpn., Ind. Chem. Sect.* **56**, 344 (1953); *CA* **48**, 10646 (1954).

TABLE II

LIGHTFASTNESS OF AZO DYES DERIVED FROM α-NAPHTHYLAMINESULFONIC ACIDS ON WOOL

Position of sulfonate in α-napthylamine	*Lightfastness with various coupling components*			
	α-Naphthol	*β-Naphthol*	*α-Naphthylamine*	*β-Naphthylamine*
2	2	5	3	4
3	3	4	3	3
4	4	5	3	3
5	3	4	3	2
6	3	4	3	3
7	3	4	3	3
8	2	3	2	2

The effects of sulfonic acid groups on the lightfastness of azo dyes have been investigated by several workers. In the group of dyes formed by coupling each of the seven possible α-naphthylaminesulfonic acids with α- and β-naphthol and α- and β-naphthylamine (Table II), it was found[27] that the position of sulfonation had little effect, except that sulfonate groups in the 8-position of the diazo component generally decreased the stability to light. It is noteworthy that the dyes based on β-naphthol had the highest average lightfastness on wool. With the series of dyes prepared by coupling α-naphthylamine or naphthionic acid to β-naphthol, Schaeffer's acid, or R-salt, it was shown[28] that the lightfastness was not dependent on the number of sulfonate groups and only marginally dependent on their position in the β-naphthol coupling component.

Giles and co-workers[29] have examined the way in which the surface activity of an azo dye, as determined by the sulfonation pattern, affects the lightfastness. Earlier studies[30] had indicated that the physical state of a dye in a fiber affected the lightfastness of the dyeing; aggregated dye particles generally faded less rapidly than the dye in a monomolecular dispersed state. It was proposed that if a dye contained sulfonate groups at one end or along one edge of a planar molecule

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[27] B. M. Bogoslovskii and F. I. Sadov, *Tekst. Promst.* (*Moscow*) **12**, 31 (1952); *CA* **47**, 5685 (1953).

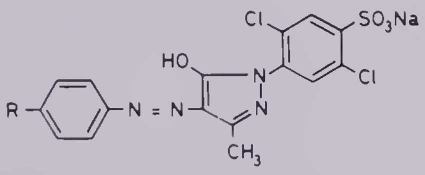
[28] M. Sekido and T. Iijima, *Sen'i Gakkaishi* **14**, 46 (1958); *CA* **52**, 14174 (1958).

[29] C. H. Giles, G. Baxter, W. A. Black, N. Macauley, and S. M. K. Rahman, *Text. Res. J.* **30**, 934 (1960).

[30] G. Baxter, C. H. Giles, and W. J. Lewington, *J. Soc. Dyers Colour.* **73**, 386 (1957).

(unsymmetrically substituted), the surface activity so generated would increase the proportion of dye in the dispersed state, thereby lowering the lightfastness. On the other hand, if the sulfonate groups were located more uniformly over the molecule (symmetrically substituted), the absence of surface activity would favor an increase in the extent of aggregation with a consequent increase in fastness. Various structural examples from CI were collated in support.

The lightfastness variations brought about by changes in surface activity of azo dyes are highlighted when large alkyl groups are introduced as a means of increasing washfastness of wool dyeings. For example, the lightfastness of the dye (II, R = H) is 6 on wool, whereas that of the dye (II, R = $C_{12}H_{25}$) is 4–5. Giles and co-workers[30] have examined the effect of alkyl groups on lightfastness and found that fastness increased as the chain was lengthened to C_4–C_8, and then decreased as the chain was further lengthened to C_{16}. This finding was explained in terms of aggregation; the dyes with short alkyl chains tend to form aggregated particles or micelles, whereas longer chains, which are able to increase the surface activity of the host dye molecule, tend to destabilize the aggregated state in favor of a monomolecular dispersion within the fiber.



(II)

The relation between the lightfastness and the chain length of an attached alkyl group can be seen from Fig. 2 to vary with the dye structure[31]; the decrease in fastness as the chain is lengthened beyond the optimum is also found to depend on the structural type.

The diazo and coupling components that are known from the patent literature to yield dyes of high lightfastness have been surveyed by Stead.[21] It is known, for example, that γ-acid (acid coupled), 2-naphthylaminesulfonic acids and 5-pyrazolones are able to impart photostability to azo dyes, particularly if used in conjunction with diazo components that provide a sulfonate or sulfonamide substituent ortho to the azo group. Photochemical explanations for these empirical observations have not yet been advanced.

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[31] J. Meybeck, P. Ruckstuhl, and J.-M. Thumann, *Teintex* **25**, 241 (1960).

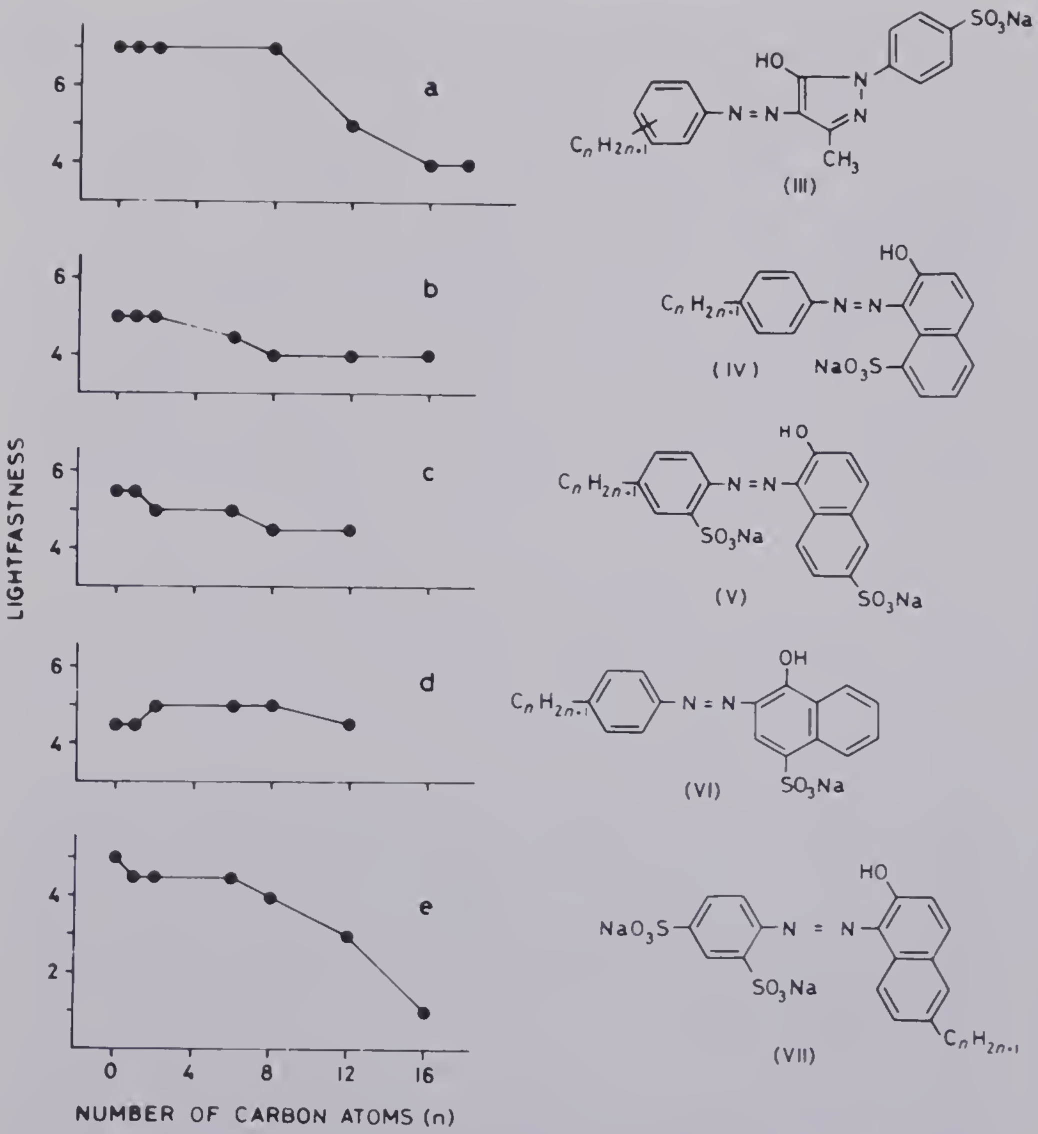


FIG. 2. Effect of the length of an alkyl chain on the lightfastness of azo dyes on wool.[31]

Azo dyes fade less rapidly on protein fibers than on cellulosic fibers.[32] Two explanations have been advanced for this behavior: (a) fading on cellulose is an oxidative process, whereas on wool it is reductive, the histidine residue acting as a hydrogen donor in the latter case[33]; (b) it is possible that particular amino acid residues in wool retard photooxidation of the dye by reacting preferentially with oxidants generated on exposure of the dyed fiber.

[32] Yu. A. Ershov and G. E. Krichevskii, *Usp. Khim.* **43**, 537 (1974); *CA* **81**, 4281 (1974).

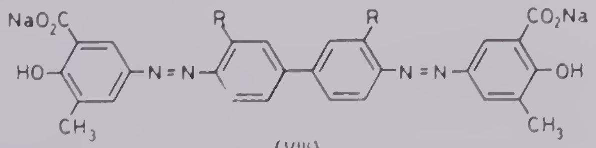
[33] J. W. Cummings, C. H. Giles, and A. E. McEachran, *J. Soc. Dyers Colour.* **72**, 373 (1956).

B. DIRECT DYES

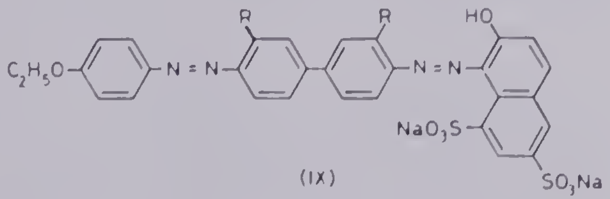
The detection of possible structure–lightfastness relationships in direct cotton dyes is made difficult by the structural complexity of this class of dye and the multitude of examples (over 200 in CI) available for examination. Because of the wide structural diversity in the trisazo class of direct dye and the limited data for the monoazo types, only examples of the disazo class will be considered.

1. *Benzidine Series*

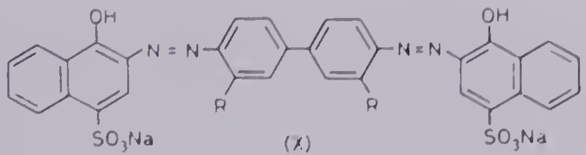
Of all the CI structures derived from tetrazotized benzidine or its analogs, 85% were rated at lightfastness 3 or less. No conclusions could be drawn from a study of dye structures in the higher fastness group as to the possibility of any molecular feature contributing to greater photostability; on the contrary, many confusing aspects were apparent. For example, CI Direct Yellow 20 (VIII; R = H) has lightfastness 3, while the related dye (VIII; R = CH_3) has lightfastness 5. Therefore, it could be concluded that methyl groups ortho to the azo group confer photostability to a dye molecule but for the fact that CI Direct Red 37 (IX; R = H) and its tolidine analog (IX; R = CH_3) are of equal fastness, 2.



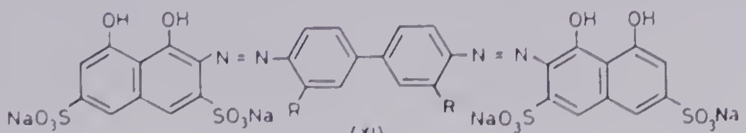
(VIII)



(IX)



(X)

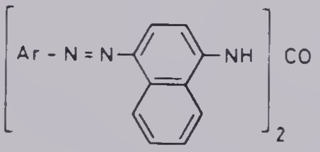


(XI)

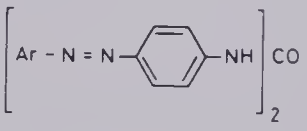
Similar anomalies are found when comparing dyes derived from benzidine and from dianisidine. For example, CI Direct Violet 43 (X; R = H) and CI Direct Violet 8 (X; R = MeO) have lightfastness 1, but the introduction of methoxyl groups into CI Direct Violet 49 (XI; R = H) raises the fastness from 1–2 to 3.

2. *Bisdiazoarylureas*

This class, which is usually formed by phosgenation of a monoazo dye containing a primary amino group, exhibits a wide range of lightfastness (1 to 6–7). The naphthylurea dyes (XII) were noted to possess an average fastness of 2–3, whereas the dyes with a phenylurea central grouping (XIII) showed an average fastness to light of 4–5.



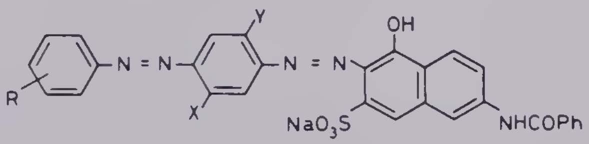
(XII)



(XIII)

3. *Disazo Dyes of the Type* A → M → E

This large group of dyes uses many types of components A and E, but relatively few for M. As with other direct dyes, replacement of groups within the same skeletal structure leads to inconsistent changes in lightfastness. It can be seen from Table III that replacement of a methoxy by a methyl group in (XIV) results in a lightfastness increase of 2 points, whereas the same alteration in a closely related structure produces no change.



(XIV)

Giles and co-workers[30,34,35] have produced kinetic evidence suggesting that the lightfastness of a cotton dyeing is dependent to a significant extent on the physical state of the dye within the fiber. Dyes that tend to form crystalline aggregates or are induced to form aggregated particles by various aftertreatments will be more resistant to fading than the same dye in a monomolecular dispersed state formed, for

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[34] G. Baxter, C. H. Giles, M. N. McKee, and N. Macauley, *J. Soc. Dyers Colour.* **71**, 218 (1955).

[35] C. H. Giles, *J. Soc. Dyers Colour.* **73**, 127 (1957).

TABLE III

LIGHTFASTNESS OF DIRECT AZO DYES (XIV) ON COTTON

CI direct color	*R*	*X*	*Y*	*Lightfastness*
Violet 34	3-SO_3Na	OMe	Me	2
Violet 41	3-SO_3Na	Me	Me	4
Violet 51	2,4-$(Me)_2$-5-SO_3Na	OMe	Me	3–4
Violet 9	2,4-$(Me)_2$-5-SO_3Na	Me	Me	3–4

example, by a cationic detergent aftertreatment. More direct evidence in support of this concept was provided by an electron microscopic examination of ultrathin films of direct-dyed viscose.[36] Among the range of dyes examined, it was observed that some dyes were present as aggregated particles of 30 Å diameter or greater, while other dyes gave no evidence of aggregation. Fading rates were measured on the same films, and the results show very strikingly that the state of aggregation as observed in the electron micrographs bears a strong correlation with rate of fading of the dye. Thus, it would appear that the lightfastness of direct dyes on cotton is determined more by their state of aggregation than any substituent influences on the chromophoric system.

C. AZOIC DYES

The lightfastness of azoic cotton dyeings, which varies over the range 1–2 to 7–8, depends on the nature of both the diazo and coupling components.[37] Although CI discloses the structures of about fifty azoic diazo components and the same number of azoic coupling components, lightfastness data are listed for only approximately one-half of the possible combinations.

The problem of searching for structure–lightfastness relationships of these one thousand or so dyeings would be formidable were it not for the fact that the majority of the azoic colors are produced from diazotized aniline derivatives coupled with substituted anilides of 2-hydroxy-3-naphthoic acid (Naphthol AS). While it is known that the extent of aggregation of a dye within a fiber can affect the lightfastness,[34] a factor very significant in azoic dyeings, the following discussion will be concerned only with the effect of the chemical structure of the coupled dye. It will be assumed that this value corresponds to the maximum fastness that is achieved by the usual aftersoaping treatments.

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[36] L. Weissbein and G. E. Coven, *Text. Res. J.* **30**, 58,62 (1960).

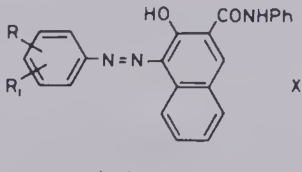
[37] *CSD I*, p. 684.

TABLE IV

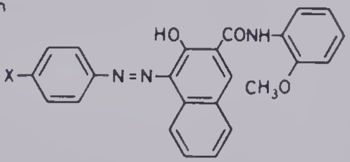
Lightfastness of Azoic Dyes (XV) on Cotton

CI azoic diazo component	*Aniline derivative*	*Lightfastness*
17	2-Trifluoromethyl-4-chloro	6–7
49	5-Trifluoromethyl-2-chloro	6
16	3,5-Bistrifluoromethyl	6
6	2-Nitro	6
8	2-Nitro-4-methyl	6
9	2-Nitro-4-chloro	6
3	2,5-Dichloro	5–6
34	4-Nitro-2-methyl	5–6
37	4-Nitro	5
12	5-Nitro-2-methyl	5
11	4-Chloro-2-methyl	4–5
32	5-Chloro-2-methyl	4
44	2-Chloro	4
10	5-Chloro-2-methoxy	4
42	5-Diethylsulfonamido-2-methoxy	3

The effect of the diazo component on the lightfastness of dyeings formed from CI Azoic Coupling Component 2 (Naphthol AS) was first considered (Table IV). It is apparent that those substituents on the aniline component that withdraw electrons from the azo group, notably trifluoromethyl and nitro groups, increase the lightfastness; on the other hand, electron-donating substituents, such as methyl and methoxy groups ortho to the azo group, decrease the lightfastness. Fluorine-containing substituents in the diazo component have been observed[38] to increase significantly the lightfastness of azoic dyes (XVI); the rating increases from 3 when X = CH_3S to 4–5 when X = CF_3O or CF_3S.



(XV)



(XVI)

Substituents in the anilide portion of Naphthol AS (XVII) can also influence the lightfastness, as shown in Fig. 3. It is clear that the

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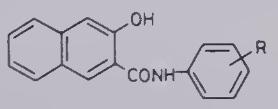
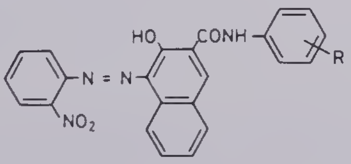
[38] L. M. Yagupolskii, B. M. Krasovitskii, V. A. Blinov, K. M. Sidneva, and D. G. Pereyaslova, *Ukr. Khim. Zh.* **26**, 389 (1960); *CA* **55**, 3063 (1961).

FIG. 3. Lightfastness of azoic dyeings derived from various substituted anilides as coupling components (XVII): (×) R = *p*-OMe, (○) R = *p*-Cl, (△) R = *m*-NO_2.

electron-donating methoxyl substituent tends to enhance lightfastness, whereas the electron-withdrawing nitro group has the opposite effect; the chloro substituent has an intermediate effect, presumably because of the lower electronegativity of chlorine as compared to that of the nitro group. Similar results were obtained with a series of dyes (XVIII), where it was found that the lightfastness was maximum for R = *p*-methoxy and minimum for R = *m*-nitro.[39]



(XVII)



(XVIII)

In summary, the above results suggest that maximum lightfastness is obtained when the azoic diazo component contains strongly electron-withdrawing substituents and the anilide ring in Naphthol AS contains electron-donating substituents. Similar conclusions can be drawn from fastness data reported for fluorene-based azoic dyes[40] and dyes derived from various 2-acyl-1-naphthols.[41]

While the influence of substituents in the phenylazo part of the dye molecule is consistent with the accepted oxidative mechanism of

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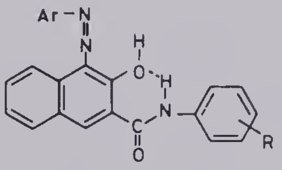
[39] J. Monheim and R. Lowenfeld, *Melliand Textilber.* **53**, 1134 (1972).

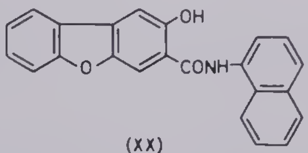
[40] N. Ishikawa, N. Izawa, and M. Okazaki, *Sen'i Gakkaishi* **15**, 209 (1959); *CA* **53**, 9673 (1959).

[41] R. D. Desai and R. M. Desai, *J. Sci. Ind. Res., Sect. B* **14**, 498 (1955).

fading on nonprotein substrates,[33,42] the enhanced fading rate observed with electron-donating groups in the anilide ring is not readily understood in terms of transmission of electronic influences through the amide bond to the azo linkage. It may be that the anilide ring can alter (by substituent inductive effects) the electron density at the amide nitrogen, thereby controlling the propensity of the amide hydrogen to hydrogen bond with the phenolic oxygen (XIX). Indeed, it is known from studies on other chromophoric systems that intramolecular hydrogen-bond formation increases photostability, possibly as a result of an increased rate of vibrational decay to the ground state (see Sections III,B, IV, and VII,D).

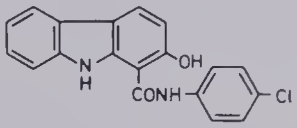


(XIX)



(XX)

The lightfastness of azoic dyeings formed from the heterocyclic coupling components (XX; CI Azoic Coupling Component 15) and (XXI; Component 37) is not affected by the nature of the diazo component, and values in the range 6–7 are reported for dyeings on cotton



(XXI)

and acetate rayon.[43] Conclusions concerning structural variations in azoic dyes based on acetoacetylamino coupling components cannot be drawn due to insufficient data. Azoic dyeings on acetate[43] usually exhibit marginally lower lightfastness than cotton dyeings. In addition, the influence of diazo component substituents is less pronounced than for cotton dyeings.

D. Disperse Dyes

From an early extensive review[44] of the properties of disperse dyes, it is clear that the nature of the substrate is a significant factor in determining the stability to light of a disperse dyeing. In general, the

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[42] H. R. Chipalkatti, N. F. Desai, C. H. Giles, and N. Macauley, *J. Soc. Dyers Colour.* **70**, 487 (1954).

[43] I. M. S. Walls, *J. Soc. Dyers Colour.* **70**, 429 (1954).

[44] J. M. Straley and D. G. Carmichael, *Can. Text. J.* **76**, 49 (1959).

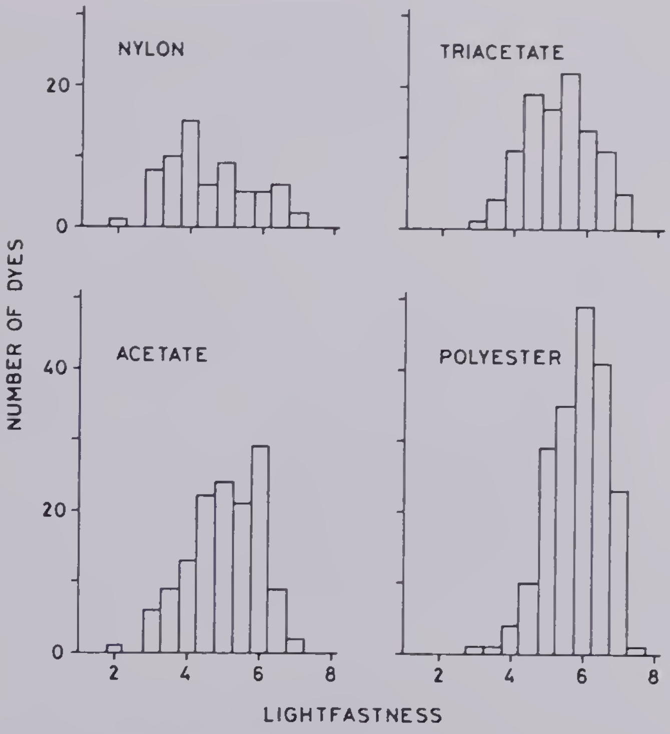

FIG. 4. Lightfastness of azo disperse dyes on various substrates (CI data).

highest lightfastness was found on a polyester substrate and the lowest on nylon, with cellulose triacetate and secondary acetate yielding intermediate fastness. Secondary acetate dyeings gave marginally higher ratings than triacetate. These conclusions are supported by a survey of the fastness data listed for disperse dyes in CI. The results of this survey are shown in Fig. 4 in which the lightfastness distributions on four different fibers using the fastness data of all dyes classified as disperse azo are plotted.

Hydroxyl groups ortho to the azo group in simple azobenzenes lower the lightfastness of polyester dyeings, particularly when a 2′-nitro and, to a lesser extent, a 4′-nitro group is present (Table V).[45] A 3-nitro group increases the lightfastness, particularly when a 2′- or 3′-methoxy group is also present.

Most commercial disperse dyes are (substituted aniline → *N*,*N*-dialkylaniline). Some lightfastness–structure correlations on such dyes (Table VI) indicate that the fastness increases as the substituent in the para position is made more electronegative,[46] the *p*-nitro dye being the most lightfast. The inclusion of a second substituent in the ortho

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[45] S. V. Sunthankar and V. Thanumoorthy, *Indian J. Chem.* 8, 598 (1970).

[46] M. F. Sartori, *J. Soc. Dyers Colour.* 83, 144 (1967).

TABLE V

LIGHTFASTNESS OF SUBSTITUTED AZOBENZENES ON POLYESTER[45]

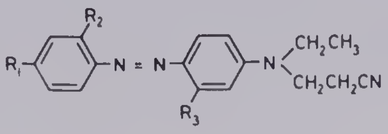
Substituents	*Lightfastness*[a]
None	6
2-Nitro	6
3-Nitro	7
4-Nitro	6–7
2-Nitro-3′-methoxy	6
3-Nitro-3′-methoxy	7–8
4-Nitro-3′-methoxy	7
2-Nitro-2′-hydroxy-5′-methyl	3
3-Nitro-2′-hydroxy-5′-methyl	6–7
4-Nitro-2′-hydroxy-5′-methyl	5
2-Nitro-2′-methoxy-5′-methyl	4–5
3-Nitro-2′-methoxy-5′-methyl	7–8
4-Nitro-2′-methoxy-5′-methyl	7–8

[a] The lightfastness ratings apply to AATCC standards.

TABLE VI

LIGHTFASTNESS OF AZO DYES (XXII)[46,47]

Substituents			*Lightfastness*	
R_1	*R_2*	*R_3*	*Polyester*	*Nylon*
H	H	Me	2	—
OMe	H	Me	2	—
SO_2NEt_2	H	Me	3	—
COMe	H	Me	4	—
SO_2Me	H	Me	4	—
NO_2	H	Me	5	—
NO_2	NO_2	H	2	1
NO_2	OMe	H	3–4	4
NO_2	Me	H	4–5	4–5
NO_2	H	H	5	4
NO_2	Cl	H	6	3–4
NO_2	CN	H	6–7	1–2



(XXII)

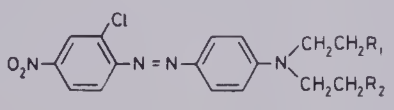
position can have a profound effect on lightfastness; a difference of 4–5 points is to be noted between the 2-nitro and 2-cyano dyes shown in Table VI,[47] even though the two substituents are of similar electronegativity. This anomalous effect is not observed when the same dyes are applied to nylon, where the lightfastness increases with increasing electron-donating power of the ortho substituents and is a minimum for both nitro and cyano ortho substituents.

Various studies have shown that the nature of the *N*-alkyl groups in the coupling component has a significant effect on the lightfastness of polyester dyeings.[47] As can be seen from Table VII, the lightfastness is a maximum for *N*-cyanoethyl groups and minimal for *N*-hydroxyethyl groups. In a similar study,[48] one of the terminal substituents (R_1 in XXIII) was varied by derivatization of the hydroxyl group, and the other was maintained as a nitrile. The dyes containing a free hydroxyl group or the derived phenylsulfonate ester were rated at lightfastness 4 on polyester, whereas a range of other derivatives (esters, carbonate esters, and thiocarbamates) were all of higher fastness (5 to 6–7).

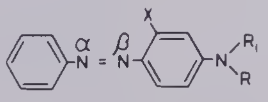
TABLE VII

LIGHTFASTNESS OF AZO DYES (XXIII) ON POLYESTER[47]

Substituents		
R_1	R_2	*Lightfastness*
H	OH	3
H	H	3–4
OH	CN	4
H	CN	6
OCOMe	CN	7
CN	CN	7



(XXIII)



(XXIV)

An extension of this area of investigation can be seen in a comparison of the electron impact-induced fragmentation patterns of 4-(*N*,*N*-dialkylamino)azobenzene dyes (XXIV) with their lightfastness on

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[47] C. Muller, *Am. Dyest. Rep.* **59** (3), 37 (1970).

[48] S. Al-Kassim and A. T. Peters, *J. Soc. Dyers Colour.* **89**, 359 (1973).

polyester and secondary acetate.[49] Two of the principal ion fragments in the mass spectra of the dyes were found to be m/e 77 (I_{77}) and m/e 105 (I_{105}) resulting from fission at the α- and β-azo nitrogen atoms, respectively. The ratio (I_{77}/I_{105}) of the relative abundances of these ions is believed to be an indication of the relative positive charge localization on the azo nitrogen atoms in the molecular ion.[49] There was a direct correlation between this ratio and the lightfastness of a range of these dyes on polyester and acetate (Table VIII and Fig. 5), indicating that the two modes of fission—electron impact and photochemical—are related. Introduction of additional groups, such as nitro, into the diazo component creates complexities that make correlations between mass spectral behavior and lightfastness less obvious. It is of interest to note that the lightfastness of these dyes (XXIV) is higher on acetate than polyester in all examples.

Bridgeman and Peters[50] have investigated the photochemical degradation of these dyes in ethanolic solution and compared the rates of photodecomposition with the pK_a of the dye (Fig. 6). The dissociation constant was taken to be a measure of the electronegativity of the β-azo nitrogen atom, and therefore, if photodecomposition is initiated here, a negative slope in a plot of pK_a values versus fading rate (Fig. 6) is consistent with a reductive fading mechanism in ethanolic solution.

TABLE VIII

LIGHTFASTNESS AND MASS SPECTRAL DATA FOR AZO DYES (XXIV)[49]

Dye number	*X*	*R*	*R_1*	*I_{77}/I_{105}*	*Lightfastness*	
					Acetate	*Polyester*
1	H	H	Me	4.89	5	4
2	H	H	Et	3.43	5	3
3	H	H	C_2H_4OH	0.74	4	3
4	H	C_2H_4OH	C_2H_4OH	1.60	4	2
5	H	C_2H_4CN	C_2H_4CN	6.47	6	5
6	H	C_2H_4OH	C_2H_4CN	3.1	4–5	3
7	Me	C_2H_4OH	C_2H_4CN	6.0	5–6	4
8	H	Et	C_2H_4CN	3.65	5	4
9	H	Me	C_2H_4CN	4.0	5	4
10	Me	H	C_2H_4CN	6.0	5–6	5
11	Me	Et	C_2H_4CN	4.67	5–6	4
12	Me	C_2H_4CN	C_2H_4CN	7.0	6.	5

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[49] H. P. Mehta and A. T. Peters, *Appl. Spectrosc.* **28**, 241 (1974).

[50] I. Bridgeman and A. T. Peters, *Text. Res. J.* **44**, 645 (1974).

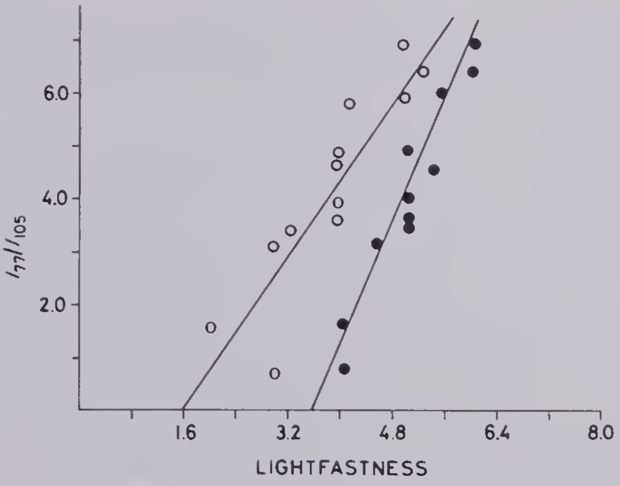


FIG. 5. Relationship between ratios of the relative abundance of fragment ions m/e 77 (I_{77}) and m/e 105 (I_{105}) and the lightfastness of dyes XXIV on secondary cellulose acetate (●) and polyester (○) fibers.[49] Compare Table VIII.

This finding contrasts markedly with the results on polyester and acetate fibers. Dyes exhibiting the lowest photostability in ethanolic solution are those with the highest lightfastness on polyester (compare Table VIII with Fig. 6), thus indicating an oxidative pathway operating from the β-azo nitrogen atom on polyester. The data shown in Table VI for polyester are consistent with such a mechanism, with the exception of the 2,4-dinitro-substituted dye, whose fastness would be expected to be similar to that of the 2-cyano-4-nitro dye. From the limited data

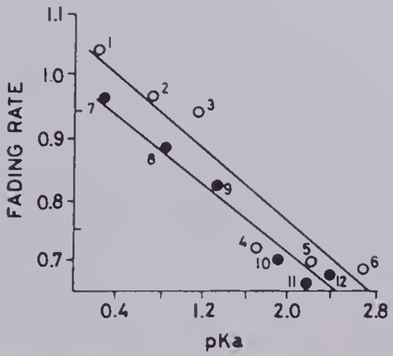


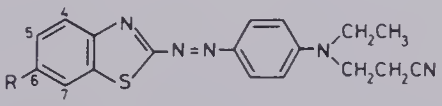
FIG. 6. Relationship between fading rate in ethanolic solution and pK_a values for dyes: aniline diazotized and coupled to (1) N,N-bis-β-cyanoethylaniline, (2) N,N-bis-β-cyanoethyl-m-toluidine, (3) N-ethyl-N-β-cyanoethylaniline, (4) N-β-cyanoethyl-N-β-hydroxyethyl-m-toluidine, (5) N-β-cyanoethyl-m-toluidine,[50] (6) N-ethylaniline; and for dyes (7) o-cyanoaniline, (8) o-nitroaniline, (9) m-nitroaniline, (10) o-hydroxyethylaniline, (11) p-aminoacetanilide, (12) o-anisidine diazotized and coupled to N-β-cyanoethyl-m-toluidine.

available on the fading behavior of azo disperse dyes on nylon (Table VI), we suggest that the photochemical mechanism on this fiber may well be a reductive process, but this possibility needs further experimental verification.

The fading rates of substituted 4-phenylazo-1-naphthylamines in cellulose acetate films[51,52] are also indicative of a photooxidative mechanism of decomposition, i.e., Hammett plots have a negative slope. In contrast, the fading of a series of phenylazo-β-naphthol dyes in polypropylene films appears to be a photoreductive process[53]; i.e., a positive slope is observed in a plot of relative fading rates versus Hammett sigma constants. In a later study,[54] evidence for photoreduction was found when the dyed polypropylene support was irradiated under nitrogen. However, in the presence of oxygen, no definite conclusion could be drawn from the Hammett plot. Thus, the mechanism of fading of azo dyes on polypropylene must remain undecided until further results are available.

Substituents containing fluorine[55] and silicon[56] located at specific positions in a dye molecule have been found to improve the light fastness of acetate dyeings.

Increase in the photostability of the somewhat fugitive thiazole and benzothiazole azo types by structural modification has been reported in several investigations. Modena[57] has shown that the dyes formed from diazotized 2-aminothiazole, 2-aminobenzothiazole, and naphthothiazoles with various amines gave higher lightfastness on nylon than acetate. It was also found that *N*,*N*-dialkylanilines as coupling components gave dyes of higher fastness than naphthylamines with thiazole and benzothiazole diazo components, and that the fastness of naphthothiazole azo dyes depended on the position of ring fusion.



(XXV)

The lightfastness of the benzothiazole azo dyes (XXV) was greatly improved by the incorporation of electron-withdrawing groups in

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[51] E. Atherton and I. Seltzer, *J. Soc. Dyers Colour.* **65**, 629 (1949).

[52] E. Atherton and R. H. Peters, *J. Soc. Dyers Colour.* **68**, 64 (1952).

[53] M. Ahmed and V. Mallett, *J. Soc. Dyers Colour.* **84**, 313 (1968).

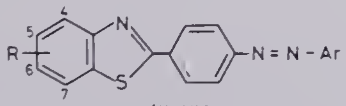
[54] V. N. Mallet and B. T. Newbold, *J. Soc. Dyers Colour.* **90**, 4 (1974).

[55] J. B. Dickey, E. B. Towne, M. S. Bloom, G. J. Taylor, H. M. Hill, R. A. Corbitt, M. A. McCall, W. H. Moore, and D. G. Hedberg, *Ind. Eng. Chem.* **45**, 1730 (1953).

[56] S. V. Sunthankar and H. Gilman, *Text. Res. J.* **23**, 53 (1953).

[57] G. Modena, *Gazz. Chim. Ital.* **85**, 922 (1955); *CA* **50**, 2175 (1956).

the 6-position[46]; for example, the introduction of a nitro group in this position increases the fastness from 2 to 6 on polyester. When the nitro group was located at the 4-position, the fastness was lowered, irrespective of the nature of the substituent occupying the 6-position. In 2-(4′-phenylazo)benzothiazole dyes (XXVI; Ar = Ph), electron-donating groups such as methoxy and dimethylamino resulted in increased lightfastness for dyeings on nylon.[58] The results indicate an oxidative fading process on polyester and a reductive one on nylon.



(XXVI)

In the case of a series of halogenobenzothiazolylazo dyes[59] [XXVI; Ar = 4-(*N*-hydroxyethyl-*N*-cyanoethyl)-3-toluidinyl], the lightfastness was found to be considerably higher on secondary acetate than on polyester, but was found to be relatively unaffected by the nature of the halogen (XXVI; R = Cl, Br, F) and its position in the benzo ring (4, 5, 6, or 7).

Numerous studies have been reported on the structure–lightfastness relationships of experimental monoazo disperse dyes not found in commercial ranges and include coupling components such as substituted phenols and 2-acetyl-1-naphthol,[60] 5-hydroxynaphtho[1,2-*d*]triazole,[61] 4-hydroxyquinaldine,[62] indolizine and imidazolo[1,2-*d*]pyrimidine,[63] and diazo components such as *p*-amino-α-methylcinnamaldehyde,[64] 5-nitro-2-aminobenzothiazole 3*N*-oxide,[65] and aminonaphthothiazoles.[66]

E. Cationic Dyes

Azo dyes containing a charged amino function are used widely for dyeing basic-dyeable polyacrylonitrile fibers. Since very few structures

[58] A. M. Osman and S. A. Mohamed, *U.A.R.J.Chem.* **14**, 493 (1971).

[59] A. T. Peters, *J. Soc. Dyers Colour.* **85**, 507 (1969).

[60] M. Kamel, R. M. Issa, L. Abdel-Wahab, S. Shakra, and A. Osman, *Textilveredlung* **6**, 224 (1971).

[61] M. A. Allam and H. Mustafa, *Egypt. J. Chem.* **15**, 255 (1972).

[62] S. H. Gole and S. V. Sunthankar, *Indian J. Technol.* **12**, 571 (1974).

[63] L. Pentimalli, L. Greci, and G. Milani, *Ann. Chim.* (*Rome*) **63**, 95 (1973); *CA* **80**, 146957 (1974).

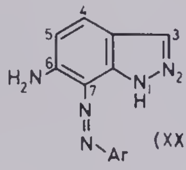
[64] E. Barni and G. DiModica, *Ann. Chim.* (*Rome*) **63**, 379 (1973); *CA* **81**, 38914 (1974).

[65] K. Nishida, T. Takeuchi, K. Shimizu, T. Hotsuta, and H. Iwamoto, *J. Soc. Dyers Colour.* **89**, 406 (1973).

[66] K. Nishida, H. Tashiro, T. Ohtsu, T. Hotsuta, H. Iwamoto, and H. Toda, *J. Soc. Dyers Colour.* **90**, 441 (1974).

are disclosed in CI, it is not possible to formulate any structure–fastness relationships.

The azoindazole class of dye (e.g., XXVII) has been extensively studied with the aim of correlating lightfastness and color with various structural features.[67] The indazole coupling component, containing an amino group in the 4-, 5-, 6-, or 7-position, was either *N*-methylated in the 1- or 2-position or free in these positions. A correlation was found between the pK_a of the parent aminoindazole and the lightfastness of the derived dye on Orlon (Table IX). The structural factor that most affected both these parameters was the position of *N*-methylation, dyes with 1-methyl groups having low lightfastness and low basicity and those with 2-methyl groups having high fastness and high basicity. The lightfastness was controlled to a lesser extent by the position of the amino group, the order of fastness being 5- < 7- < 4- < 6-amino.



(XXVII)

TABLE IX

STRUCTURE–LIGHTFASTNESS–BASICITY CORRELATION OF INDAZOLE AZO DYES (XXVII) ON ORLON[67]

Indazole substitution pattern						
1	2	4	6	7	*Lightfastness*	pK_a[a]
H	—	H	NH_2	*o*-Chlorphenylazo	3	2.08
Me	—	H	NH_2	*o*-Chlorphenylazo	1	−3.15
—	Me	H	NH_2	*o*-Chlorphenylazo	5	5.15
H	—	H	NH_2	*o*-Methoxyphenylazo	6	4.52
Me	—	H	NH_2	*o*-Methoxyphenylazo	2	−3.00
—	Me	H	NH_2	*o*-Methoxyphenylazo	6–7	6.85
H	—	*o*-Chlorphenylazo	H	NH_2	4	2.63
Me	—	*o*-Chlorphenylazo	H	NH_2	3	1.37
—	Me	*o*-Chlorphenylazo	H	NH_2	4	2.8
H	—	*o*-Methoxyphenylazo	H	NH_2	4	3.4
Me	—	*o*-Methoxyphenylazo	H	NH_2	3	2.37
—	Me	*o*-Methoxyphenylazo	H	NH_2	4	3.76

[a] Dissociation constant of parent aminoindazole.

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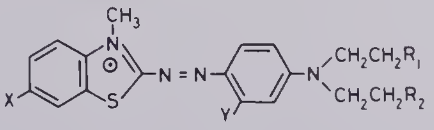
[67] R. Sureau, *Chimia* **15**, 195 (1961).

The lightfastness of the dyes on Courtelle was usually lower than on Orlon and was not as clearly related to the basicity of the indazole.

A series of cationic azo dyes (XXVIII) on Leacril 16 (an acrylic fiber) showed maximal lightfastness when X = OCH_3, $R_1 = R_2 =$ CN. The fastness rating was diminished by 1 or 2 points when X = Cl.[68]



(XXVIII) X = OCH_3, SCH_3, CH_3, Cl
Y = H, CH_3
R_1 and R_2 = OH, CN, H

F. Metallized Dyes

1. *After-Coppered Direct Dyes*

The posttreatment of direct dyed cotton with copper salts has been employed for many years as a method for improving wash- and lightfastness.[69] In order to ensure that the copper complex possesses maximum stability, it is necessary for the dye to contain an *o,o'*-dihydroxyazo or *o*-hydroxy-*o'*-carboxyazo grouping.[70] Dyes derived from dianisidine are also effectively after-coppered as a result of the conversion of methoxyl to hydroxyl groups during the dyeing. An additional complexing site for copper ions is provided by a dye formed from salicylic acid, but in this case there is little change in lightfastness observed due to the separation of the chromophoric azo group from the metal (Table X). The *o,o'*-dihydroxy(or methoxy)azo group provides the largest increase in lightfastness of a dyeing aftertreated with copper. Aftertreatment with chromium salts is used with some direct dyes to improve washfastness, but usually the lightfastness is relatively unaffected, as can be seen from Table X.

2. *Mordant Azo Dyes*

The great majority of chrome mordant colors have a lightfastness of at least 6 on wool, which indicates that this type of complexation effectively insulates the azo group from photochemical attack. In certain types of azo dye, however, the reverse is true; for example, the

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[68] G. Alberti, A. Cerniani, and G. Seu, *Chim. Ind. (Milan)* **56**, 495 (1974); *CA* **81**, 171311 (1974).

[69] *CSD I*, p. 544.

[70] *CSD I*, p. 601.

TABLE X

EFFECT OF METAL AFTERTREATMENTS ON LIGHTFASTNESS OF AZO DYES ON COTTON

		Lightfastness		
			Aftertreatment	
CI direct color	*Chromophore ligands*	*Direct*	*Copper*	*Chromium*
Blue 166	*o*,*o*′-Dihydroxyazo	1	6	—
Blue 8	*o*-Hydroxy-*o*′-methoxyazo	1	4–5	—
Blue 22	*o*-Hydroxy-*o*′-methoxyazo	1	5–6	—
Blue 58	Mono-*o*-hydroxyazo	2–3	3–4	2–3
Violet 45	Mono-*o*-hydroxyazo	1	4	—
Yellow 2	Salicylic acid	5	7	5
Yellow 33	Salicylic acid	6	6–7	—
Red 7	*o*-Amino-*o*′-methoxyazo	1	1	—
Green 1	Mono-*o*-aminoazo	1–2		2
Red 33	Salicylic acid and *o*-hydroxyazo	3	4	4

lightfastness of several 3-arylazo-4-hydroxynaphtho[1,2-*d*]triazole dyes on wool is markedly reduced by an afterchrome treatment.[71]

3. *Premetallized Azo Dyes*

Most preformed metal-complex dyes produce dyeings of high lightfastness on wool (mostly between 6 and 7). From an inspection of the limited number of structures disclosed in CI, it appears that the variations in fastness between dyes of similar constitution are not related to changes in substituents. It is possible that the lightfastness of metallized dyes, as in the case of direct cotton dyes, is related to their degree of aggregation within the fiber rather than to the chemical structure.

The nature of the metal in the complex does not seem to be a major factor in determining lightfastness, although it is clearly related to other properties of the dye. Acid Violet 92 and Acid Blue 193 which are 1:2 cobalt and chromium complexes, respectively, containing the same chromophoric ligand system, have identical lightfastness ratings (6–7) on wool; 1:2 chromium and nickel complexes (Acid Green 62 and Acid Brown 234) of the same chromophore are also of identical lightfastness (6).

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[71] M. A. Allam and H. Mustafa, *Egypt. J. Chem.* **15**, 255 (1972).

III. Anthraquinonoid Dyes

A. ACID DYES

Sulfonated 1,4-diaminoanthraquinones are of particular importance as they impart brilliant blue, green and violet shades to wool, silk, and synthetic polyamide fibers.[72]

1. *Lightfastness on Wool, Silk, and Nylon*

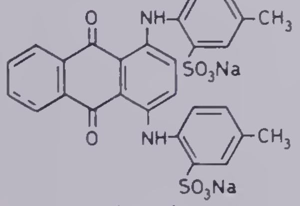
A survey of CI showed that the lightfastness of anthraquinone acid violets, greens, and blues on wool is distributed over a fairly narrow range, the majority being rated between 5 and 6. The nature of the substrate has minimal influence on the lightfastness of the dyeing.

2. *Effect of Substituents on Lightfastness of Wool Dyeings*

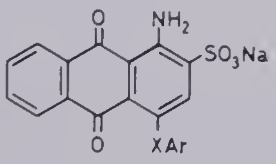
Although substituents in general have little effect on the lightfastness of anthraquinones, it is apparent that *N*-alkyl groups are present in those dyes of lower fastness. It is known that photodealkylation is a significant pathway in the fading process of alkylamino anthraquinones[73–75]; the lightfastness is increased by replacing an alkylamino by an arylamino group (cf. CI Acid Blue 27, CI 61530 and CI Acid Green 25, CI 62055).

If one or two hydroxyl groups are introduced in the 5- or 5,8-positions of CI Acid Green 25 (XXIX), the lightfastness is increased from 5–6 to 6 and 6–7 (cf. CI Acid Greens 38 and 41). This is a contrary finding to an early investigation of the fading rates of some hydroxyanthraquinones.[76]

The sulfonation pattern has a small but significant influence on the lightfastness of anthraquinone dyes on wool. This effect is in accordance with the theory of Giles and co-workers,[29,77] which states that an



(XXIX)



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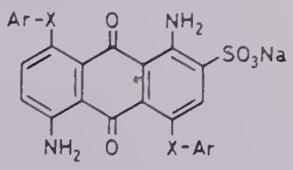

(XXXI)

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[72] *CSD V*, p. 57ff.

[73] M. Couper, *Text. Res. J.* **21**, 720 (1951).

[74] C. H. Giles and R. S. Sinclair, *J. Soc. Dyers Colour.* **88**, 109 (1972).

[75] D. Wegerle, *J. Soc. Dyers Colour.* **89**, 54 (1973).

[76] K. Gebhard, *J. Soc. Dyers Colour.* **25**, 276 (1909).

[77] C. H. Giles, *J. Soc. Dyers Colour.* **76**, 587 (1960).

unsymmetrically sulfonated dye (one or two groups localized in one region of the molecule) will possess a degree of surface activity that will tend to promote the formation of monomolecular dispersions. On the other hand, symmetrically substituted dyes (sulfonate groups distributed over the molecular framework) will possess no inherent surface activity, and therefore the tendency of dye particles to aggregate will be unimpeded; the lightfastness of a dye is generally greater when it is in the aggregated state than in a dispersed state.[7] Data from CI for 27 acid anthraquinone dyes support Giles' theory, since symmetrically sulfonated dyes gave on the average $\frac{1}{2}$ point higher ratings than dyes having an unsymmetrical sulfonation pattern. The presence of a halogen attached to the chromophoric nucleus appears to have little influence on the lightfastness. Dyes containing arylthio groups (XXX; X = S) have a lightfastness 2 points higher than dyes containing aryloxy groups (XXX: X = O).[78] In contrast, the fastness of disubstituted dyes (XXXI) is unaffected by the nature of the substituent connecting atom (X = S or O).

B. Disperse Dyes

Originally introduced as dyes for acetate fibers, disperse anthraquinone dyes are now used for a wide range of fiber types, such as polyamide, polyester, triacetate, and acrylics. The lightfastness of this class of disperse dye is dependent on the substrate. Dyeings on acetate exhibit marginally higher lightfastness than those on nylon 66, while those on polyester are highest. Giles and Rahman[79] suggest that one parameter controlling the lightfastness of a disperse-dyed fiber is the regain of the substrate. Hence, the rate of photofading on polyester may be retarded because access of water vapor to the dye particle is restricted.

Most anthraquinone disperse dyes contain either one or two amino groups (free or substituted), usually in the 1- and 4-positions. The substitution pattern can have a marked effect on the lightfastness of acetate dyeings as shown in Table XI. Although the range of examples is not very comprehensive, it is clear from Table XI that the nature and position of both *N*- and nuclear substituents have a controlling influence on the lightfastness. The chromophoric modifications that increase lightfastness are: (1) introduction of hydroxy groups para to an amino group, (2) replacement of an alkylamino by an arylamino group, and (3) acetylation of a free amino group. It is to be noted that

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[78] J. Degani and A. Tundo, *Boll. Sci. Fac. Chim. Ind. Bologna* **17**, 55 (1959); *CA* **54**, 13667 (1960).

[79] C. H. Giles and S. M. K. Rahman, *Text. Res. J.* **31**, 1012 (1961).

TABLE XI

LIGHTFASTNESS OF SOME COMMERCIAL ANTHRAQUINONE DISPERSE DYES ON ACETATE

CI disperse color	*Substituents*	*Lightfastness*
	One amino group	
Orange 11	1-Amino-4-methyl	4
Red 15	1-Amino-4-hydroxy	5–6
Red 9	1-Methylamino	4
Red 3	1-(β-Hydroxyethyl)amino	4–5
Red 22	1-Anilino	6–7
Red 4	1-Benzoylamino-4-methoxy	6–7
	Two amino groups	
Violet 1	1,4-Diamino	5–6
Red 11	1,4-Diamino-2-methoxy	5
Violet 8	1,4-Diamino-5-nitro	6
Violet 4	1-Amino-4-methylamino	4–5
Blue 5	1-Amino-4-methylamino-2-amido	7
Violet 6	1-Amino-4-acetylamino	6–7
Blue 6	1-Amino-4-cyclohexylamino-2-amido	7–8
Blue 19	1-Amino-4-anilino	5–6
Blue 28	1-Amino-4-anilino-2-*N*-hydroxyethylamido	7
Blue 14	1,4-Di(methylamino)	5
Blue 3	1-Methylamino-4-hydroxyethylamino	5
Blue 23	1,4-Di(hydroxyethylamino)	4–5
Blue 24	1-Methylamino-4-anilino	6
Blue 26	1,5-Di(methylamino)-4,8-dihydroxy	6
	Four amino groups	
Blue 1	1,4,5,8-Tetraamino	3–4
Blue 31	1,4,5,8-Tetra(methylamino)	3

tetraamino derivatives have lower fastness than mono and diamino types.

A comprehensive synthetic program involving aminoanthraquinones was undertaken by Naiki[80] with the aim of investigating the relation between structure, fastness properties, and dyeing behavior. It is evident from this work that modification (1) above has general validity and also that alkoxy substituents can influence the lightfastness of monoaminoanthraquinones, depending on their location in the dye molecule; for example, the lightfastness of 4-methoxy-1-aminoanthraquinone on acetate is $2\frac{1}{2}$ points lower than that of 1-aminoanthraquinone

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[80] K. Naiki, *Sen'i Gakkaishi* **15**, 203 (1959); *CA* **53**, 9675 (1959).

whereas a 2-methoxy group raises the lightfastness by $2\frac{1}{2}$ points compared to the parent chromophore. The author concludes that substituents affect the light-fastness of anthraquinone dyes on acetate in the order: 1-amino-4-hydroxy > 1,4-diamino > 1,4,5-triamino-8-hydroxy > 1-amino > 1,4,5,8-tetraamino.

TABLE XII

EFFECT OF SUBSTITUENTS ON LIGHTFASTNESS OF ANTHRAQUINONES ON POLY(ETHYLENE TEREPHTHALATE)[81]

High lightfastness (6–8)	*Moderate lightfastness* (3–5)	*Low lightfastness* (1–2)
1-Hydroxy	1-Amino	2-Amino
1,4-Dihydroxy	1-Methylamino	2-Methylamino
1-Arylamino	1-Piperidino	2-Methoxy
1-Acylamino	1-Amino-4-methoxy	2-Hydroxy
1-Amino-4-hydroxy	1-Amino-5-chloro	2-Piperidino
	1,4-Diamino	2-Acetylamino
	1-*N*-Methylanilino	1-Amino-4-chloro
		1-Methoxy

In a similar survey, Allen *et al.*[81] determined the lightfastness of a number of highly purified anthraquinone disperse dyes on polyester fabric; the results are summarized in Table XII, where the dyes have been collected into three groups depending on their lightfastness. The substituents found in high lightfast dyeings are similar to those producing the same effect on acetate (see above). It was proposed[81] that the photostability imparted by arylamino and hydroxy substituents in the 1- and 4-positions is due to their ability to hydrogen bond to the carbonyl group, thereby allowing the excited singlet state to be rapidly deactivated through a reversible proton transfer. Hydrogen bonds are also thought to stabilize nitrodiphenylamine (Section IV) and quinophthalone dyes (Section VII,D). The authors further propose[81] that the variation in lightfastness within the group of dyes containing substituted 1-amino groups is a function of the electron density on the nitrogen atom. High electron density generally lowers lightfastness, whereas low electron density brings about an increase. As evidence for this proposal, a linear relationship was demonstrated between the lightfastness of 1-(N-R,R′)-aminoanthraquinone on poly(ethylene terephthalate) and the pK_a of the species $RR'NH_2^+$.

Dyes in the low lightfast group in Table XII contain 1- or 2-methoxy, 2-hydroxy, or 2-amino substituents, all of which are incapable of

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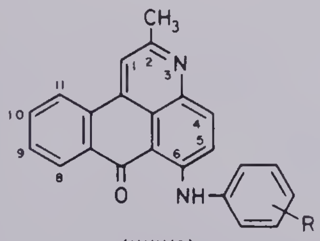
[81] N. S. Allen, P. Bentley, and J. F. McKellar, *J. Soc. Dyers Colour.* **91**, 366 (1975).

forming intramolecular hydrogen bonds with the *peri*-carbonyl oxygen. As a consequence, they are able to abstract an electron from their immediate environment. The fact that the dyes within this group redden on exposure (an indication that the π-electron system has been extended) is forwarded as indirect evidence supporting this proposition.

A remarkable dependence of lightfastness on substituents[82] has been found for a series of 6-substituted benzanthrones on polyester. When the 6-substituent was NH_2 or $NHCH_2CH_2OH$, the fastness was 2, and it was increased to 6–7 when the substituent was NHPh or NHC_6H_4OMe. The two dyes of high photostability gave neither observable transients in flash photolysis of solutions nor observable fluorescence and/or phosphorescence emission, which is consistent with an extremely fast deactivation process from the excited singlet state. Even more remarkable is the finding that 8-hydroxybenzanthrone has a lightfastness of 8 on polyester,[83] whereas the 6-hydroxy derivative has a fastness rating of 1–2. No mechanism was advanced to account for this enormous difference in photostability, which was thought to arise as a result of a rapid deactivation process operating in the 8-hydroxy derivative, but not with any efficiency in 6-hydroxybenzanthrone.

By analogy with the arylaminoanthraquinones and benzanthrones, it would be reasonable to expect the 2-methyl-6-arylaminopyridinoanthrone dyes (XXXII) to be of high lightfastness; the ratings,[84] however, range from 2 for the *o*-anisidine to 6 for the *p*-anisidine derivative, which cannot be explained on the basis of intramolecular hydrogen bonding as applied to the previous class of dyes. Another group of dyes, the lightfastness of which shows an unexplained dependence on substituent position, is a series of 1-hydroxy-4-arylaminoanthraquinones,[85] where the substituents in the aryl ring are varied.



(XXXII)

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[82] A. H. Berrie, J. F. McKellar, and E. Young, *Chem. Ind.* (*London*) p. 791 (1973).

[83] P. Bentley, J. F. McKellar, and G. O. Phillips, *Chem. Ind.* (*London*) p. 919 (1974).

[84] M. R. Patki, D. W. Rangnekar, and S. V. Sunthankar, *Indian J. Technol.* **12**, 540 (1974).

[85] V. S. Salvin and R. A. Walker, *Am. Dyest. Rep.* **48**, 35 (1959).

The fact that certain anthraquinone disperse dyes (notably those containing alkylamino substituents) fade more rapidly on polyester than on acetate or nylon prompted Giles and Sinclair[74] to examine the photoproducts of some dyes in polyester films. They found that the marked reddening that occurred during exposure could be attributed to *N*-dealkylation and proposed a reaction sequence to account for the products isolated (Fig. 7). The most plausible photodealkylation mechanism is one involving, as the first step, dehydrogenation to form an imine, which is subsequently hydrolyzed to form the free amine and formaldehyde (in the case of *N*-methyl dyes). The variation in lightfastness with polymer substrate was ascribed to the ability of the polymer or adsorbed water molecules (or both) to stabilize an excited state of the dye, thereby reducing the probability of photodealkylation.

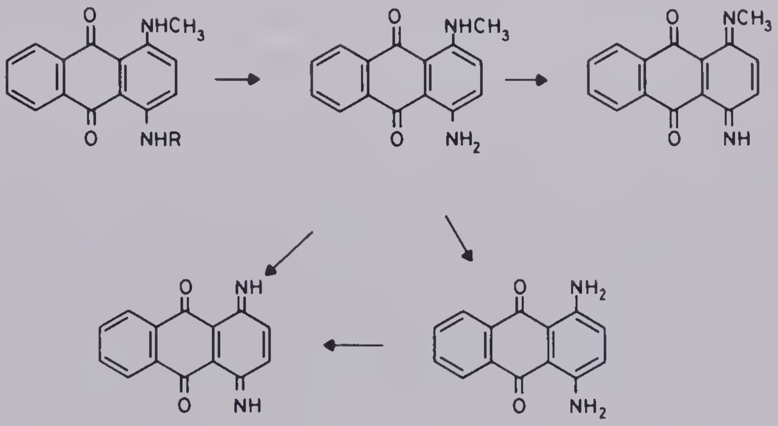

Fig. 7. Photoproducts from anthraquinone disperse dyes.[74]

In a study on the photochemistry of Disperse Blue 14 (1,4-bismethylaminoanthraquinone) on cellulose acetate, Couper[73] was able to identify several products in which hydroxyl groups had either replaced the amino function or been introduced elsewhere in the chromophore. Wegerle[75] has claimed that *N*-formylaminoanthraquinones are a photoproduct of *N*-methylamino dyes, resulting from oxidation of the *N*-methyl group or reaction of an amino group with an unspecified formylating agent.

C. Vat Dyes

Extensive surveys of the chemistry and dyeing properties of anthraquinonoid vat dyes have been published.[86,87] A very wide range of structural types are included in this classification, which provides

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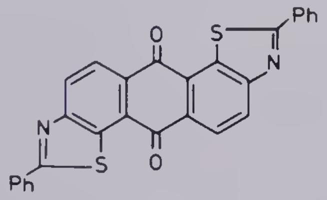
[86] M. R. Fox, *J. Soc. Dyers Colour.* **65**, 508 (1949).
[87] *CSD V*, p. 131ff.

colorations of moderate to high lightfastness ranging in shade from yellow to black. Most of the fastness data in CI apply to cotton dyeings in which it is assumed that maximum fastness has been attained by the appropriate aftertreatments, e.g., soaping, steaming.[88]

Although the majority of anthraquinone vat dyes provide intrinsically high lightfast dyeings on cotton, useful observations have been made on groups of related chromophores where the placement of substituents has an influence on the lightfastness.

Among the acylaminoanthraquinones, the lightfastness for the yellow dyes is 5–6, and for the orange and red dyes 7–8. A structural difference between these two groups is the placement of the benzoylamino functions in the anthraquinone nucleus; the yellow dyes possess 1- or 5-benzoylamino or 1,5-dibenzoylamino groups, whereas the red dyes have the substituents in a 1,4 arrangement. The introduction of hydroxyl groups in the 4- and 8-positions appears to have no effect on the lightfastness; compare CI Vat Yellow 3 (CI 61725) with Vat Violet 15 (CI 63355).

The lightfastness of the anthraquinonethiazoles on cotton and silk (Table XIII) appears to be influenced by the position of ring fusion. The yellow dyes (XXXIII) and (XXXIV), which are based on a [1, 2-*d*] ring fusion, have a fastness on cotton and silk about 3 points lower than that exhibited by dyes (XXXV–XXXVII) with a [2, 3-*d*] fusion.



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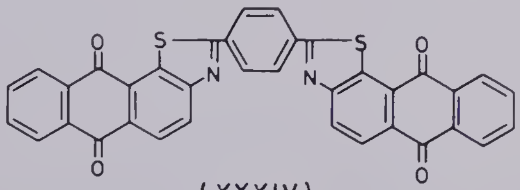

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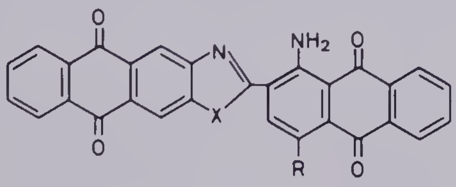

(XXXV) X=S, R=H
(XXXVI) X=O, R=H
(XXXVII) X=S, R=PhCONH

Changes in substitution patterns have little significant effect on the lightfastness of anthraquinonylamines (anthrimides) and anthra-

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[88] *CSD II*, p. 874.

TABLE XIII
LIGHTFASTNESS OF ANTHRAQUINONETHIAZOLES AND ANTHRAQUINONEOXAZOLES

		Lightfastness	
CI vat color	*Structure*	*Cotton*	*Silk*
Yellow 2	XXXIII	3–4	—
Yellow 11	XXXIV	4	4–5
Red 20[a]	XXXV	7	6–7
Red 10	XXXVI	6–7	6–7
Blue 30	XXXVII	7–8	—

[a] Lightfastness of 8 on wool.

quinonecarbazoles. The indanthrone group of vat dyes give dyeings of high lightfastness on cotton irrespective of the nature and position of substituents. Vat dyes incorporating the acridone ring likewise show high intrinsic fastness on cotton and moderate fastness on wool. Little comment can be made concerning the influence of substituents on the lightfastness of violanthrone dyes, except to note that the average ratings are higher than those found for the isoviolanthrones.

Although the pyrimidanthrones (*CSD II*, p. 996) are now obsolete, it is of interest to note that enhancement of lightfastness is apparent when an acylamino group is shifted from the 6- to the 8-position. A similar effect has been observed with hydroxyl groups in benzanthrones (see Section III,B), although the magnitude of the enhancement is much greater in the latter case.

D. PHOTOTENDERING OF VAT DYES

Phototendering is the dye-sensitized photodegradation of the fiber. The tendering of cotton by anthraquinone vat dyes has been investigated by many authors,[6] and on the basis of a survey of the information available at that time, Venkataraman[89] concluded that no relationship was discernible between the structure and tendering activity of anthraquinone vat dyes. The problem confronting anyone seeking such a relationship is best highlighted by considering the dyes shown in Table XIV.[86] Although all the dyes are simple benzamido derivatives, the range of phototendering activity varies from "active" to "protective." A more recent study[90] on the effects of substituents and their

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[89] *CSD II*, p. 1243.

[90] V. A. Titkov and T. A. Kolobalotskaya, *Zh. Prikl. Khim.* **36**, 843 (1963); *CA* **59**, 6544 (1963).

TABLE XIV

PHOTOTENDERING ACTIVITY OF SOME ANTHRAQUINONE VAT DYES[86] ON COTTON

CI vat color	*CI constitution number*	*Activity*
Yellow 26	65410	Active
Yellow 3	61725	Moderately active
Yellow 13	65425	Mildly active
Yellow 12	65405	Inactive
Orange 17	65415	Protective

location on the tendering activity of anthraquinone vats further emphasized the difficulties encountered in making logical deductions from an examination of structural formulas.

Two principal mechanisms have been proposed[6,9] to account for phototendering behavior: (1) abstraction of hydrogen atoms from the substrate by the triple state of the dye and subsequent degradation of the fiber from the resultant radical site; and (2) reaction of singlet molecular oxygen generated by energy transfer from the dye triplet state to ground state oxygen with certain groups in the substrate. In both mechanisms there are certain assumptions that have not yet been completely verified. For example, most of the evidence for the hydrogen-abstraction mechanism comes from model studies of dyes in solution. However, deductions made from solvent systems may not be applicable to dyed cellulosic fibers, where the mobility of species is severely restricted. With regard to the singlet oxygen mechanism, no experimental evidence exists that demonstrates that singlet oxygen causes chemical degradation of cellulosic fibers. Moreover, neither mechanism is able adequately to explain the variation in the tendering activity of dyes with closely related structures such as those given in Table XIV.

It is conceivable that phototendering occurs by a variety of mechanisms, including those described above and that the relative importance of any one mechanism depends on such parameters as the irradiation wave-lengths, regain of the fiber, and accessibility of water and oxygen to the dye molecule. Dual mechanisms have been advanced for many dye-sensitized photooxidation reactions in solution.[91–93]

[91] C. S. Foote, *Science* **162**, 963 (1968).

[92] N. A. Evans and I. H. Leaver, *Aust. J. Chem.* **27**, 1797 (1974).

[93] R. S. Davidson and K. R. Trethewey, *J. Chem. Soc., Chem. Commun.* p. 674 (1975).

IV. Nitrodiphenylamine Dyes

The nitrodiphenylamines, although few in number, have been the subject of a systematic study of the effect of structure on lightfastness. The way in which structure influences the lightfastness (Table XV) may be summarized as follows: (a) 2,4-dinitrodiphenylamines are markedly less fast to light on secondary acetate than are the 2-nitrodiphenylamines; (b) within the dinitrodiphenylamine series, electron-donating groups such as hydroxyl and amino increase the lightfastness when located in the 4-position. Conclusion (a) is also valid for the limited number of related acid wool dyes in CI.

A more detailed understanding of the structure–fastness relationship has emerged from the studies of Asquith, Peters, and co-workers,[94–98] who proposed that the lightfastness and extinction coefficient data (Table XVI) may be interpreted partly in terms of the presence of photolabile quinonoid structures (XXXIXb) and (XLb) of the 4-nitro

TABLE XV

LIGHTFASTNESS OF DISPERSE NITRODIPHENYLAMINE DYES ON ACETATE

Dye structure (XXXVIII)[a]			
R	*R_1*	*CI disperse color*	*Lightfastness (CI)*
NO_2	H	Yellow 14	3–4
NO_2	OH	Yellow 1	4–5
NO_2	NH_2	Yellow 9	5
SO_2NHPh	H	Yellow 42	6–7
H	Cl	Yellow 22	7
Cl	H	Yellow 26	7
Cl	OMe	Orange 15	7

[a]

(XXXVIII)

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[94] R. S. Asquith and B. Campbell, *J. Soc. Dyers Colour.* **79**, 678 (1963).

[95] R. E. Todd, R. S. Asquith, and A. T. Peters, *Am. Dyest. Rep.* **55**, 560 (1966).

[96] R. S. Asquith, E. Coates, A. T. Peters, and R. E. Todd, *J. Soc. Dyers Colour.* **81**, 360 (1965).

[97] R. S. Asquith, A. T. Peters, and F. Wallace, *J. Soc. Dyers Colour.* **84**, 507 (1968).

[98] A. T. Peters, *J. Appl. Chem. & Biotechnol.* **23**, 751 (1973).

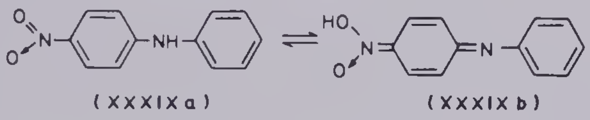
TABLE XVI

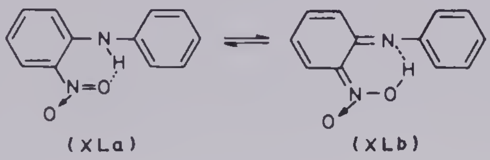
EFFECT OF NITRO SUBSTITUTION ON LIGHTFASTNESS OF SOME NITRODIPHENYLAMINE DYES ON SECONDARY CELLULOSE ACETATE[97]

Position of nitro groups	$\epsilon_{\max}$[a]	*Lightfastness*
2	7762	8
3	1125	2–3
4	26920	1–2
2,2′	8172	8
3,3′	1504	2
4,4′	39792	1
2,4′	13680	2 or 2–3
3,4′	22616	1–2
2,3′	6572	8
2,6	7943	8
2,4	16220	2

[a] Extinction coefficient at the longest wavelength absorption maximum of the dye in ethanol solution.

(XXXIX) and 2-nitrodiphenylamines (XL). It was suggested that the extinction coefficient of the longest wavelength absorption maximum in these dyes is an approximate measure of the proportion of the dye present in the quinonoid form. On this basis, the extent of quinonoid formation in mononitrodiphenylamines is in the order: 3-nitro < 2-nitro < 4-nitro, while the order with respect to lightfastness on secondary acetate is found to be 4-nitro < 3-nitro < 2-nitro. However, the quinonoid theory does not explain the high lightfastness of 2-nitrodiphenylamines, which are able to form intramolecular hydrogen bonds, and it is believed that these bonds are able to stabilize the *ortho*-quinonoid structure (XLb) in its excited state, presumably by increasing


(XXXIXa) (XXXIXb)


(XLa) (XLb)

the rate of nonradiative decay to the ground state. Intramolecular hydrogen bonding has been proposed to explain the enhanced photostability of a range of organic compounds,[99,100] including anthraquinone (Section III,B) and quinophthalone dyes (Section VII,D).

The existence of internal hydrogen bonding in 2-nitrodiphenylamines has been deduced from PMR spectroscopy in both polar and nonpolar solvents, whereas 2,4-dinitrodiphenylamines appear to be hydrogen bonded only in nonpolar solvent.[101] However, when a strongly electron-donating substituent is present in the non-nitrated ring (R′ in structure XXXVIII) of the dinitro dyes, evidence for intramolecular hydrogen bonding is found in both types of solvent. This type of substitution pattern can also be seen from Table XV to confer high lightfastness on a nitrodiphenylamine dye, thereby supporting the concept of hydrogen bonding as a photostabilizing influence.

The lightfastness ratings of a series of 2,6-dinitrodiphenylamines on acetate, triacetate, and polyester (in the range 3–4) indicate that this nitration pattern lowers the photostability in comparison to the 2-nitro dyes[98]; the electronic absorption spectra of the 2,6-dinitro dyes indicated that stabilization by hydrogen bonds is less favored in comparison to 2-nitrodiphenylamines. However, the inclusion of a 4-methoxyl group, which is known to stabilize intramolecular hydrogen bonds (see above), brought about a marginal improvement in lightfastness within the series.

The effects of substitution pattern on the order of lightfastness ratings of nitrodiphenylamines are independent of the nature of the substrate,[95] which suggests that the operative mechanism of fading is consistent for all fibers. In general, however, this class of dye is most stable on Courtelle and least stable on nylon, polyester, and Acrilan. However, this may be due to the presence of the delustering agent titanium dioxide, which is known to reduce the lightfastness of some disperse dyes.[35]

V. Triarylmethane Dyes

The triarylmethane (TAM) dyes are characterized by their brilliance of shade and high tinctorial strength. Their great disadvantage, in most cases, is their low lightfastness on natural fibers. The vast majority of cationic TAM dyes in CI are of lightfastness 1 on wool, silk, or cotton,

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[99] R. Pater, *J. Heterocycl. Chem.* 7, 1113 (1970).

[100] B. Ranby and J. F. Rabek, "Photodegradation, Photooxidation and Photostabilization of Polymers," pp. 372–378. Wiley, New York, 1975.

[101] D. J. Gale and J. F. K. Wilshire, *Aust. J. Chem.* **25**, 2145 (1972).

while the anionic dyes (those containing two or more sulfonate groups) show a wider range in fastness on wool (1 to 4–5), with an average value around 2. Since the 1950s, the interest in cationic TAM dyes has steadily increased due to the moderately high lightfastness they show when applied to basic-dyeable polyacrylonitrile fibers.

Apart from the substrate, external agents such as oxygen and water have a marked effect on the rate of fading of TAM dyes. Two dyes of this class, CI Basic Blue 18 and CI Basic Blue 26 were selected by Schwen and Schmidt[102] for an investigation into the relative importance of substrate and atmospheric components in determining lightfastness. The results are shown in Table XVII. Both dyes can be seen to give a higher daylightfastness on Orlon than other fibers, while oxygen, especially in the case of Orlon, has a profound influence on the fading rate. The presence of water can also be seen to influence the fastness but to a lesser degree than oxygen. Schwen and Schmidt

TABLE XVII

EFFECT OF ENVIRONMENT ON SUNLIGHT-FADING OF TRIARYLMETHANE DYES[a]

	Lightfastness				
		Oxygen		*Nitrogen*	
Substrate	*Open tube*	*Moist*	*Dry*	*Moist*	*Dry*
	CI Basic Blue 18 (CI 42705)				
Cotton	1	$\ll 1$	1	2–3	3
Viscose rayon	2	$\ll 1$	1–2	1	2
Cellulose acetate	1–2	$\ll 1$	2–3	5–6	6
Silk	2–3	<1	2–3	4	5–6
Wool	1–2	1	2–3	3	3–4
Orlon	4	1–2	3–4	7	7
	CI Basic Blue 26 (CI 44045)				
Cotton	<1	<1	<1	1–2	3–4
Viscose rayon	$\ll 1$	$\ll 1$	$(<)<1$	$\ll 1$	<1
Cellulose acetate	<1	<1	1	3–4	4
Silk	<1	$(<)<1$	$(<)1$	2	3–4
Wool	1	$(<)<1$	1	2–3	3–4
Orlon	2–3	2	2–3	6	6

[a] Taken from Schwen and Schmidt.[102] Parentheses indicate intermediate values; Thus, $(<)<1$ lies between <1 and $\ll 1$.

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[102] G. Schwen and G. Schmidt, *J. Soc. Dyers Colour.* **75**, 101 (1959).

concluded from these results: "The normal lightfastness value is, as we have shown, obviously a composite value, and the relationship between the individual values seems to be governed by laws which are as yet unknown." In many respects, this statement is just as valid today as it was in 1959. Many proposals have been advanced to account for the roles water and oxygen play in the photofading reaction of TAM dyes, but a definitive proof is still awaited.

The reason for the higher lightfastness shown by TAM dyes on basic-dyeable polyacrylonitrile fibers (e.g., Orlon) compared to that exhibited on other substrates has been investigated in some detail by several workers.[103–108] Wegmann[103] claimed that a relationship exists between the lightfastness of TAM dyes on Orlon and the basicity of the dye cation—the more basic the cation, the lower the lightfastness of the dyed fiber (Table XVIII). In the case of 4-aminotriphenylcarbonium chloride the following modifications resulted in a decrease in lightfastness: (a) methylation of the amino group, and (b) the introduction of

TABLE XVIII

LIGHTFASTNESS OF *N*-METHYLATED MONO-, DI, AND TRIAMINOTRIPHENYLMETHANE DYES ON POLYACRYLONITRILE (ORLON 42) AND WOOL

Number of N-methyl (or phenyl) groups*	*Number of amino groups*			*Fiber*[a]
	1	2	3	
0	7	6	5	Orlon
	1	1	2	Wool
1	2	1–2	—	Wool
2	6	3	2	Orlon
	2	1–2	1	Wool
1*	—	6–7	6	Orlon
	—	2–3	—	Wool

[a] Ratings for Orlon taken from Wegmann[103]; ratings for wool by Evans and Stapleton (unpublished).

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[103] J. Wegmann, *Melliand Textilber.* **39**, 408 (1958).

[104] D. Bitzer and H. Brielmaier, *Melliand Textilber.* **41**, 62 (1960).

[105] J. J. Porter and S. B. Spears, *Text. Chem. Color.* **2**, 191 (1970).

[106] H. Zollinger, *Am. Dyest. Rep.* **54**, 634 (1965).

[107] R. F. Johnson, O. A. Stamm, and H. Zollinger, *Opt. Anregung Org. Syst., Int. Farbensymp., 2nd, 1964* p. 375 (1966).

[108] M. Pestemer, *Opt. Anregung Org. Syst., Int. Farbensymp., 2nd, 1964* p. 475 (1966).

further amino functions. Both substituent modifications were found to increase the basicity of the dye. Such a correlation does not hold when wool is the substrate (Table XVIII), a result that suggests that different fading mechanisms may be operating on the two fibers.

Wegmann[103] explains the basicity–fastness relationship by a consideration of the nature of the bond between the dye cation and the fiber sulfonate group; as the basicity of the dye decreases, the dye–fiber interaction becomes less electrostatic in character. This change in bond type is thought to lead to a closer union between the dye molecule and the fiber binding site, such that the absorbed energy is dissipated through nondestructive pathways, which in turn results in a dyeing of higher lightfastness.

On the basis of this concept, Bitzer[104] modified cotton by the introduction of carboxyl groups in an attempt to provide similar bonding interactions to those prevailing in modified polyacrylonitrile fiber. The carboxyl groups were introduced by several methods—oxidation of primary hydroxyl groups, carboxyethylation, and carboxymethylation. Only in the last modification was an increase in lightfastness (1 point) observed for TAM dyes.

In a detailed examination of the photodecomposition of Malachite Green (CI Basic Green 4) on cellulosic substrates, Porter and Spears[105] reported that the fading rate on sulfoethylated cotton was slower by a factor of 5–10 compared to that observed on carboxymethylated or untreated cotton. These workers also isolated and identified the major photodecomposition products and found them to be identical for each of the three substrates. This finding implied that the mechanism of photodecomposition was the same on both modified substrates, and therefore, the difference in the fading rate was believed to be due to the change in concentration of the carbinol base (Ar_3COH) as determined by the pK_a of the dye binding site (0.5 in the case of sulfoethylated cotton and 3.7 for carboxymethylated cotton). A decomposition mechanism was proposed in which the excited state (possibly triplet) was generated from the carbinol form of Malachite Green. Consequently, strongly anionic binding sites, which can force a high proportion of the dye to be present as the carbonium ion (Ar_3C^+), will impart an increased photostability to the dye.

Zollinger[106] has put foward an alternative proposal to account for the difference in lightfastness shown by cationic–TAM-dyed fibers, where the binding sites are either carboxyl or sulfonate groups. When a carboxylate group is the counterion, it is postulated that an excited state of the dye abstracts an electron, forming a carboxyl radical (which readily decomposes to carbon dioxide) and a residual radical within the fiber. A recombination reaction with the dye radical is no longer possible, and therefore, the dye radical decomposes irreversibly. On the other hand, sulfonate ions have little tendency to form radicals and lose SO_3, and therefore, the excited state of the dye decays back to the ground state.

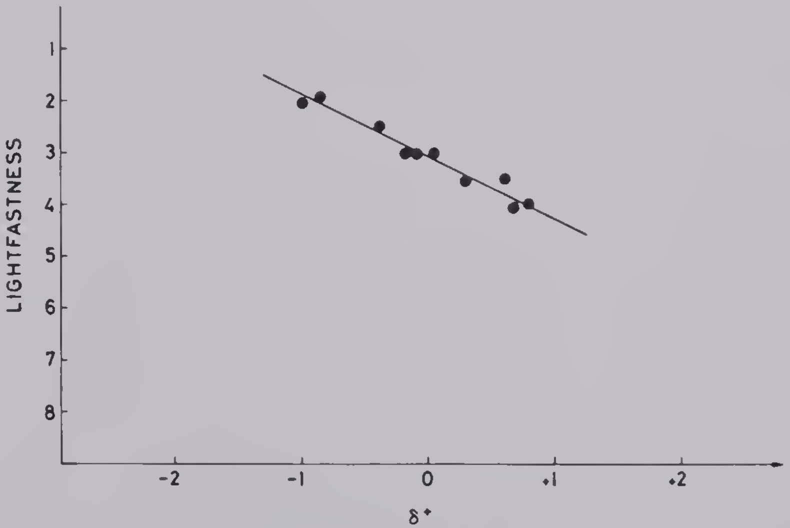

FIG. 8. Lightfastness of substituted Malachite Green on Orlon 42 as a function of the Hammett substituent constant δ^+.[106]

Investigations[106,107] of Malachite Green carrying a substituent in the third benzene ring have shown that if δ^+ substituent constants are used, a Hammett free energy relationship can be applied to the rates of fading on basic-dyeable acrylic and polyester substrates (Orlon 42 and Dacron 64) (Fig. 8); δ^+ substituent constants have been used[109] for reactions in which a positive charge is localized on the group involved in the reaction. The negative ρ value as revealed by the Hammett plot indicated that the fading reaction is an oxidation process, although Zollinger[106] has discussed several alternative explanations of the observed substituent effects. It is to be noted that the Hammett relationship is observed only for fibers containing sulfonate groups and does not hold for TAM dyes on modified cotton[106,107] or wool.[110]

A systematic study aimed at identifying the factors responsible for the higher lightfastness (compared to triphenylmethane acid dyes) shown by the indolyldiphenylmethane dye CI Acid Blue 123 on wool[110] showed that the series of structural variants (XLI) could be divided into two groups according to the nature of their *N*-substituents: (a) the

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[109] H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.* **80**, 4979 (1958).

[110] N. A. Evans and I. W. Stapleton, *J. Soc. Dyers Colour.* **89**, 208 (1973).

(XLI)

N-aryl series, which exhibited a lightfastness 2–3 or higher; and (b) the *N*-alkyl series, which exhibited a fastness of 1–2 or lower. Within the *N*-aryl group (Table XIX), minor improvements in fastness were apparent when the dye was converted into an acid type by the introduction of two sulfonic acid groups (see above). Other structural features, such as methylation of the indole nitrogen, presence of an ethoxy group on the *N*-aryl ring and a phenyl group at the 2-position of the indole ring, all appear to have minor additive roles in improving the lightfastness of the parent chromophore up to the ultimate rating of 3–4 for a wool dyeing.[110]

TABLE XIX

LIGHTFASTNESS OF INDOLYLDIPHENYLMETHANE DERIVATIVES (XLI) ON WOOL[110]

R_1	R_2	R_3	R_4	*Lightfastness*
Me	Ph	$C_6H_3(OEt)(SO_3Na)$	H	3–4[a]
Me	Ph	p-$(EtO)C_6H_4$	H	3
Me	Ph	$C_6H_4SO_3Na$	H	3
Me	Ph	Ph	H	2–3
Me	Me	p-$(EtO)C_6H_4$	H	2–3
Me	H	p-$(EtO)C_6H_4$	H	2–3
H	Ph	p-$(EtO)C_6H_4$	H	2–3
n-Bu	p-$(C_6H_4)Ph$	p-$(EtO)C_6H_4$	H	2–3
Me	Ph	Me	Me	1
Me	Ph	Me	H	1–2[b,c]
H	Me	Me	Me	1
H	Me	Me	H	1–2[b]

[a] CI Acid Blue 123.

[b] These dyes contain a methyl group ortho to the amino group.

[c] CI 44520 (Brilliant Rhoduline Violet R).

Some insight into the structural factors affecting the lightfastness of TAM dyes has been obtained from an examination of the photoproducts of Malachite Green (CI Basic Green 4; CI 42000) in aqueous solution,[105,111,112] in the solid state,[112,113] and on chemically modified cellulose[105] and wool.[114] Two modes of photodegradation have been observed: (a) *N*-dealkylation in aqueous solution[111] and on wool[114] and (b) oxidation to yield 4-dimethylamino and 4-monomethylaminobenzophenone in aqueous solution,[105,112,114] in the solid state,[112,113] and on carboxymethylated and sulfoethylated cotton[105]; *p*-dimethylaminophenol was also found in the last study. The phenomenon of photodealkylation provides the basis for an alternative mechanism to that proposed by Wegmann[103] for the lightfastness variation shown by TAM dyes on Orlon (Table XVIII). *N*-Dealkylation, which is a common event in dye photochemistry, having been observed with *N*-methylaminoanthraquinones,[73–75] rhodamines,[115] and thiazines,[116,117] has also been suggested as an explanation for the lower lightfastness exhibited by certain anthraquinone disperse dyes on polyester compared with acetate or nylon.[74] However, as those dyes that contain *N*-alkyl groups are also the most basic, it is difficult to distinguish between these two mechanisms.

The identification of benzophenone derivatives and *p*-dimethylaminophenol as photoproducts from the irradiation of Malachite Green enabled Porter and Spears[105] to propose a fading mechanism in which the excited state (derived from the dye carbinol base) either fragments into radicals (which eventually form the isolated products) or reacts directly with oxygen and water.

The significance of the carbinol base has been mentioned earlier in the discussion on the variation in fading rates found on certain modified cellulose substrates. Evidence in support of the involvement of this species, rather than the cation, in the photolytic pathway is provided by results of fading rate studies in solution, which show that the rate becomes slower as the acidity of the solvent is increased (over the pH range 1–5). This hypothesis is strengthened by the fact that phloracetophenone, which absorbs in the same spectral region as the carbinol base, protects the dye from photodegradation.[104] The observation that certain TAM dyes on Dacron T-64 fabric are stable to sunlight irradiation when wavelengths below 420 nm are filtered out[14] also

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[111] P. C. Henriquez, *Rec. Trav. Chim. Pays-Bas* **52**, 991 (1933).

[112] C. M. Desai and B. K. Vaidya, *J. Indian Chem. Soc.* **31**, 261 (1954).

[113] K. Iwamoto, *Bull. Chem. Soc. Jpn.* **10**, 420 (1935).

[114] N. A. Evans and I. W. Stapleton, unpublished data.

[115] N. A. Evans, *J. Soc. Dyers Colour.* **89**, 332 (1973).

[116] Z. Yoshida and K. Kazami, *Kogyo Kagaku Zasshi* **59**, 1418 (1956); *CA* **53**, 2821 (1959).

[117] H. Obata, *Bull. Chem. Soc. Jpn.* **34**, 1057 (1961).

supports the involvement of the carbinol and not the colored carbonium ion as the species that absorbs destructive radiation. On the basis of this mechanism, the enhanced lightfastness of TAM dyes on Orlon can be explained in terms of a rapid deactivation of the excited state of the carbinol base by the sulfonate anion according to the manner suggested by Zollinger.[106]

It is not yet known how structural modifications to TAM dyes affect the rates of formation of benzophenones or the excited states in the photochemical reactions.

VI. Polymethine and Methine Dyes

Interest in the cationic polymethine dyes was stimulated by the finding that these dyes show a significantly higher lightfastness on polyacrylonitrile fibers (such as Orlon 42) than on most other fibers;[102,103] examples of this are shown in Table XX. The influence of oxygen and water on the lightfastness of polymethine dyes is marked, with fastness

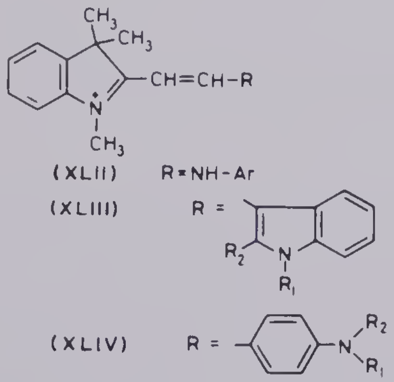
TABLE XX

Effect of Dye Environment on Lightfastness of Some Polymethine Dyes[a]

	Lightfastness				
		Oxygen		Nitrogen	
Substrate	*Open tube*	*Moist*	*Dry*	*Moist*	*Dry*
CI Basic Orange 22 (CI 48040)					
Cotton	1	$\ll 1$	1	3–4	5
Viscose rayon	3–4	2	3	4	5–6
Acetate	5	4	4–5	5	6
Silk	4–5	2–3	3	4–5	5–6
Wool	4	2–3	3	4	4–5
Orlon	5	3–4	4–5	6	6–7
Astra Violet FN Extra (CI 48075)					
Cotton	< 1	< 1	1–2	4–5	5–6
Viscose rayon	$\ll 1$	$\ll 1$	< 1	4–5	5
Acetate	$\ll 1$	$\ll 1$	< 1	5–6	4–5
Silk	$\ll 1$	$\ll 1$	< 1	6	6
Wool	$\ll 1$	$\ll 1$	< 1	6	6
Orlon	3	1	2	6	6

[a] Taken from Schwen and Schmidt.[102]

being observed to vary from 1 to 6–7 depending on the fiber and atmospheric components. The reasons for such a wide variation are not yet known, although the indications are that the dye is photodegraded by an oxidation process in which molecular oxygen plays a more significant role than water.



(XLII) R = NH–Ar

(XLIII) R =

(XLIV) R =

The lightfastness of the dyes derived from Fischer's base is dependent on the other half of the dye molecules. The fastness ratings are commonly 6 for dyes of structure (XLII), 5 for (XLIII), and 4 for (XLIV) on basic-dyeable polyacrylonitrile fibers.[103,118] On wool, the respective lightfastness ratings are in the ranges 3–4, 3–4, and 1–2.[119] The extent of conjugation in the chromophore appears to have some influence on the lightfastness of polymethine dyes on wool; the dyes with the shortest conjugate chain length (XLII) show the highest fastness, while those with the most extended conjugate chain length (XLIV) are the least fast.[119]

Little attention appears to have been paid to the reasons underlying the enhanced lightfastness shown by this class of dye on Orlon-type fibers compared with other substrates.

Only three disperse methine (or styryl) dyes are listed in CI, and they show a lightfastness of at least 5 on synthetic fibers. Irick and Straley[120] have synthesized a range of yellow to red methine dyes (XLV) by the reaction of 1,3-indandione with a substituted *p*-aminobenzaldehyde. The color of the dyeings and their fastness to light were related to the electron-donating character of the amino function. As the substituent became more electron-donating in character, the wavelength of the absorption maximum was observed to increase, and

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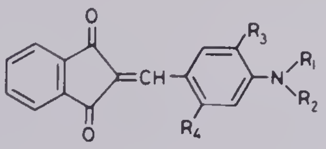
[118] S. N. Nagaraji and S. V. Sunthankar, *J. Sci. Ind. Res., Sect. D* **20**, 378 (1961).

[119] J. B. Caldwell, N. A. Evans, D. J. Gale, I. W. Stapleton, and J. F. K. Wilshire, *J. Soc. Dyers Colour.* **89**, 94 (1973).

[120] G. Irick and J. M. Straley, *Text. Chem. Color.* **1**, 278 (1969).



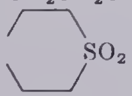
(XLV)

at the same time, the lightfastness of a dyeing on cellulose ester (Estron) and polyester (Dacron and Kodel II) decreased (see Table XXI). Those dyes with an absorption maximum at 473 nm or lower showed an average lightfastness of 2–3, while those which absorbed at 475 nm or higher showed an average fastness of 1. These results contrast with those given by cationic dyes derived from Fischer's base, where variations in amino substituents showed little influence on the lightfastness.

The variation in lightfastness resulting from changes in the electronic character of the substituents on the disperse dyes (XLV), is consistent with a photooxidative mechanism, since the ease of oxidation increases with the electron density at the site of oxidation, presumably the ethylenic bond.

TABLE XXI

Lightfastness and Absorption Maxima of Some Methine Dyes (XLV) Derived from Indandione[120]

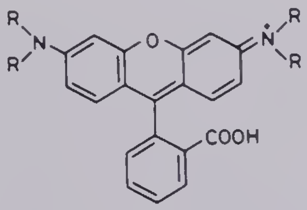
Structure				λ_{max} (*acetone solution*)	*Lightfastness*[a]		
R_1	R_2	R_3	R_4	(*nm*)	*Estron*	*Kodel II*	*Dacron*
CH_2CH_2Cl	CH_2CHF_2	H	H	456	3	4	4
CH_2CH_2Cl	CH_2CH_2CN	H	H	460	1	4	4
CH_2CH_2Cl	CH_2CH_2Cl	H	H	460	1	2	2
CH_2CH_2Cl	CH_2CH_2Cl	H	Cl	461	3	3	3
	 SO_2	H	Me	463	3	1–2	3
CH_2CH_3	CH_2CH_2CN	H	H	468	2	1	2
CH_2CH_2Cl	CH_2CH_2Cl	H	Me	473	2	4	4
CH_2CH_2Cl	CH_2CH_2Cl	H	OMe	473	2	1	3
p-$EtOC_6H_4$	Me	H	H	475	1–2	1	2
Ph	CH_2CH_2Cl	H	OMe	476	1	1–2	1–2
Me	Me	H	H	480	1	1	1
CH_2CH_3	CH_2CH_3	H	MeCOO	482	1	1	1
CH_2CH_2Cl	CH_2CH_2Cl	OMe	OMe	496	1	1	1

[a] Lightfastness ratings are based on a visual scale of 1 (considerable fading) to 5 (no fading) after 20 hours of exposure in an Atlas carbon-arc Fade-Ometer.

VII. Heterocyclic Dyes

A. Xanthene Dyes

The most commonly used xanthenes in textile dyeing are the rhodamines (XLVI; R = alkyl or aryl) and certain sulfonated derivatives.



(XLVI)

Those rhodamines containing *N*-alkyl groups possess unique coloration properties as a result of their narrow visible absorption band, combined with a strong fluorescence emission from the first singlet excited state. It seems that the structural features of rhodamine dyes that contribute to their unique shade are also those responsible for the low lightfastness.

Two types of photochemical reaction have been observed with Rhodamine B (XLVI; R = Et) in solution and on wool[115]: (a) *N*-dealkylation as evidenced by a hypsochromic shift in the absorption maximum of the dye solution and isolation of dealkylated photoproducts and (b) destruction of the chromophore itself. The possible significance of the *N*-dealkylation reaction as an underlying cause for the low lightfastness of rhodamine dyes on wool, can be seen from the higher fastness shown (Table XXII) by dyes lacking alkyl groups (with the exception of *N*,*N*-diethylrhodamine).

TABLE XXII

Lightfastness of Rhodamine Dyes (XLVI) on Wool[115]

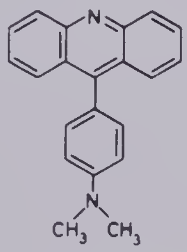
Dye	*Lightfastness*
Rhodamine (R = H)	3
N,*N*-Diethylrhodamine	3
N,*N*′-Diethylrhodamine	1
N,*N*,*N*′-Triethylrhodamine	1
Rhodamine B (R = Et)	1
N,*N*′-Diphenylrhodamine	2–3

It is of interest to note that those members of the series that give a relatively high lightfastness on wool also exhibit a less intense fluorescence; two relatively lightfast dyes, rhodamine and its *N*-diethyl analog, while fluorescent in solution, are nonfluorescent on wool. This observation suggests that the first excited singlet states of the lightfast rhodamine dyes are much shorter lived than those of the fugitive fluorescent dyes, which have more opportunity to undergo chemical reaction from the singlet or triplet (formed by intersystem crossing) excited states.

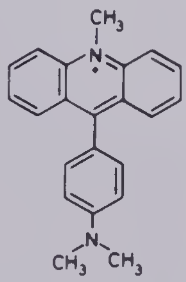
By analogy with the structurally related triarylmethane dyes, it would be expected that the lightfastness of rhodamine dyes would be dependent on the nature of the substrate. There is some evidence in support of this view; in lacquers, Rhodamine B and 6G show markedly different fastness properties: 1–2, 3–4, and 5 on shellac, nitrolac, and polyurethane, respectively.[108] In polymer films[121] and in solution,[122,123] the photostability of rhodamine dyes is markedly dependent on the immediate environment. Certain conclusions regarding the substrate properties that can influence lightfastness were drawn from studies on the photostability of Rhodamine 6G in a range of polymer films.[121] Most significant was the effect of acidic groups within the polymer; for example, the photostability of the dye was increased by a factor 40 in sodium poly(styrene sulfonate) compared with polystyrene and was reduced by a factor of 286 in poly(styrenesulfonic acid) compared with polystyrene. It is possible that the sulfonate anion stabilizes the dye in the manner suggested by Zollinger[106] to account for the enhanced photostability of TAM dyes on basic-dyeable polyacrylonitrile (see Section V).

B. ACRIDINE DYES

Most of the acridine dyes in CI are derived from salts of 3,6-diaminoacridine, but because of their poor fastness properties, they are seldom used as textile dyes. Recently, however, derivatives of 9-phenylacridine and their salts have been described as dyes for acrylic and modacrylic



(XLVII)



(XLVIII)

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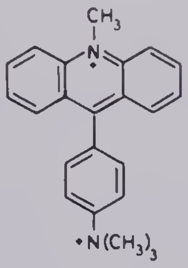
[121] N. A. Evans and P. J. Waters, *Proc. Int. Wool Text. Res. Conf., 5th, 1975*, **III**, 567 (1977).

[122] W. Schultze, *Melliand Textilber.* **47**, 537 (1966).

[123] N. A. Evans, *Text. Res. J.* **46**, 144 (1976).



(XLIX)

fibers.[124] In general, the lightfastness can be related to the number of unit charges on the chromophore. For example, the fastness (based on a 1 to 5 assessment scale) of the acridine (XLVII) is 3, the monocation (XLVIII) 3–4, and the dication (XLIX) 5. This increase in photostability with increasing cationic charge is consistent with the proposal that the lone-pair electrons on the nitrogen atoms are implicated in the photodegradative pathway of the fading reaction.

TABLE XXIII

Effect of Substrate, Oxygen, and Water on Lightfastness of Oxazine Dyes[102]

	Lightfastness[a]				
		Oxygen		*Nitrogen*	
Fiber	*Open tube*	*Moist*	*Dry*	*Moist*	*Dry*
CI Basic Blue 3 (CI 51005)					
Cotton	2–3	1	1–2	3–4	4–5
Viscose	2–3	1–2	2	2	3
Acetate	3–4	3	4–5	3–4	3–4
Silk	2	2	3	1	2–3
Wool	1–2	< 1	2	< 1	1–2
Orlon	5–6	4	4–5	> 7	> 7
CI Basic Blue 12 (CI 51180)					
Cotton	2	1	2–3	4–5	6
Viscose	1	≪1	1–2	3–4	5
Acetate	2–3	1–2	2–3	3–4	4–5
Silk	1	(<)1	1–2	2–3	4–5
Wool	2	1	2–3	3–4	4
Orlon	3	2	2	> 6	> 6

[a] Parentheses indicate intermediate values; thus, (<)1 lies between 1 and < 1.

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[124] G. Irick, *Text. Chem. Color.* 1, 423 (1969).

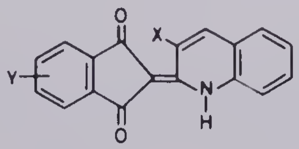
C. OXAZINES AND THIAZINES

Oxazine dyes, such as CI Basic Blue 3 and 12, belong to a small group of little significance in textile applications. While little is known concerning the structural factors that influence their photostability, it has been shown that the substrate, water, and oxygen can affect the rate of fading (Table XXIII).[102] The dyes show the highest lightfastness on Orlon, which may be due to factors already mentioned in connection with other basic dyes (see Sections V and VII,A). The presence or absence of oxygen can be seen to affect the lightfastness more markedly on certain substrate fibers than on others. No explanation is available to account for this behavior.

Thiazine dyes, which are formally related to the oxazines by replacement of oxygen by sulfur in the hetero ring (Methylene Blue is a well-known example) are of generally low lightfastness. For example, Methylene Blue has a lightfastness of 1 on wool or silk, 3 on tannin-mordanted cotton (data from CI), and 3 on Orlon.[103]

D. QUINOPHTHALONES

The fastness to light of quinophthalone (sometimes classed as quinoline) dyes (L) on polyester[125] and on polyvinyl chloride (PVC)[126] depends mainly on the nature of the substituent X (Table XXIV). In most cases, the lightfastness is low when X is hydrogen and high when X is hydroxyl; two exceptions to this rule are the dyes in which positions 4 to 7 are all substituted by chlorine or bromine.



(L)

The effect of the hydroxyl group is presumably related to its ability to form an intramolecular hydrogen bond with the adjacent carbonyl oxygen atom, thereby increasing the rate of internal conversion from the first excited singlet state. This would effectively decrease the lifetime of this reactive photochemical intermediate and hence slow the rate of fading. It has been established that intramolecular hydrogen bonding increases the rate of internal conversion of a wide range of compounds,[99,100] and is thought to be the reason for the high photostability of certain nitrodiphenylamine dyes (see Section IV) and

---

[125] M. Matsuoka, H. Shiozaki, T. Kitao, and K. Konishi, *Kogyo Kagaku Zasshi* **74**, 1390 (1971); *CA* **75**, 110983 (1971).

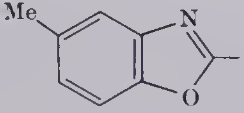
[126] B. K. Manukian, P. Nicklaus, and H. Ehrsan, *Helv. Chim. Acta* **52**, 1259 (1969).

TABLE XXIV

LIGHTFASTNESS OF QUINOPHTHALONE DYES (L) ON POLYESTER[125] AND PVC[126]

Substituents		*Lightfastness*	
X	*Y*	*Polyester*	*PVC*
H	H	1	1
OH	H	>6	8
H	4-NO_2	3	—
OH	4-NO_2	>6	—
H	5-COOH	3–4	1
OH	5-COOH	>6	6–7
H	5-R[a]	4	—
OH	5-R	>6	—
H	Cl_4	>6	2–3
OH	Cl_4	>6	8
H	Br_4	>6	—
OH	Br_4	>6	—

[a] R =



hydroxy- and aminoanthraquinones (Section III,B). A survey of CI reveals that the average lightfastness of sulfonated quinophthalones on wool is about 2, and on Orlon 6 to 7.

E. INDIGOID DYES

The chemistry of indigoid dyes has been extensively reviewed,[127] and CI lists fastness data for an extensive range of structures. There are three major classes of indigoid dye—indigo and its derivatives, thioindigo and its derivatives, and indolethianaphthene dyes. The lightfastness of the indigo series, with one exception, is relatively independent of the substituents attached to the aromatic rings. The exception is sulfonated indigo, which has a lightfastness of 1–2 on wool; indigo has lightfastness 7–8. This is probably the most dramatic example of the way in which simple substitution can affect lightfastness. Another unusual facet of the photochemical behavior of indigo derivatives is the fact that their lightfastness on wool is generally much higher (3–4 points) than on cotton, and 1–2 points higher than on silk.

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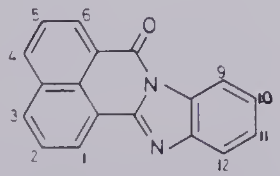
[127] *CSD II*, p. 1003.

The thioindigo and indolethianaphthene dyes show 1–2 points higher fastness on cotton than the indigo derivatives, while their light stability on wool seems to be somewhat dependent on the substitution pattern, although it is not clear which positions and substituents are critical.

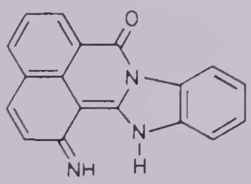
The photochemical reactions of indigo and thioindigo have been studied in several laboratories. Hibbert *et al.*[128,129] have isolated isatin and dibromoisatin from photodegraded cotton fabric dyed with indigo and tetrabromoindigo, respectively; the authors suggested that an oxidative pathway is involved in the fading of indigo-dyed cotton. This conclusion conforms to the general principle outlined by Giles,[130] who states that the fading of dyes on nonprotein substrates is an oxidation process and on protein substrates, such as wool, a reduction process.[33,130] If the chromophore is resistant to photoreduction, as could be the case with indigoid dyes, then wool dyeings would be expected to show a high fastness to light.

F. Dyes Derived from Naphthalene 1,8-Dicarboxylic Anhydride

Several photochemical studies have been reported on heterocyclic dyes based on the naphthalene 1,8-dicarboxylic anhydride ring system. Yellow, orange, and red fluorescent disperse dyes of the general structure (LI), have been applied to polyester, polyamide, and, to a lesser extent, acrylic fibers.[131] Their lightfastness properties (Table XXV) depend to a marked extent on the substituents attached to the aromatic rings and on the nature of the fiber substrate.[131,132] The dyeings on polyester are faster to light than on nylon for reasons not yet explained, and among the substituents, it appears that only amino and nitro groups have an adverse effect on the fastness. The loss in photostability arising from the amino group may be partly explained by its participation in quinonimine structures such as (LII), which are believed to be



(LI)



(LII)

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[128] E. Hibbert, *J. Soc. Dyers Colour.* **43**, 292 (1927).

[129] F. Scholefield, E. Hibbert, and C. K. Patel, *J. Soc. Dyers Colour.* **44**, 236 (1928).

[130] C. H. Giles, C. D. Shah, W. E. Watts, and R. S. Sinclair, *J. Soc. Dyers Colour.* **88**, 433 (1972).

[131] J. Arient, J. Marhan, and L. Havlickova, *J. Soc. Dyers Colour.* **85**, 246 (1969).

[132] P. H. Grayshan and A. T. Peters, *J. Heterocycl. Chem.* **10**, 705 (1973).

TABLE XXV

LIGHTFASTNESS OF DISPERSE DYES (LI)[131,132]

Substituent[a]	Lightfastness[b]	
	Polyester	*Polyamide*
None	6–7	4
1-Nitro	4–5	1
2-Nitro	5–6	1
3-Nitro	3 or 4–5*	2
4-Nitro	5	2
5-Nitro	7	1
6-Nitro	6–7	1
1-Amino	2–3	—
3-Amino	5*	2–3*
2,10-Diamino	1*	1–2*
3-Acetamido	6*	5–6*
11-Acetamido	6–7*	3*
11-Methoxy	6–7*	5–6*
2- and 5-bromo	6–7	—
10- and 11-carbomethoxy	7	2–3
11-Methyl	6–7*	4*

[a] Where two structures are given, the dye sample was a mixture of two isomers.

[b] Ratings marked by an asterisk were taken from Arient *et al.*,[131] the remainder from Grayshan and Peters.[132]

photochemically reactive [quinonoid structures have been implicated in the fading mechanism of certain nitrodiphenylamine dyes (see Section IV)]. The low lightfastness of the nitro-substituted dyes may also be a result of the reactivity of a quinonoid structure.

The benzimidazothioxanthenoisoquinolinones (LIII) are a related series of dyes whose lightfastness properties on polyester have been investigated.[133] In general, the substituent R has no effect on lightfastness, with the exception of the nitro group which had a moderate lowering effect.

Disperse dyes of structure (LIV) show a lightfastness dependence on the substituents X and Y and not on the substituent pattern in the diaminonaphthalene portion of the molecule (Table XXVI).[134]

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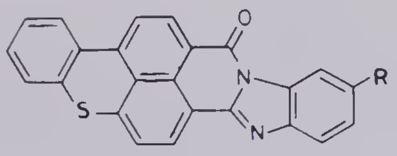
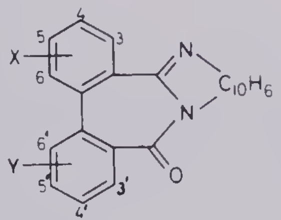
[133] A. M. Kadhim and A. T. Peters, *J. Soc. Dyers Colour.* **90**, 199 (1974).

[134] T. Sekiguchi, M. Tanaka, and H. Umezu, *Nippon Kagaku Kaishi* p. 1389 (1975); *CA* **83**, 149082 (1975).



(LIII)



(LIV)

(LV)

TABLE XXVI

LIGHTFASTNESS OF DYES (LIV)[134]

Substituent			*Lightfastness (on PVC)*
X	*Y*	*Naphthalene*	
H	H	1,2	
5-Cl	5′-Cl	1,2	7
4-Cl	4′-Cl	1,2	7
H	H	1,8	3
5-Cl	5′-Cl	1,8	7
4-Cl	4′-Cl	1,8	8
H	H	2,3	3
5-Cl	5′-Cl	2,3	6–7
4-Cl	4′-Cl	2,3	7

The lightfastness of 4-amino-3-nitro-1,8-naphthalimides (LV) on polyester has been shown to be responsive to the type of substituent R_1 attached to the 4-amino group[135]; when R_1 is a *p*-methoxyphenyl group, the dye shows a rating of 5–6, which is lowered to 1–2 when an alkyl group is present. The variation in fastness that results from an alkylarylamino substituent group replacement is common to several classes of dyes, for example, TAM dyes (see Section V) and anthraquinone acid and disperse types (see Sections III,A and B). As already discussed, this variation may be due either to a change in basicity or to a photochemical dealkylation reaction.

[135] A. M. Kadhim and A. T. Peters, *J. Soc. Dyers Colour.* **90**, 153 (1974).

VIII. Reactive Dyes

If a reactive dye is considered as a solubilized chromophore to which is attached a reactive group, then intuitively one would expect the lightfastness to be essentially identical to the nonreactive dye constituted from the identical chromophore (this assumes that the reactive group is not electronically integrated with the chromophore). A number of recent publications contest this assumption; for example, Daruwalla[136] has reported on the unpublished results of a study by Daruwalla and Rastogi, who compared the lightfastness of representatives of a range of reactive dyes with their hydrolyzed nonreactive analogs on cotton. The reactive dyes included examples from the Procion, Cibacron, Remazol, Reactone, Levafix, Primazine, and Procinyl classes, and in all cases the covalently-bound dye showed a substantially higher lightfastness (Table XXVII). Independent studies on a range of Procion dyes[137,138] and Remazol dyes on cellophane films[139] gave similar results. It has been suggested that the covalent bond between a dye and the fiber facilitates the transfer of energy from an excited state of the dye to the fiber, thereby reducing the rate of photodegradation of the dye.[136]

Studies on reactively dyed wool have shown that there is little or no difference in lightfastness attributable to dye–fiber binding. For example, covalently bound Remazol and Lanasol reactives showed no

TABLE XXVII

LIGHTFASTNESS OF REACTED AND HYDROLYZED UNREACTED DYES[136] ON COTTON

	Lightfastness	
Dye	*Unreacted*	*Reacted*
Procion Brilliant Yellow H5GS	4	6–7
Cibacron Turquoise Blue G	3–4	5–6
Remazol Brilliant Orange RR	4	5–6
Reactone Red 2B	3	5–6
Levafix Brilliant Red E-2B	3–4	5–6
Primazine Yellow P-GL	3–4	6
Procinyl Scarlet G	4–5	6

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[136] E. H. Daruwalla, *Colour Annu.* **17**, 118 (1969).

[137] W. Ingamells, *J. Soc. Dyers Colour.* **79**, 651 (1963).

[138] T. D. Zakharova, V. B. Soloveva, and V. N. Zaitseva, *Zh. Prikl. Khim.* **44**, 2771 (1971); *CA* **76**, 128589 (1972).

[139] G. S. Baranova, M. G. Romanova, and M. A. Chekalin, *Tekst. Promst.* (*Moscow*) **32**, 70 (1972); *CA* **76**, 142364 (1972).

difference in photostability compared to the hydrolyzed dye,[140] and in some cases a decrease was observed. Similar findings apply to wool dyed with reactive polymethine dyes[141] (α-chloroacetamido reactive group). Covalent attachment of Procinyl reactive dyes to nylon has been shown to bring about little or no change in lightfastness compared with unbound dyes.[142]

Studies by Russian workers on the lightfastness of reactive dyes has been reviewed by Krichevkii *et al.*[143] On the basis of fading rates of monochlorotriazine and vinylsulfone dyes in polyamide and cellulose films, the conclusion was reached that the nature of the dye–substrate bond (covalent or adsorption) has little effect on the lightfastness. This finding contrasts with that of Daruwalla (Table XXVII), who found that a dye bound covalently to cellulose increased in lightfastness by 2 points in the case of monochlorotriazine types. A possible explanation of this anomaly may lie in the methods of assessment of photostability. The studies on film entail measurement of the radiation transmitted through the film at the absorption maximum of the dye, whereas the lightfastness of dyed fabrics is based on a visual assessment of a color change. The results from these two methods could differ for the following reason: If a photoproduct of the dye is highly colored and absorbs in a different spectral region from the test dye, then it will not be recognized in the instrumental method on films; on the other hand, a change of color in the visual assessment method contributes very significantly to the rating accorded in the test sample.

In summary, there is evidence that the covalent bonding between cotton and a reactive dye increases the lightfastness of the resultant dyeing, but that covalent binding of a dye to wool or polyamide has little or no effect on the fastness to light. An understanding of the mechanism by which the covalent dye–fiber bond increases lightfastness in reactive cotton dyes awaits further experimental results.

Acknowledgments

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[140] N. J. J. van Rensburg, *S. Afr. Wool Text. Res. Inst., Tech. Rep.* No. 155 (1971).

[141] D. J. Gale and J. F. K. Wilshire, *J. Soc. Dyers Colour.* **90**, 97 (1974).

[142] C. D. Shah and R. Srinivasan, *Text. Res. J.* **45**, 486 (1975).

[143] G. E. Krichevskii, B. Vachobov, Yu. A. Ershov, and E. V. Dovbii, *Text. Res. J.* **45**, 608 (1975).

CHAPTER VII

RELATIONS BETWEEN THE MOLECULAR STRUCTURES OF DYES AND THEIR TECHNICAL PROPERTIES

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I. Introduction

The qualities a dye must possess for successful commercial exploitation are desirable color, good application property, and adequate fastness to various agencies. Each of these properties is a function of the molecular constitution of the dye molecule. The relation between constitution and color of dyes has been studied in considerable depth (see S. F. Mason in *CSD III*). In this chapter we deal with the influence of the constitution on the other two properties, which in effect are those determining the suitability of the dye for practical use and comprise the substantivity of the dye for the fiber and its rate of diffusion therein and the fastness properties of the colored material to dry and wet influences. Light fading is not included, since this is dealt with in Chapter VI. However, the attention devoted to the relation of dye constitution to the properties we cover has been much less than that given to light fastness, probably because the physical chemistry of the actions involved is simpler and less challenging than that of light fading.

II. Application Properties of Dyes

The most familiar method of assessing dyeing properties is probably the use of the so-called time–temperature curve, in which the uptake of dye by the fiber is plotted against both time and rising temperature. The more fundamental measures of practical suitability are substantivity or thermodynamic affinity and rate of diffusion within the fiber. The interplay of the two factors—affinity and diffusion—determines the quality of the end product, i.e., its levelness of dyeing and its wet-fastness properties. Levelness is the result of a high rate of diffusion, and generally with low substantivity, whereas the highest wet fastness is achieved with dyes having low rates of diffusion. Sections A and B deal in a general manner with the relations between molecular structure on the one hand and affinity and rate of diffusion on the other.

A. RELATION BETWEEN MOLECULAR STRUCTURE AND DYE AFFINITY

1. *Cellulose*

The affinity of dyes for cellulose has been a subject of investigation for a long period.[1] Hodgson[2] made the first real advance in clearly demonstrating that the dye molecule must be planar for marked affinity for cellulose to be manifest. Consideration of other facts led to the hypothesis that hydrogen bonds are formed between the dye and fiber molecules[1] either directly or subsequent to adlineation and close approach of dye and fiber molecules caused by strong van der Waals attraction.[3]

Later evidence[4–11] threw doubt on the hydrogen bond hypothesis,

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[1] T. Vickerstaff, "The Physical Chemistry of Dyeing." 2nd ed. Oliver & Boyd, Edinburgh, 1954; see also *CSD II*, pp. 1253–1296; *CSD VII*, pp. 191–275; I. D. Rattee and M. M. Breuer, "The Physical Chemistry of Dye Adsorption." Academic Press, New York, 1974.

[2] H. H. Hodgson, *J. Soc. Dyers Colour.* **49**, 213 (1933).

[3] H. Zollinger, *Discuss. Faraday Soc.* **16**, 123 (1954); A. N. Derbyshire and R. H. Peters, *J. Soc. Dyers Colour.* **71**, 530 (1955).

[4] M. M. Allingham, C. H. Giles, and E. L. Neustädter, *Discuss. Faraday Soc.* **16**, 92 (1954).

[5] J. Wegmann, *Am. Dyest. Rep.* **51**, P276 (1962).

because the cellulose hydroxyl groups are too firmly attached to water to allow their bonding to polar groups in a dye. The unique ring structure of glucose, the building unit of cellulose, ensures maximum retention of an "atmosphere" of water molecules around it, though the aldehyde group in the open-chain form, not significantly present in cellulose, can form bonds in water.

The results of a monolayer experiment[4] supported this suggestion. When a surface-active benzidine disazo dye is spread as a monolayer on water containing cellobiose, the area per dye molecule rises to the value required to accommodate a single layer of water molecules between each dye and cellobiose molecule, thus preventing hydrogen bonds forming between them, whereas no such layer is evident when mannitol is used instead of cellobiose. Mannitol, unlike cellobiose, does form hydrogen bonds with other solutes in water, and so can form them with dyes.

The following additional hypotheses have been proposed to account for dye–cellulose affinity.

a. Ion–Dipole Interaction. Wegmann[5] postulated attraction between dipoles on the cellulose ether groups and ionic groups in the dye molecules. This does seem a possible contribution to the attractions involved, but no extensive research has been carried out to investigate it.

b. Hydrogen π Bonds. Supporting a suggestion of this type of bond, Yoshida *et al.*[6] found that sucrose, glucose, and cellobiose form 1:1 complexes in water with simple aromatic but not aliphatic sulfonate anions, the inference being that the bond involves the aromatic nucleus. Yoshida's observations have recently been confirmed, and extended to a sulfonated anthraquinone dye, which was found to form a 1:1 complex with sucrose in water.[7] The entropy of formation is high, 314 J (75 cal) K^{-1} mol^{-1}; suggesting that the complex is formed by two cooperating molecules oriented parallel to each other and face to face. The evidence was in favor of the operation of this bond in cellulose dyeing, until it was found that typical sulfonated azo dyes, including Sky Blue FF (CI. 24410; CI Direct Blue 1), do not form any complex with methyl-β-D-glucopyranoside (a water-soluble model of cellulose) or with sucrose, so that its importance in cellulose dyeing is ruled out. It appears that the presence of an azo group in an aromatic structure

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[6] Z. Yoshida, E. Ōsawa, and R. Oda, *J. Phys. Chem.* 68, 2895 (1964).

[7] C. H. Giles and A. McIntosh, *Text. Res. J.* **43**, 489 (1973).

[8] R. H. Peters and H. H. Sumner, *J. Soc. Dyers Colour.* **71**, 130 (1955).

[9] V. G. Agnihotri and C. H. Giles, *J. Chem. Soc., Perkin Trans.* **2**, p. 2241 (1972).

[10] C. H. Giles and A. S. A. Hassan, *J. Soc. Dyers Colour.* **74**, 846 (1958).

[11] T. H. Morton, *J. Soc. Dyers Colour.* **62**, 272 (1946).

prevents formation of the π bond complex,[7] but the cause of this prevention is not known.

The linear relation between affinity of anionic dyes for cellulose and the (log) length of conjugate chain in the dye molecules (Fig. 1) suggests that the source of affinity lies in either, or both, fiber–dye or dye–dye van der Waals forces, rather than in hydrogen-bonding groups, since many of the dyes concerned do not differ in their content of the latter, yet differ markedly in affinity. Peters and Sumner[8] found a similar relation between affinity of some of these dyes and the (log) extinction coefficient.

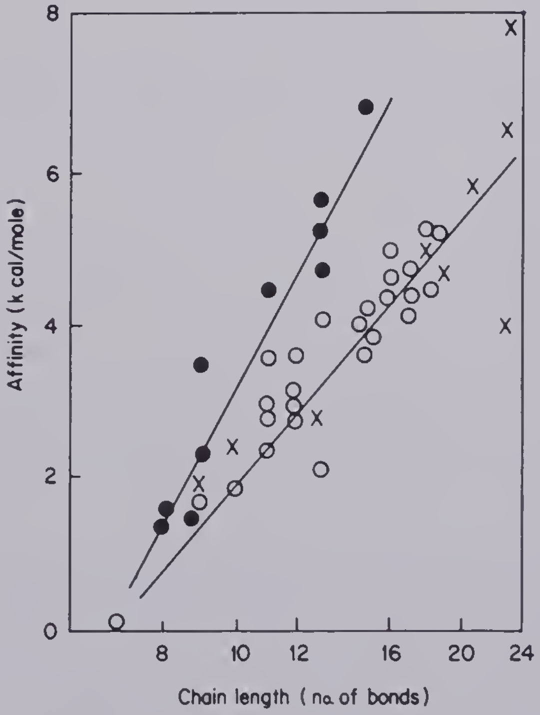

FIG. 1. Relationship between affinity for regenerated cellulose and molecular conjugate chain length of dyes. (○, ●) Affinities at 40° of planar leuco vat dyes and related compounds for cuprammonium rayon; (×) affinities at 50° of planar sulfonated azo dyes for viscose rayon (○ and ● represent dyes with, respectively, one and no —NHCO— group in the conjugate chain). Affinity data from Peters and Sumner,[8] and Giles and Hassan.[10]

c. Acid–Base Bonds. New evidence of a possible bond between cellulose and free hydrogen atoms on amino groups in dyes has been obtained recently.[9] Refractometric tests with Sky Blue FF dissolved in a solution of cellulose in alkaline Cadoxen solvent showed the presence of a 1:1 complex between the dye molecule and the cellobiose unit of the cellulose chain. This complex seems to be very weak—it has no influence on the surface viscosity of a monolayer of cellulose—and it may be the result of a weak acid–base reaction between the cellulosic hydroxyl groups and the amino groups in the dye.

This hypothesis is supported by the following three observations: (1) CI Direct Blue 10 (CI 24340), which is very similar in structure to CI. Direct Blue 1 (CI 24410), but has OH and no NH_2 groups, gives no evidence of a complex with cellulose in Cadoxen solution; (2) other ionic bonds do not affect surface viscosity, e.g., those between a protein monolayer on acid solutions and disulfonated acid dyes; (3) the hydrogen bonds between cellulose acetate in a monolayer and a disperse dye do considerably increase the viscosity of the monolayer.

It therefore appears that a type of acid–base ionic attraction is exerted by cellulosic hydroxyl groups and free hydrogen atoms on basic groups in a dye.

d. Van der Waals Attraction. Further understanding of cellulose dyeing comes from monolayer experiments. Direct dyes in the water subphase beneath a monolayer of cellulose cause the film to expand without change in its compressibility: moreover the expansion is proportional to the width of the dye molecule[9] (Fig. 2). Both these facts are in agreement with the hypothesis that the dye molecules are oriented flat, face to face with, and parallel to the cellulose chains on the water surface. A similar suggestion was made by Morton[11] to account for the dichroic effects shown by dyed cellulose. The evidence from the monolayer tests is in favor of an attraction between cellulose and dye, and not merely a chance juxtaposition of the two, each tending to float on the water surface. The question still remains as to what the nature of this attraction is. The evidence points to the simultaneous operation of several weak forces.

2. *Hydrophobic Fibers*

a. The Solubility Effect.[12–14] The (log) saturation adsorption of disperse dyes adsorbed from water by cellulose acetate rises with (log) dye solubility (Fig. 3) suggesting that there is only weak competition for dye between substrate and water and that the dye–fiber attraction is of the same nature as the dye–water attraction and is therefore mainly polar. The relation appears to be linear for several dye series; the lines have slopes less than unity, which implies that increase in adsorption is more difficult to achieve than increase in solubility, i.e., that a dye molecule must have more energy to penetrate between fiber

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[12] L. H. Griffiths and S. M. Neale, *Trans. Faraday Soc.* **30**, 395 (1934); **29**, 6 (1959).

[13] C. H. Giles, *Text. Res. J.* **31**, 141 (1961).

[14] C. L. Bird and P. Harris, *J. Soc. Dyers Colour.* **73**, 199 (1957).

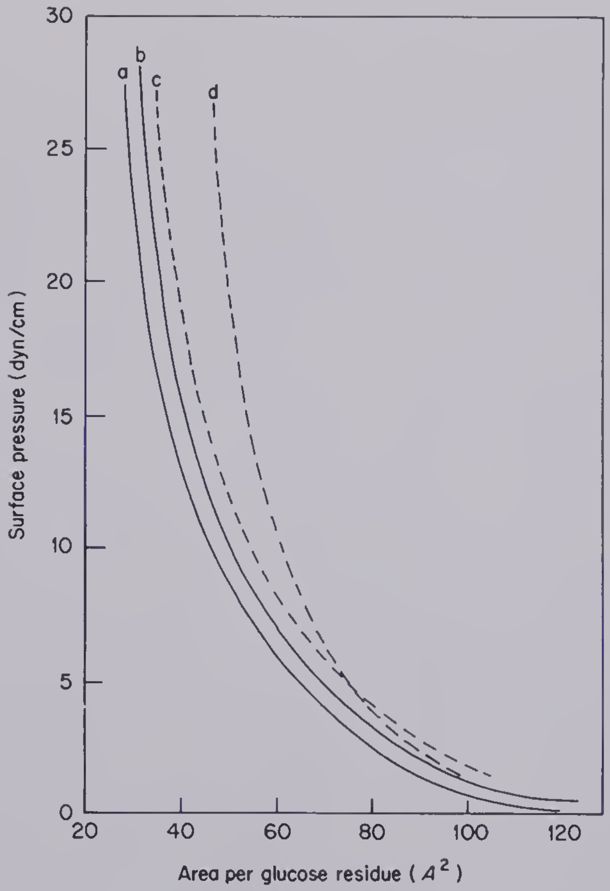

FIG. 2. Pressure–area curves for cellulose monolayers[9]: (a) control (on water); (b) on solutions (10^{-5}–10^{-4} M) of azo direct or acid dyes CI. Direct Yellow 12, Red 2, Blue 1, Acid Orange 7 (Orange II), Reds 1, 88; (c) same as b, +0.1 M NaCl; (d) same as b, CI. Direct Green 26.

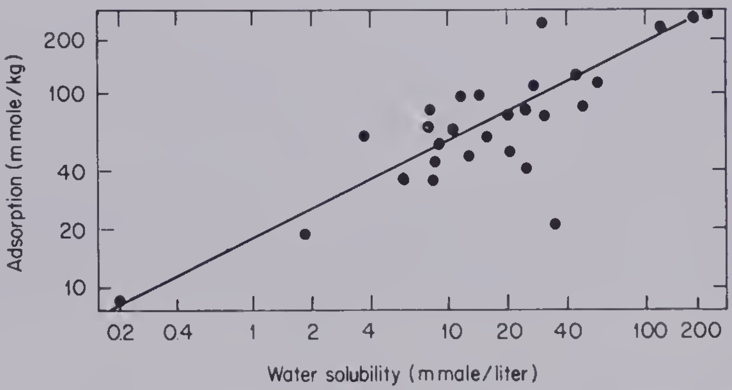

FIG. 3. Relation between water solubility (80°) of some disperse dyes and their saturation adsorption (80°) in cellulose acetate.[13,14]

molecules than between water molecules. Figure 3 shows thus that nylon is more difficult for a disperse dye to penetrate than cellulose acetate, which agrees with the fact that nylon is the more crystalline fiber. This direct correlation between solubility and adsorption is evidence that both parameters are directly related to a third, which must be the number and nature of the polar groups in the dye molecule.

The reverse relation is shown by water-soluble dyes on a hydrophilic fiber, cellulose. Griffiths and Neale[12] found that the saturation adsorption of direct dyes by viscose (regenerated cellulose) falls with increase in sulfonation of the dye molecule and therefore with increase in its water solubility.

b. Evidence for Requirement of Planarity. Determination of affinity and saturation values for disperse dyes synthesised by Daruwalla, Rao, and Tilak[15] showed clearly that planarity in the dye molecule is essential for adequate depth of shade to be built up.

c. Free Hydrogen Atoms. Free hydrogen atoms capable of forming intermolecular bonds between the dye and the fiber have a very marked effect on adsorption, especially if they are capable of forming very strong hydrogen bonds, e.g., phenols. This suggests that hydrogen bonding (to the keto or ether oxygen of the acetyl group) is one of the principal adsorption forces.

d. Hydrogen-Accepting Groups.[16–18] Hydrogen-acceptor groups can, when suitably oriented, increase adsorption. The cause is the hydrogen-donating power of the CH_3 group in esters activated by the $C{=}O$ group.

The ability of polymers to act as both proton donors and proton acceptors in bonding with polar groups or the π electron system in the dye molecule can be demonstrated in several ways, including monolayer experiments and tests of various physical properties of binary mixtures of dyes and polymers or model compounds. One method is gas–liquid chromatography as developed by de Vries *et al.*[19–21] for measuring the heat of reaction between cellulose acetate as stationary phase and a large number of model compounds.

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[15] E. H. Daruwalla and V. R. Limaye, *J. Soc. Dyers Colour.* **74**, 464 (1958); E. H. Daruwalla, S. S. Rao, and B. D. Tilak, *ibid.* **76**, 418 (1960).

[16] F. M. Arshid, C. H. Giles, and S. K. Jain, *J. Chem. Soc.* p. 1272 (1956).

[17] A. Cameron, C. H. Giles, and T. H. MacEwan, *J. Chem. Soc.* p. 4304 (1957).

[18] A. Cameron, C. H. Giles, and T. H. MacEwan, *J. Soc. Dyers Colour.* **73**, 511 (1957).

[19] M. J. de Vries and J. H. Smit, *J. S. Afr. Chem. Inst.* **20**, 11 (1967).

[20] J. H. Smit and M. J. de Vries, *J. S. Afr. Chem. Inst.* **20**, 144 (1967).

[21] M. J. de Vries, J. H. Smit, and H. G. Raubenheimer, *J. S. Afr. Chem. Inst.* **21**, 47 (1968).

The conclusions these authors reach are: (1) phenols and aliphatic alcohols act as proton donors to the carbonyl oxygen atom of the acetate group and the hydroxy group in secondary cellulose acetate; (2) aromatic hydrocarbons act as electron donors and the acetate group as an electron acceptor (other hydrocarbons are adsorbed only by weak dispersion forces); (3) the halogen compounds are adsorbed by electron transfer from the carbonyl oxygen atom of the acetate group to the protons of the haloforms and the chlorine atoms of carbon tetrachloride, respectively.

It is thus possible to account for the adsorption of all disperse dyes on all hydrophobic polymers by the combined action of weak dispersion forces together with strong hydrogen bond and electron transfer forces. On polypropylene, only the weak dispersion forces can operate.[22] It is now clear that for all disperse dyes and all hydrophobic fibers every polar substituent group in the dye molecule and the aromatic system as a whole contributes to the strength of the dye–fiber bond, if the dye molecule is planar and thus can lie flat against the polymer molecule. This accounts for the much higher affinity that planar disperse dye molecules have, compared with nonplanar ones, as stated above, and also for the evidence, given by measurement of monolayer areas and viscosities, that a strong 1:1 complex is formed by face-to-face packing between planar disperse dyes and the hexacetylcellobiose residues in cellulose triacetate.[23,24]

Most of the evidence for the hydrogen-bonding mechanism in the dyeing of disperse dyes has been gained from experiments with cellulose acetates, but there seems no reason to doubt that nylon and polyester absorb these dyes by the same general mechanism. In confirmation, there is a linear relation between the solubilities of a range of such dyes in cellulose acetate and nylon, respectively[13] and this indicates a similar mechanism (Fig. 4).[25] Certainly both nylon and polyester have more hydrocarbon groups than cellulose acetate. These groups, however, in nylon are in the form of alkyl chains, and it follows from the very low affinity of disperse dyes for the purely alkyl hydrocarbon polymer polypropylene,[22] that they must have a negligible effect on dye affinity. Nevertheless, the aromatic nuclei in polyester may take part in hydrogen bonding through the π electron system, as described above.[19–21]

[22] C. L. Bird and A. M. Patel, *J. Soc. Dyers Colour.* **84**, 560 (1968).

[23] C. H. Giles, *Br. Polym. J.* **3**, 279 (1971).

[24] C. H. Giles, V. G. Agnihotri, and A. S. Trivedi, *J. Soc. Dyers Colour.* **86**, 451 (1970).

[25] T. Vickerstaff, "The Physical Chemistry of Dyeing," 2nd ed., p. 442. Oliver & Boyd, Edinburgh, 1954.

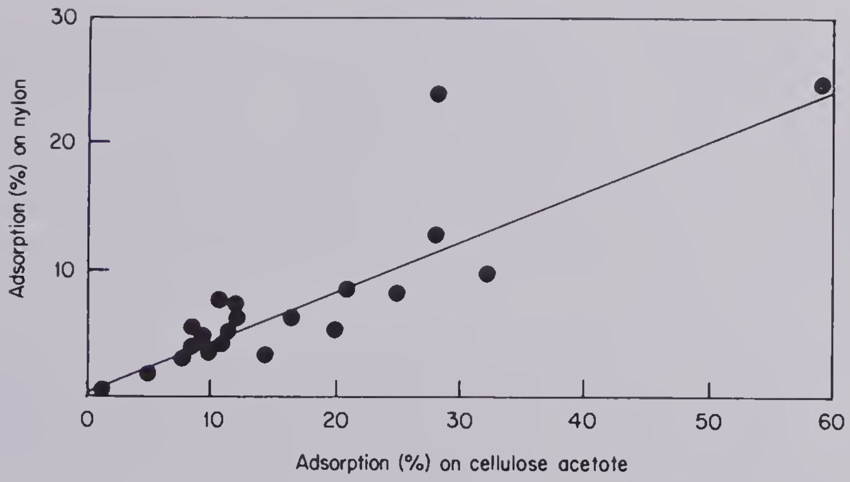

FIG. 4. Relation between saturation adsorption of disperse dyes on cellulose acetate and on nylon[25] at 85°.

e. Adsorption Forces Other than Hydrogen Bonds. Nonpolar (van der Waals) forces and dipole–dipole forces almost certainly contribute to the adsorption energy. The evidence for van der Waals forces is the tendency for the partition coefficient between cellulose acetate and water to rise with molecular weight (cf. data in Bird and Harris[26]). There is no direct evidence of dipole–dipole forces, but in any case they would be much weaker than the hydrogen bond forces. In a series of intermolecular reactions between small organic molecules studied by Sutton and collaborators,[27] the association constants of those involving a hydrogen bond were found to lie between 3.5 and 230 (moles/liter) but those for dipole-dipole (non-hydrogen bond) reactions were much lower, ~0.2–0.4.

f. Interaction Effects. Adsorption normally rises with increase in number of hydrogen-acceptor groups, but if there is a methyl group ortho to the azo group, adsorption, which is at first very high, falls with increase in number of hydrogen-acceptor groups.[13] The *o*-methyl group increases the electron density at the azo group and thus enhances its ability to accept a bonding hydrogen atom. Addition of electron-attracting groups (Cl, NO_2) then, progressively neutralizes this effect, and adsorption generally falls, in spite of the hydrogen-accepting power of these groups themselves. The influence of an *o*-methoxy group on adsorption is even more marked than that of the *o*-methyl group, in accordance with its greater power of electron release.

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[26] C. L. Bird and P. Harris, *J. Soc. Dyers Colour.* **73**, 201 (1957).

[27] R. L. Denyer, A. Gilchrist, J. A. Pegg, T. E. Smith, and L. E. Sutton, *J. Chem. Soc.* p. 3889 (1955).

Other interaction effects, which may be compared with appropriate Hammett σ values,[28] are that the nitro group promotes adsorption (by facilitating $—NH_2\cdots$bonding) better in the 4′ than in the 3′-position in an aminoazobenzene derivative, and that the *p*-nitro group promotes adsorption more effectively than the *p*-phenylazo group in aniline derivatives, but less effectively in dimethylaniline derivatives. The amino group in aniline donates hydrogen and is therefore activated by an electron-attracting group, but the dimethylamino group accepts hydrogen.

g. Steric Effects.[13,29] When either hydrogen-donating or accepting groups are widely spaced in the solute molecule (especially in the para position), their ability to promote both adsorption and solubility is usually reduced. Normally, an increase in number of (unchelated) polar groups in a molecule increases its solubility in water.

There are at least two reasons for such effects:

1. Intermolecular association with face-to-face packing, is easier for 1,4-substituted aromatic molecules than for the 1,2 or 1,3 isomers. This makes the crystal lattice energy of the 1,4-compounds higher and their molecules are thus less readily broken away to pass into solution.
2. In adsorption, cross-linking of adjacent substrate molecules could occur most readily with 1,4-disubstituted solute molecules. Thus, access to the internal structure of the substrate would be more restricted.

h. Additivity of Dye Adsorption. It is well known that the saturation adsorption of some disperse dyes on hydrophobic fibers may be additive,[15,30–32] but only in the case of selected dyes. Thus, dye A may be additive with B, but not with C (Fig. 5). The cause is probably connected with the geometry of dye molecules. Additive dye molecules may be able, respectively, to penetrate different regions of the fiber, and therefore they will not compete. Their ability to penetrate different regions may be determined, e.g., by molecular geometry, energy of dye–fiber binding or of dye–solvent binding.[13] Those dyes that have similar characteristics, however, (e.g., similarly shaped molecules) may enter the same regions of the fiber, and so will compete with each other, and their saturation adsorptions will not be additive.

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[28] L. P. Hammett, "Physical Organic Chemistry," 2nd ed., p. 355. McGraw-Hill, New York, 1970.

[29] T. G. Majury, *J. Soc. Dyers Colour.* **70**, 442 (1954).

[30] C. L. Bird and P. Rhyner, *J. Soc. Dyers Colour.* **77**, 12 (1961).

[31] M. J. Schuler and W. R. Remington. *Discuss. Faraday Soc.* **16**, 201 (1954).

[32] A. Johnson, R. H. Peters, and A. S. Ramadan, *J. Soc. Dyers Colour.* **80**, 129 (1964).

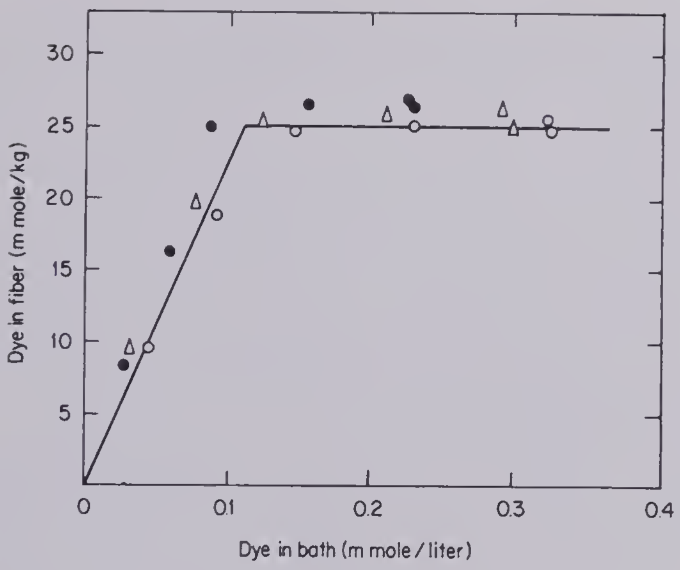
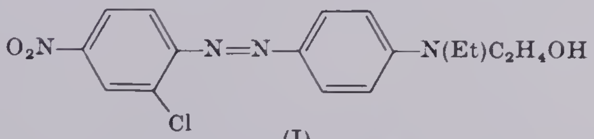
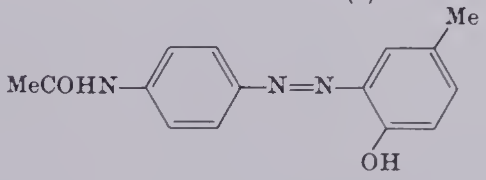


FIG. 5. Adsorption isotherms of additive disperse dyes on nylon (90°)[32]: (——) dye I; (○) dye I in presence of dye II; (●) dye I in presence of dye III; (△) dye I in presence of dye IV.

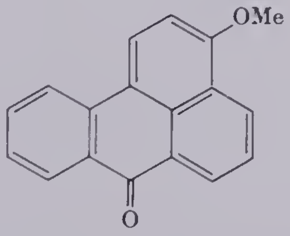
Formulas:



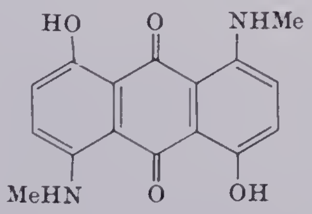
(I)



(II)



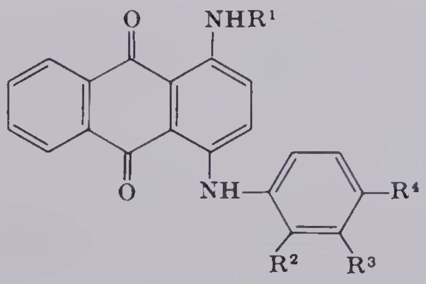
(III)



(IV)

These suggestions are in fact confirmed by experiment; dyes with different molecular structures are nonadditive.[18,32] These properties, however, appear to be rather critically dependent on the detailed structure of the dye molecule. Johnson *et al.*,[32] in an interesting investigation, examined the melting point diagrams for pairs of disperse dyes of nonadditive and additive properties, respectively. They found that dyes that are nonadditive form mutual solid solutions in all proportions in the crystal phase. Additive dyes do not: they form eutectic mixtures. In the latter case, the melting point of each pure compound is depressed as the proportion of the second compound is increased, until at a certain composition a minimum melting point is obtained. This is the eutectic point. At this point, in the solid phase, each component is present in its own crystalline form. The ability to interact and form mixed crystals was seen in this investigation to be critically dependent on the shape of substituent groups in the dye molecule. This fact is shown by the results of Johnson *et al.*, with their dyes V–IX of the following general formula.

Mixtures of V + VII, VI + VII, VII + IX, and X + XI interact and are thus nonadditive and mutually interfering on the fiber.



Dye	R^1	R^2	R^3	R^4
V	Me	H	H	H
VI	C_2H_4OH	H	H	H
VII	Et	H	H	H
VIII	Me	H	H	Me
IX	Me	Me	H	H
X	Quinizarin			
XI	1-Amino-4-hydroxyanthraquinone			

More exact explanation of the cause of additivity may be possible when the detailed morphology of the hydrophobic polymers is better understood than it is now.

B. Relation between Molecular Structure and Diffusion Rate

1. *Dye Structure*

Park[33] derived an equation to describe the diffusion of an organic vapor into polystyrene

$$\log D = \log K - A V_{\mathrm{m}} - Bd$$

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[33] G. S. Park, *Trans. Faraday Soc.* **47**, 1007 (1951).

where D is the diffusion coefficient, V_m the molar volume of the vapor, d its minimum molecular diameter, and K, A, and B are constants. Merian[34] found a similar relation between log D for disperse dyes and a function of their molecular size and shape, based on this equation.

Rate of dyeing data for various acid dyes on wool and gelatin also show a similar relation in that the molecular volume is inversely proportional to the logarithm of the dyeing rate (Fig. 6).[35b]

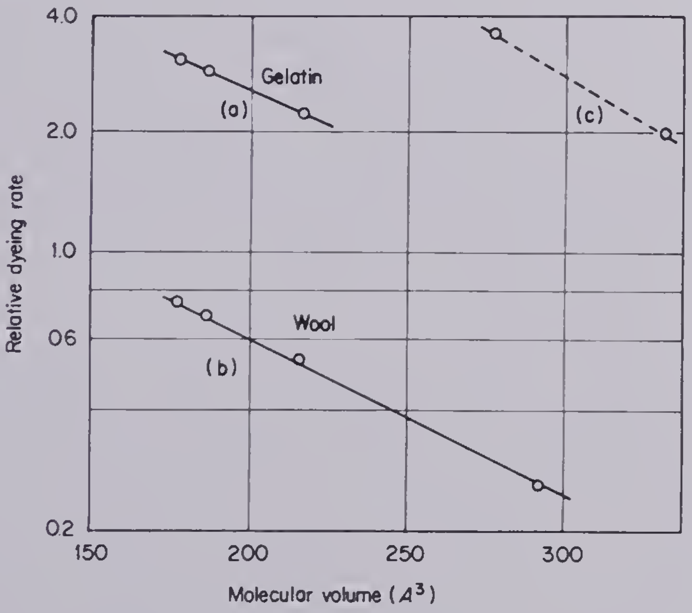
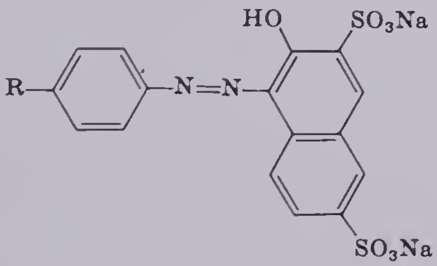


FIG. 6. Illustrating influence of porosity of substrate, and molecular volume and ionic character of dye on rate of dyeing,[35] at 70°.



R = H, CH_3, n-C_4H_9, n-$C_{12}H_{25}$, respectively. Lines a and b are for these dyes: (a) gelatin; (b) wool; line c is for a different type of dye, namely two 2:1 dye–chromium complexes of similar structure to each other, with shielded anionic charge. The relative dyeing rate is obtained by dividing the slope of the curve relating the square root of the dyeing time to the amount adsorbed by the specific surface of the substrate.

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[34] E. Merian, *Text. Res. J.* **36**, 612 (1966); cf. K. Odajima, *J. Soc. Dyers Colour.* **75**, 255 (1959).

[35a] J. B. Speakman and S. G. Smith, *J. Soc. Dyers Colour.* **52**, 121 (1936); [b] C. H. Giles, A. P. Montgomery, and A. H. Tolia, *Text. Res. J.* **32**, 99 (1962).

McGregor and Peters[36] have found that "*m*-benzopurpurine" diffuses more slowly in cellulose than benzopurpurine (CI 23500) itself. The cause must again be the difference in minimum cross-sectional areas, which are ~75 Å^2 and ~48 Å^2, respectively.

It also appears that if the ionic charge of the dye molecule is sterically shielded, as in 2:1 dye–metal complexes, where the negative charge is located on the central metal atom, the dyeing rate is increased (Fig. 6). Presumably this occurs because coulombic forces between dye anion and charged cationic groups in the fiber are attenuated. Dye–fiber polar attractions, including hydrogen bond forces, are still present, but these attenuate more rapidly with distance than the coulombic forces and thus are less effective in retarding dye diffusion along the pores. This type of research has not received much attention, yet it could be most useful in determining how to tailor the geometry of dye molecules to suit practical rate-of-dyeing requirements.

2. *Porosity of the Substrate*

"Absolute" rates in different substrates can be compared by making allowance for differences in external surface. This was first done by Speakman and Smith in 1936[35a] with wool fibers from different sources. More recently, gelatin and wool have, as stated above, been compared for dyeing rates of various dyes, and found to differ by a constant factor: each dye had a rate about four times as great on gelatin as on wool (Fig. 6).

At any moment there are individual dye molecules and dye micelles bombarding the substrate from the solution at every angle relative to the surface pores. One factor determining the rate of adsorption is the proportion that happens to strike pores at the angle at which they can enter most readily. Obviously, this proportion is higher the smaller the molecular volume of the dye and the more amorphous the substrate. Thus, the constant proportionality of difference between rates in gelatin and wool, gelatin giving the higher rates, shows that gelatin has a larger average pore size than wool. A bombarding dye molecule has a better chance of entering a pore in gelatin than in wool.

3. *Hydrophobic Fibers—Diffusion Coefficient*

Recent kinetic work on dyes, especially by the Manchester school (e.g., ref. 36), has been concerned with detailed theoretical and experimental study of the diffusion coefficient of dyes and its variation with

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[36] R. McGregor and R. H. Peters, *Trans. Faraday Soc.* **60**, 2062 (1964); R. H. Peters, J. H. Petropoulos, and R. McGregor, *J. Soc. Dyers Colour.* **77**, 704 (1961).

concentration in the fiber. The coefficient determined directly from rate measurements is an apparent value, sometimes called the integral diffusion coefficient. This is calculated assuming the applicability of Fick's first law of diffusion,

$$dQ/dt = -DA\ dc/dx$$

where dQ/dt is the rate of transport of a substance across a given area A under a concentration gradient dc/dx, D being the diffusion coefficient. Deviations from this law can arise in dyeing, because the concentration c may not represent the concentration of dye molecules free to diffuse, since some of these molecules in any given element of volume in the fiber may already be adsorbed on the internal surface and thus be immobile, and only the remaining unadsorbed dye molecules still in solution are free to diffuse.

Deviation from Fick's law occurs when the concentration of adsorbed molecules is not a linear function of the concentration of free molecules, and also if the dye molecules associate either with themselves or with inorganic ions in the internal solution.

The real diffusion coefficient is the value for specified invariable conditions, and its determination requires complex theoretical and experimental treatment. Peters *et al.*[36] found that this real coefficient for an anionic dye in nylon tends to increase with amount of dye adsorbed (Fig. 7), presumably because diffusion becomes easier as more sites in the fiber are filled and they can therefore no longer exert a drag

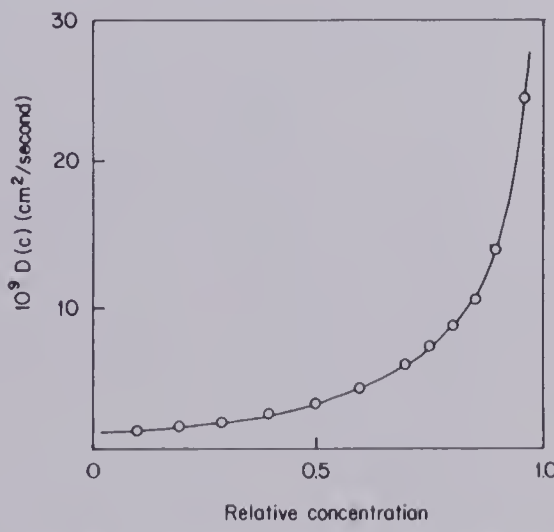

FIG. 7. Relation between relative concentration and real diffusion coefficient at pH 3.2 of a trisulfonated azo dye (CI 16150) in nylon.[36]

on the passing dye molecules. For a disperse dye in cellulose acetate, however, the real coefficient remains constant, because the linear adsorption relation applies, and the adsorbing surface expands with progress of adsorption.

The relation between the diffusion coefficient of disperse dyes in hydrophobic fibers and their structural characteristics is discussed further in Section IV,C.

III. Fastness Properties of Dyes

A dye must be able to withstand treatments in manufacturing processes and normal usage when present in the fiber. Thus, it must be fast to wet treatments and light. Lightfastness is dealt with elsewhere in this volume. Wet treatments include washing, shampooing, and manufacturing processes such as milling. Sections A and B below deal with some general relations between dye structure and fastness properties. Specific dye–fiber systems are considered in Section IV.

A. Wetfastness and Diffusion Properties

These properties are related, since all depend on the rate of diffusion of dye in the fiber. The rate is a function of the geometry of the dye molecule, depending as it does on both the "slimness" of the molecule, i.e., the size of its smallest cross-section, and on the molecular weight. Rate of dyeing and washfastness are the most important of this type of diffusion-related property and may be considered to be directly related, provided that the conditions of test or exposure are the same; actually, of course, they seldom are. Thus, we may quote the conditions in the wet treatment of wool. Wool dyes are applied under acid conditions, but are washed under neutral or slightly alkaline conditions. In these circumstances, a second factor complicates that of the simple ability of the dye molecule, regarded as an inert solid body, to migrate along the internal channels of the fiber. This factor is the chemical attraction between the dye and the fiber molecule.

Affinity of dye for fiber molecules tends to reduce the rate of transport of dye into or out of the fiber. In effect, the dye–fiber attractive forces (and possibly dye–dye forces also) tend to cause the dye molecules to remain attached to fiber molecules rather than to diffuse along the pores of the fiber. Thus, Nicholls[37] found that with acid dyes of the same basicity, the desorption rate from wool into alkaline buffer solution falls with rise in dye–fiber affinity. He also found that the rate falls with reduction in basicity. Thus, the fewer sulfonate groups

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[37] C. H. Nicholls, *J. Soc. Dyers Colour.* **72**, 479 (1956).

there are in the dye molecule the more slowly it desorbs into alkaline solution, and the more of such groups are present, the more rapid is the desorption. Nicholls explains this as the result of repulsion between the anionic sulfonate groups and anionic charged sites in the fiber, i.e., negative affinity, produced by the alkaline solution. Thus, the dye–fiber affinity in alkaline solution in fact falls with increase in number of sulfonate groups in the dye. The opposite condition should apply to acid conditions, where there is positive affinity of sulfonate groups for cationic sites in the fiber, i.e., the rate of adsorption should decrease with increase in number of sulfonate groups; this does happen. Thus, each sulfonate group increases the dye–fiber affinity in acid solution. This would be expected, for though there is competition for the sulfonate group between the water of the dyebath and the cationic groups in the fiber, the balance appears to be in favor of the fiber.

During the limited period of a normal washing treatment or of the standard tests devised to imitate it, an equilibrium between dye inside and outside the fiber may not be reached. In these circumstances, the amount of dye removed from the fiber may depend largely on its rate of desorption. We should therefore expect that the washfastness of dyes with molecules of the same degree of sulfonation should increase with molecular (or anionic) weight or volume. Plots of technical data for a large number of commercial dyes on wool do show this trend, though with much scatter (Fig. 8). Another and more selective set of wool dyes

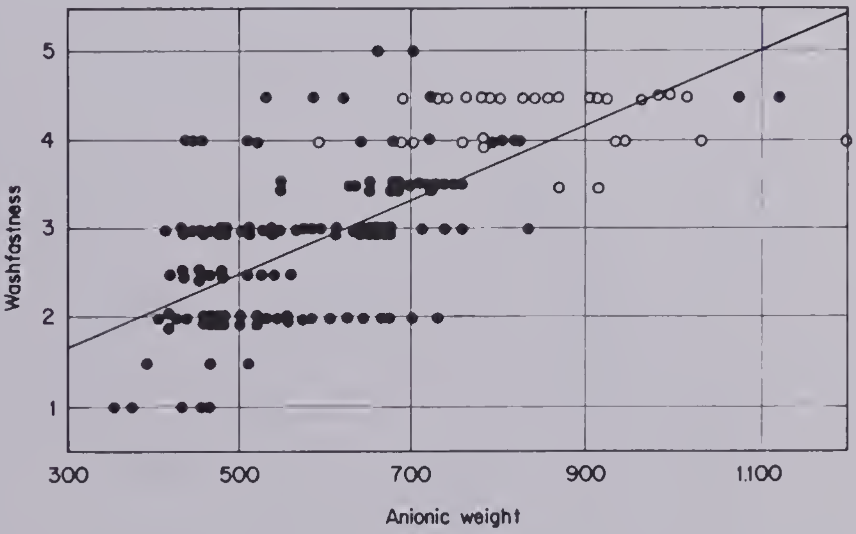

FIG. 8. Relation between washfastness of disulfonated acid dyes on wool and anionic weight. The least squares line is shown; this is highly significant and accounts for 45% of the total regression; (●) acid dyes, (○) chrome-mordanted dyes. These mordanted dyes are monosulfonates; they are here assumed to form complexes in which one chromium atom is linked with two dye molecules in a high-molecular-weight disulfonated complex.

shows a similar relation with less scatter, but the effect of the number of sulfonate groups is not clearly evident (Fig. 9).

From the user's point of view, therefore, dyes with large molecules are preferable; they are likely to be more difficult to remove from the fiber. The dyer, however, prefers those with small molecules; their ready diffusibility ensures good penetration into fabrics and levelness of shade.

It has often been thought that the superior washfastness of the metal-complex dyes on wool is due to additional forces between the metal atom and the wool protein molecules. Recent investigations[38] using monolayers of protein spread on dye solutions, however, have given no evidence of such action, and it is to be concluded that the superior fastness is due to the ability of the dye molecules to associate into large aggregates in the fiber, which then have low diffusion rates. In the tests mentioned, the compressibility of the protein film was the same whether a given dye in the water beneath the film was complexed with chromium or not. Had there been any chromium–protein reaction with the 1:1 metal complex dyes used, it would have been manifested by an increase in the rigidity, i.e., a decrease in compressibility, of the monolayer.

There is known to be a direct relation between diffusion coefficient

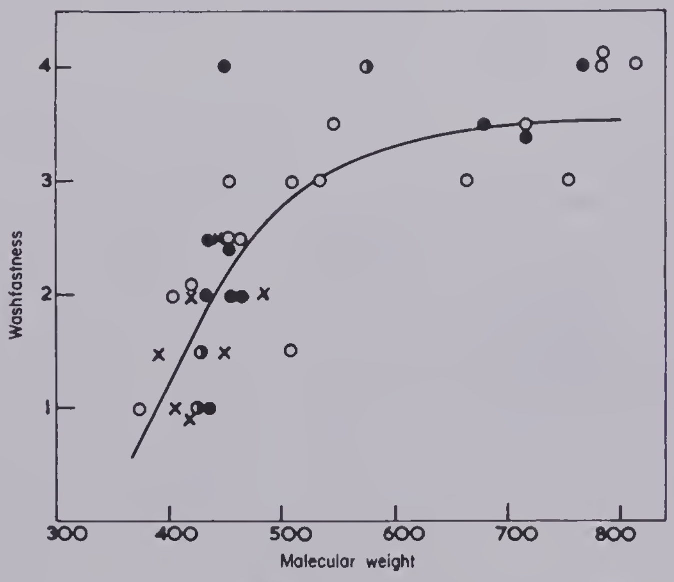

FIG. 9. Relation between washfastness of acid dyes on wool and their molecular weight; (◐) and (×) anthraquinone dyes, (○) azo from β-naphthol $(SO_3Na)_2$, (●) azo from α-naphthol $(SO_3Na)_2$.

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[38] C. H. Giles, T. H. MacEwan, and N. McIver, *Text. Res. J.* **44**, 580 (1974).

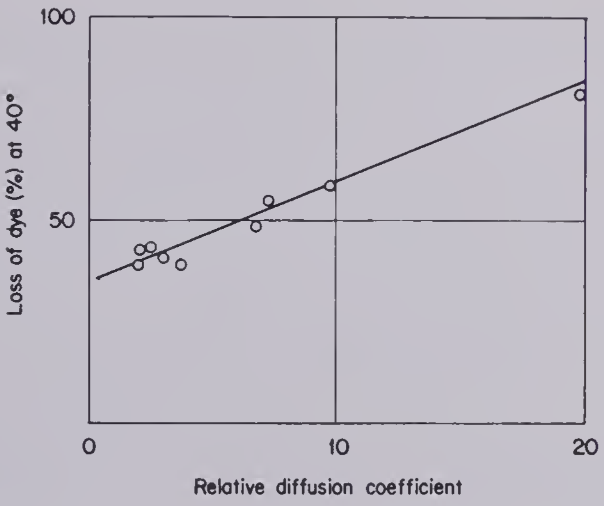

FIG. 10. Relation between washfastness and diffusion coefficient of some acid dyes on wool.[38a]

of acid dyes in wool and their washfastness (Fig. 10). Therefore, there is a direct relation between molecular volume of acid dyes and the logarithm of the rate of loss of dye in washing tests.[38a]

B. DRYFASTNESS PROPERTIES

1. *Fastness to Gaseous Impurities in the Atmosphere*

a. Burnt Gas-Fume Fading. The best known effect of this type is that due to products of combustion, usually termed (burnt) gas-fume fading, though other products can also be active. In the early years of this century, MLB investigated some unusual cases of fading of dyes on stored wool goods. This fading was most noticeable on the edges of dyed materials that had been exposed to air. The cause was traced to nitrogen oxides in the air, assisted by traces of sulfuric acid in the fiber. These oxides were formed by combination of atmospheric nitrogen and oxygen in the heat of the flames of unenclosed electric arc lamps and incandescent gas mantles. It is now known that the undiluted products of gas combustion may contain 100–200 ppm of nitric oxide, and motor car exhausts up to 500 ppm. Normal atmospheres contain 0.01–0.02 ppm, falling to ~0.003 ppm after heavy rain, but rising to ~0.15 ppm in fog. Nitric oxide slowly combines with oxygen in damp air to give higher oxides, e.g., nitrogen dioxide. The MLB research team found that all the susceptible dyes contained free or substituted amino groups, and they suggested that these might become either diazotized or nitrosated.

[38a] M. H. Fern, *Hexagon Dig.* **9**, 3 (1950).

This matter seems thereafter to have been forgotten. No doubt the 1914 war was responsible at first, but the increasing replacement of the older forms of illumination by filament electric lamps reduced the incidence of the trouble. Meanwhile, cellulose acetate was introduced as a fiber about 1920 and disperse dyes for it, several containing amino groups, appeared a few years afterward. In the 1920s, atmospheric fading on dyed cellulose acetate began to be noticed, and the cause was rediscovered and reinvestigated from about 1933 onward, the earlier work remaining apparently unknown. It is now known that dyes on cellulose acetate are more susceptible to nitrogen oxides than they are on wool. Rowe and Chamberlain[38b] made a systematic investigation of the chemistry of the dye degradation process and independently reached similar conclusions to those of the MLB team. The continued importance of this problem today reflects the increasing contamination of the urban atmosphere.

Nitric oxide itself does not react with the dyes; the effective agents are the higher oxides, probably mainly nitrogen dioxide. They react with basic groups in the dye, and the ease of reaction increases with basicity; thus, $NHAr < NH_2 < NHalk$. Hydroxyl groups do not appear to react. The primary amino groups form a diazo nitrate, and the secondary an *N*-nitrosamine. Sulfur dioxide modifies the action of nitrogen oxides (e.g., *N*-nitrosamine formation is retarded), so that fading tests in the atmosphere do not always give the same results as those made in nitrogen oxides diluted with air.

The reactions that occur in the fading may be represented as follows:
(i) With primary amino groups in the dye:

$$RNH_2 \xrightarrow{NO_2} RN_2^+NO_3^-$$

(ii) With secondary amino groups:

$$RNHR' \xrightarrow{NO_2} RN(NO)R'$$

Burnt-gas-fume fading, in contrast to sulfur dioxide fading, is irreversible, and no treatment will restore the original shade. It can be retarded, but not prevented, by the presence on the fiber of substances that preferentially react with the nitrogen oxides. Possibly the simplest inhibitors are sodium thiosulphate and sodium carbonate, but these are water soluble and therefore impermanent. Patents have appeared describing inhibitors, the aim being to produce colorless, stable, and washfast products, applicable from the dyebath during the normal

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[38b] F. M. Rowe and K. A. J. Chamberlain, *J. Soc. Dyers Colour.* **53**, 268 (1937).

dyeing operation. Also, they should not affect the lightfastness of the dye. Several such products are known. Examples are *N*,*N*′-diphenylethylenediamine (formerly widely used commercially, although it becomes pale yellow by reaction with the nitrogen oxides), diphenylacetamidine, and *N*-ω-cyanoethylspirocyclohexylethyleneimine.

Blue dyes are especially susceptible to gas-fume fading, although some violets and reds also fade. The reason for this correlation between hue and fading is that amino groups in the molecule are required to shift the light absorption band toward long wavelengths. Gray shades, which are usually produced from mixtures of dyes including blue, are especially liable to show this fading, which takes the form of an unpleasant reddening. Fast blue disperse dyes are now available, including both anthraquinone and azo compounds, but some of them have inferior lightfastness, and the gas-fugitive types are still widely used.

In theory, dyes with amino-group substituents might fade on any fiber, but in practice, fading is most noticeable on cellulose acetates and on polyester fibers, less so on wool. The determining factor is the competition between fiber and dye for the nitrogen oxides. Nitrogen oxides seem to react preferentially with amino or imino groups in nylon or wool. The water content of the fiber also seems to play a part, possibly by diluting the acid gases, because dyes are not susceptible on cellulose and are less so on cellulose diacetate than triacetate.[39] This is the order of decreasing water content of the fibers. Adsorbed nitrogen oxides readily desorb in air from the acetate, but not from cellulose. Gas-fume fading on cellulose acetate is not accompanied by any mechanical weakening of the fiber.

In the tentative standard ISO test for gas-fume fastness, the patterns are exposed in an enclosed space under controlled humid conditions to an atmosphere containing nitrous fumes, generated by adding phosphoric acid solution to sodium nitrite solution.

b. Fading by Other Gases. Atmospheric ozone is a dye-fading agent. In the stratosphere, the ozone content is 6–8 ppm; at ground level in absence of pollution, up to 0.5 ppm, and in presence of high concentrations of nitrogen oxides and organic oxidants, produced by internal combustion engines, it can rise to 20 ppm, as in Los Angeles, but it can fall to 0.005 ppm where sulfur dioxide is in excess of nitrogen oxides. Salvin[40] reports marked ozone-fading of disperse blue dyes on cellulose triacetate even in low-ozone atmospheres. Fading is accentuated if the dye has not penetrated to the center of the fiber. Motor car exhaust

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[39] J. Boulton, *J. Soc. Dyers Colour.* **71**, 451 (1955); W. J. Myles and H. Reiss, *J. Polym. Sci.* **15**, 243 (1955).

[40] V. S. Salvin, *Am. Dyest. Rep.* **56**, 421 (1967), and earlier papers.

fumes also cause marked fading of many dyes. Hydrogen sulfide contamination (0.001–0.005 ppm) is present in urban atmospheres, but nothing is known of its effect on dyed fabrics.

The effect of sulfur dioxide is most noticeable with some azo dyes (often oranges or reds) on fibers, especially wool, containing traces of alkali, weakly colored bisulfite addition compounds of the dyes being formed. Urban atmospheres in Britain contain up to 2.0 ppm of free sulfur dioxide,[41] and even this appears to be sufficient to cause fading of some dyes; fading can also be caused by contact with paper or string containing bisulfite. The original color is restored by weak ammonia solution. The dyes susceptible to this form of fading include: CI 15510, 15620, 16230, 26400. This type of fading is not common within the textile trade at the present time, perhaps because some of the susceptible dyes are less used than formerly, but it might, of course, occur in museum specimens.

Sulfuric acid is present in the atmosphere due to catalytic oxidation of sulfur dioxide and will affect dyes having indicator properties and that are present on a fiber that does not itself combine with acids by ion exchange, e.g., Congo Red on cellulose.

IV. Relations between Technical Properties and Molecular Structure—Specific Dye–Fiber Systems

The refinements of the molecular architecture of dyes that impart to the dyes desirable properties are often carefully guarded secrets; even the patent literature on the subject is difficult to probe successfully to obtain clues to the structures that are commercially exploited. Among the areas where research has been concentrated in recent years are those covering reactive, disperse, basic, and acid dyes. We now consider some developments in areas that relate to the effects of molecular structure on the technical properties mentioned in the introduction, namely, application and fastness properties.

A. FIBER-REACTIVE DYES

1. *General Remarks*

The reactive dyes afford, in principle, the greatest opportunities for the chemist to design a dye combining the properties most desirable for dyeing textile fibers. These are brightness, level dyeing properties, and high wetfastness. The first reactive dyes, which were introduced in the late 1950s, were based on simple acid dye chromophores satisfying

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[41] C. H. Giles, S. D. Forrester, and B. J. Hojiwala, *J. Colloid Interface Sci.* **50**, 588 (1975).

the first two of these requirements and that were combined with chlorine-containing heterocycles capable of reacting with the cellulose anion under alkaline conditions to give dyeings that, at least in theory, are fast to washing by virtue of the dye–fiber covalent linkage. These dyes were particularly designed for pad-dyeing systems. Developments in the chemistry of reactive dyes during the subsequent twenty years have been well documented (see *CSD VI*); the present section deals with some of the structural changes made in the dye molecules in order to influence their technical properties.

The general structural features of a reactive dye are illustrated by S—D—B—R, where D is the chromogen, B is the linking group between the chromogen and the reactive group R, and S represents one or more water-solubilizing groups. In addition to the above outlined fastness properties that a reactive dye should have, its degree of reactivity and also substantivity and its diffusion properties in the fiber are of critical importance.

2. *Relation between Molecular Structure and Reactivity*

Simultaneously with its reaction with the fiber, the reactive dye molecule undergoes hydrolysis by the water of the dyebath. The efficiency of the dyeing process has therefore been defined[42] as (rate of fixation)/(rate of hydrolysis), which is proportional to k_f/k_h, where k_f and k_h are the first-order or pseudo-first-order rate constants of the fixation and hydrolysis reactions. The reactivity of a given dye, or the above expression for the dye–fiber–water system, is governed by the nature of the reactive group. All such groups undergo one or other of two types of nucleophilic attack,[43,44] and are either (a) groups that react by nucleophilic attack on their heteroaromatic nucleus by a substitution mechanism, or (b) those which react by addition of the nucleophilic group of the substrate to a C═C double bond.

The first-order rate constants for the hydrolysis of a series of dyes having the same chromogen attached to different reactive systems illustrate the wide variation between dyes incorporating different reactive groups.[45]

Assessments of the reactivities of whole ranges of reactive dyes have been published.[46] The reactivities of dyes in each particular range are

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[42] H. H. Sumner and C. D. Weston, *Am. Dyest. Rep.* **52**, 442 (1963).

[43] I. D. Rattee, *J. Soc. Dyers Colour.* **85**, 23 (1969).

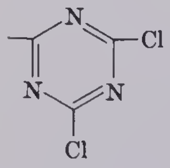
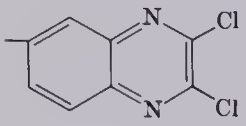
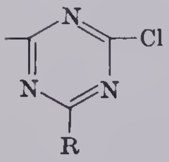
[44] P. Rhys and H. Zollinger, *in* "The Theory of Coloration of Textiles" (C. L. Bird and W. S. Boston, eds.), p. 329. Dyers Company Publications Trust, Bradford, Yorks. 1975.

[45] D. Hildebrand, *Colour. Annu.* p. 77 (1969); *CSD VI*, p. 352.

[46] J. A. Fowler and W. J. Marshall, *J. Soc. Dyers Colour.* **80**, 358 (1964).

TABLE I

PSEUDOUNIMOLECULAR HYDROLYSIS CONSTANTS K AT pH = 11[47]

	$K_w \times 10^{-3}$ (*min*$^{-1}$)			
Reactive group	20°	40°	60°	70°
 Dichlorotriazine	3.5–29	—	—	—
 Dichloroquinoxaline	0.3–1.8	5.4–23	—	—
$—SO_2CH_2CH_2OSO_3H$ Vinylsulfone	0.09–0.6	—	3.5–35	—
 Monochlorotriazine	0.02–2.3	—	—	4.1–103

designed to be similar, though in fact quite wide variations within ranges do occur (Table I).[47]

Thus, the reactivity, while primarily determined by the reactive grouping R, is also influenced by the chromogen, and any grouping in the chromogen that will, for example, increase the electron density at the point of nucleophilic attack will result in reduced reactivity. Thus, the deactivating influence of a phenolic group near the bonding linkage B, which will dissociate under the alkaline conditions employed in the application of reactive dyes to cellulose, is shown on p. 303.

The Procion M (ICI) dichlorotriazinyl dyes have also been shown[48] to possess two different reactivities for water, one at low and the other at high concentrations of OH^-. This has been interpreted by Horrobin[49] as being due to ionization of the bridging group B. This has been claimed[50] as an advantage in practice, since the substantivity of

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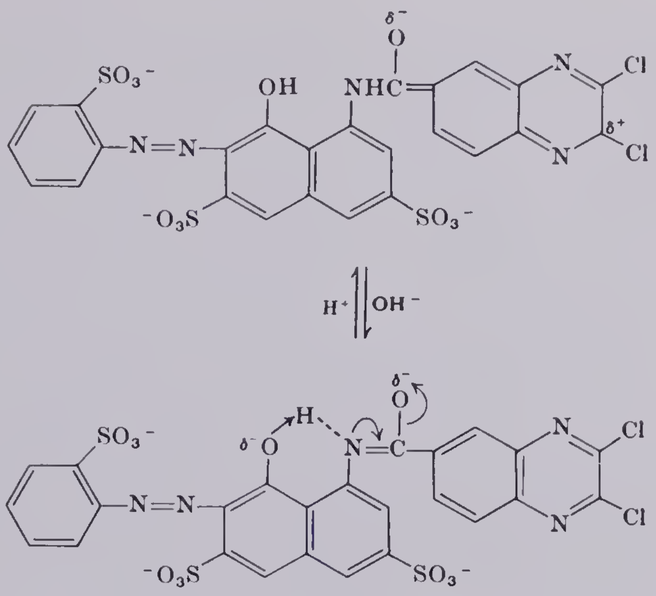
[47] D. Hildebrand, *Farben Rev.* (*USA*) 9, 29 (1964).

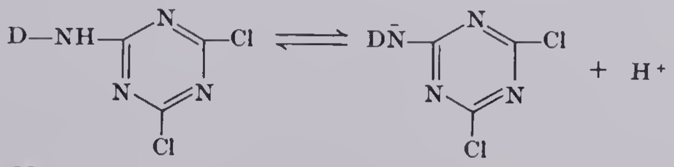
[48] W. Ingamells, H. H. Sumner, and G. Williams, *J. Soc. Dyers Colour.* 78, 274 (1962).

[49] S. Horrobin, *J. Chem. Soc.* p. 4130 (1963).

[50] W. J. Marshall, *Am. Dyest. Rep.* 58, 19 (1969).



dichlorotriazinyl dyes is often low in the pH range 10.5–12.5 at which point the dyes have acquired an adequate degree of reactivity.



More reactive form,
at low [OH⁻] values

Less reactive form,
at high [OH⁻] values

The reactivities of all dyes are increased with increase in pH and temperature, and in dyeing applications, many factors must be considered in choosing between dyes of high and low reactivity.[46] Generally speaking, high reactivity is economically desirable, e.g., in continuous dyeing methods, where highly reactive dyes require shorter steaming times or shorter batching times. In batchwise dyeing, dyes of high reactivity are more efficiently fixed, though in both cases other considerations, such as shade and penetration, may dictate the choice of monochlorotriazinyl dyes over the more reactive dichloro- types. As discussed below, the requirements for printing are somewhat different, and dyes of lower reactivity are preferred.

3. *Substantivity and Diffusion Properties*

Since the efficiency of a reactive dyeing is determined by the ratio (rate of fixation)/(rate of hydrolysis), and since the fixation rate depends ultimately on the concentration of adsorbed reactive dye, high substantivity or affinity might be considered a desirable feature in reactive dyes. However, in order to achieve suitable standards of wetfastness and levelness, most reactive dyes have only low to medium substantivity, representing a compromise between the parts played by that property in influencing the kinetics of the dye–fiber reaction, where a high value is desirable, and the requirement that hydrolyzed dye should be easily removed by washing, which demands a low value. The overall structure of the dye regulates substantivity and diffusional properties largely through the molecular weight and steric effects within the chromogen, as well as influencing other physical properties such as dye aggregation in solution. For example, a number of turquoise blue reactive dyes based on the metallized phthalocyanine chromogen, because of higher molecular weights and a tendency to aggregation, are more difficult to wash off efficiently than other dyes in the same range. Dyes of lower reactivity require larger molecules to provide sufficient substantivity for the substrate, but the ultimate choice between high and low substantivity is dictated by the application process, though, in general, most reactive dyes possess low to medium substantivity, because they contain at least two sulfonate groups to impart good solubility and washing off properties.

a. Application of Reactive Dyes to Cellulose by Batch Method. Despite their early development for continuous processing, it has been estimated that 65% of chlorotriazinyl dyes sold in 1970 were used in batch processing,[51] and in this area, a relatively high substantivity is desirable, low substantivity dyes giving high yields only when applied by pad methods. The effect of differences in substantivity on the dyeing characteristics of two dichlorotriazinyl dyes is shown in Fig. 11. With the dye of low substantivity, alkali addition is critical in controlling the dyeing, since dye is rapidly and irreversibly absorbed. This stage is much less critical with the highly substantive dye. The desire for high substantivity for efficient fixation coupled with good washing off properties to remove unfixed dye has resulted in the development of the Procion H-E (ICI) Dyes.[51] It is claimed that high fixation is obtained by modification of the chromogen to make the dyes salt sensitive, in the sense that they are applied in fairly high concentrations of electrolyte to give high exhaustion. At the same time, however, the substantivity is quite low under the low electrolyte concentrations occurring during subsequent washing. The effect on the efficiency of fixation when compared with the other Procion ranges (dichlorotriazinyl M and monochlorotriazinyl H) is shown in Fig. 12.

The above considerations of balance between high and low substantivities and different levels of reactivity apply also in a general way to those reactive dyes that undergo an addition reaction with cellulose to

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[51] M. R. Fox, *Text. Chem. Color.* 5, 197 (1973).

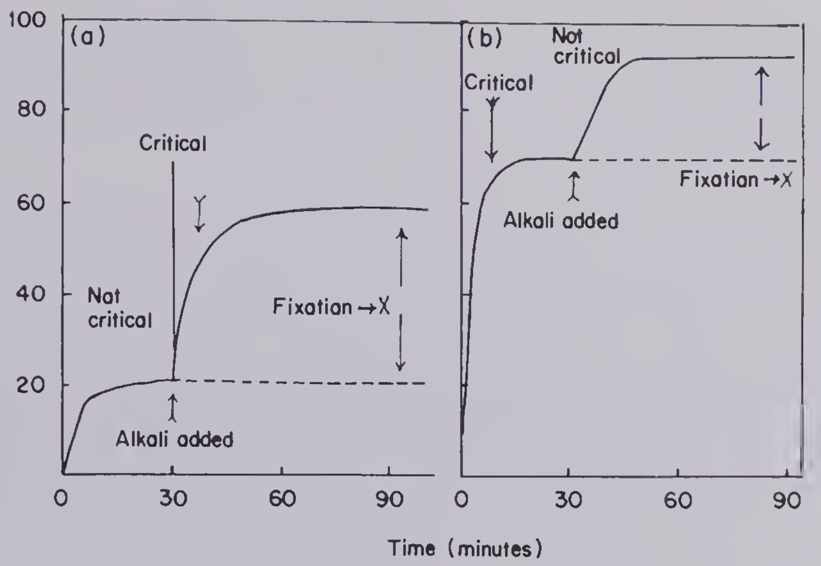

FIG. 11. Rate of exhaustion of low- and high-substantivity dyes[51]: (a) CI Reactive Blue 1; (b) CI Reactive Orange 1.

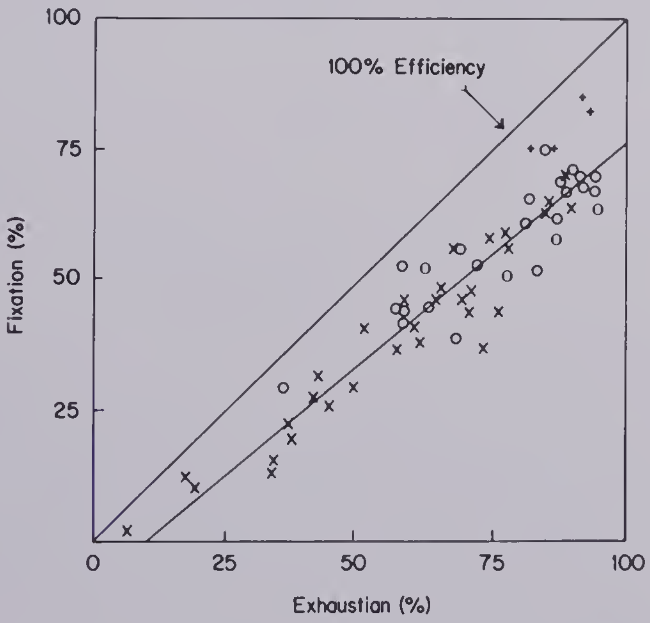

FIG. 12. Relation between fixation and exhaustion of Procion dyes[51]: (○) Procion M dyes; (×) Procion H dyes; (+) Procion H-E dyes.

form a cellulose ether. Such dyes are typified by the Remazol (Hoechst) ranges and are based on the reactivity of the vinylsulfone group, though the commercial products contain a precursor such as the β-sulfatoethylsulfone group and have the general formula $D—SO_2—CH_2—CH_2—O—SO_3Na$. These dyes have lower alkali stability than the chlorine-containing heterocyclics, and reaction with the fiber cannot take place until the reactive vinylsulfone is formed. The importance of the rate at which the latter is produced using different precursors has been described by von der Eltz[52] and the following points may be made:

1. The most versatile dyes are those based on the β-sulfatoethylsulfone precursor.

2. The application properties of the dyes can be modified by esterification with acids other than sulfuric acid. Thus, using thiosulfatoethylsulfones, the formation of the reactive vinylsulfone takes place at a higher pH than with the sulfatoethylsulfone precursor (Fig. 13), and the former offer advantages in certain exhaust dyeing methods with electrolyte owing to differences in the solubilities of the esters, as well as increased pad liquor stability in the presence of alkali.

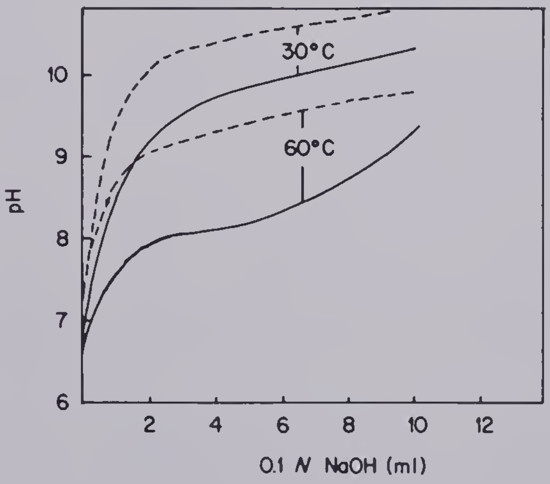

FIG. 13. Vinylsulfone formation from various esters;[52] (– – –) thiosulfatoethylsulfone, (——) sulfatoethylsulfone.

3. The use of β-dialkylaminoethylsulfone precursors of general formula $D—SO_2—CH_2—CH_2—NR_2$ reduces the reactivity of the dyes (Remazol H type) in that the conversion to the activated form is greatly retarded.[53] Such types, because of their increased alkaline stability, are particularly suited for printing and pad–batch and pad–steam dyeing processes. Dialkylaminoethylsulfones can in fact be produced from the normal β-sulfatoethylsulfone dyes by a short pretreatment with secondary amines.

4. Variations in reactivity of arylvinylsulfones can result from the introduction of a deactivating imino group (Remazol D dyes). Thus,

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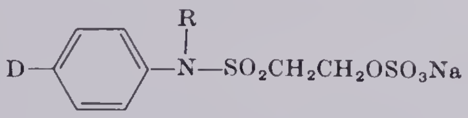
[52] H.-U. von der Eltz, *Text. Chem. Color.* **2**, 126 (1970).

[53] E. Feess, *Melliand Textilber.* **51**, 197 (1970).

with dyes of general formula shown below the application properties are largely determined by the substituent R.



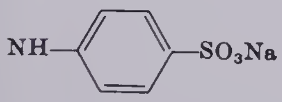
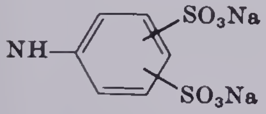
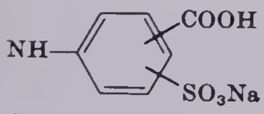
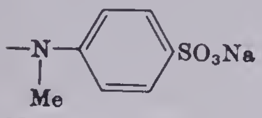
If R = H, conversion to the reactive form only occurs on thermofixation. If R is an alkyl group (CH_3 or C_2H_5), the reactivity is increased, and the dyes are suitable for pad dyeing methods and printing.

4. *Use of Reactive Dyes in Printing*

The requirements of a reactive dye that make it suitable for application by printing have been given[54] as (1) high solubility; (2) low substantivity (to assist removal of unfixed dye), coupled with good diffusional properties; (3) high degree of fixation; (4) reactivity high enough to achieve good fixation, but low enough to ensure print paste stability in all-in printing methods. Dichlorotriazinyl dyes are too reactive for printing, but dyes of the monochloro type, by virtue of the possible variations in R can be manufactured with differing degrees of

TABLE II

Effect of Substituents in Reactive System[55]

Group R	*Reactivity*
NH_2	Control
	Similar
	Similar
	Little higher
OMe	Higher
OPh	Higher
Cl	Much higher
	Lower
$N(Ph)(CH_2)_xMe$	Lower

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[54] F. R. Alsberg, H. G. Connor, W. F. Liquorice, and S. W. Milne, *Int. Dyer, Text. Printer, Bleacher Finish.* **141**, 151 (1969).

reactivity and practical behavior (Table II).[55] The degree of fixation during printing with conventional reactive dyes is, however, seldom greater than 70%.[54] Recently, improvements in this figure have been made by incorporating more than one reactive group into the dye molecule.[56,57] The Procion Supra (ICI) dyes are claimed to couple this type of modification, thus increasing fixation to ~ 90%, with a reduction in substantivity produced by introducing substituents to prevent coplanarity of the molecule. This can be achieved, e.g., by the presence of a substituent ortho to the point of attachment of a planar reactive group or by substitution of the bridging nitrogen through which the reactive group is attached.[57] Thus, by reducing the amount of unfixed dye to be washed out, advantages in washing off and wet-marking off are evident. The improvement in washing off compared with conventional reactive dyes for a range of shades from 1/1 to 4/1 ISO standard depth is shown in Fig. 14.

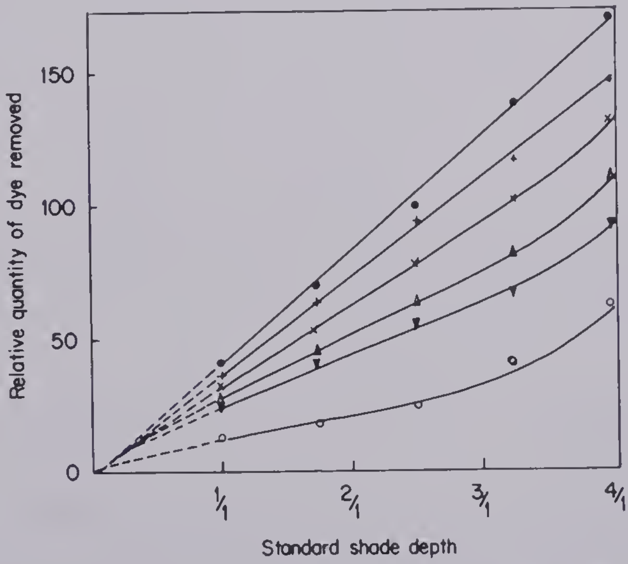

FIG. 14. Differences in washing-off properties among ranges of reactive dyes;[54] (○) Procion Supra Red 4BP (ICI); the other data are for conventional reactive red dyes.

While the reactivity of the Procion Supra dyes is very similar to the monochlorotriazinyl (Procion 'H') dyes, the high level of fixation achieved makes them ideally suited to all-in steaming processes. The severity of fixation conditions with respect to alkali, development time, and temperature is determined by the reactivity of the dye, and

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[55] B. Glover and J. A. Hughes, *J. Soc. Dyers Colour.* 87, 371 (1971).

[56] C. V. Stead, *Rev. Prog. Color.* 1, 23 (1969).

[57] R. R. Davies, *Rev. Prog. Color.* 3, 73 (1972).

generally, manufacturers choose dyes of suitable solubility, substantivity, diffusion properties, and color, varying reactivities where necessary through chemical modifications in the reactive group (see Table II). Having estimated values for substantivity, reactivity, and diffusion coefficient for a range of monochlorotriazinyl dyes, Glover and Hughes[55] correlated them with the suitability of dyes for all-in printing (Fig. 15). Thus, dyes were classified from A to D, i.e., from higher to lower reactivities. In order to modify a dye represented by x (unsuitable for development by two-stage development and only suitable for all-in processing by steaming for times in excess of 5 minutes) to make it suitable for two-stage development, it is necessary to increase the reactivity by suitable choice of R (see Table II) in Fig. 15 to move it to point z. This procedure is preferable to changing the substantivity and diffusion properties to move x to y (also in area B).

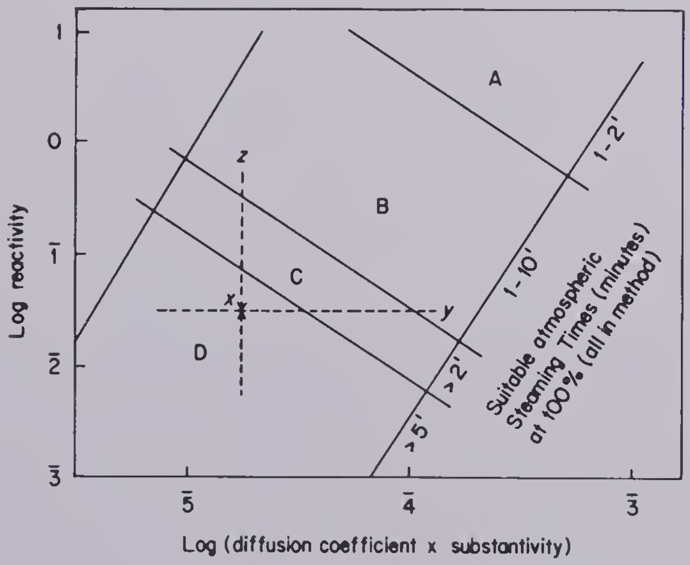
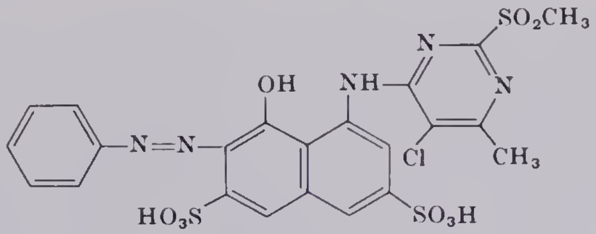


Fig. 15. Log reactivity versus log of product of diffusion coefficient and substantivity[55] (suitability for all-in method).

The possibilities for modifying reactivity by replacing one of the chlorine atoms in diazine dyes are more limited than in the triazine type, though the electronegative alkylsulfonyl group is exploited in the Levafix P (Bayer) dyes to give higher reactivity compared with the dichloro product. This, combined with low substantivity and good diffusion properties, makes these dyes particularly suited for printing as well as for pad–dyeing systems. Such dyes are typified by structures such as that shown below.



5. *Reactive Dyes for Wool*

Though reactive dyes for wool were commercially available before the introduction of the first Procion dyes for cellulose, they have become widely used only in the last ten years. The main practical difficulties facing the dyer in early trials were an unacceptable degree of unlevelness and inefficient removal of unfixed dye during subsequent washing. These dyes consisted of (1) ranges designed specially for the wool fiber and containing reactive groups such as sulfatoethylsulfone (FH) ($—SO_2CH_2CH_2OSO_3H$) and chloroacetamido (CGY)($—NHCOCH_2Cl$); and (2) existing ranges such as the monochlorotriazinyl dyes designed for cellulose dyeing, but applied to wool under acid conditions.

Some time later, ranges were introduced based on different reactive groups, such as acrylamido and fluorinated pyrimidines, which were claimed to combine level dyeing behavior with a high degree of wetfastness. In particular, the introduction of Superwash wool, with its high washfastness requirement has dictated the use of dyes covalently bound to the fiber.[58] Most of the practical problems mentioned above arise as a result of incomplete reaction of dye with the fiber. Among the reasons for this[59] are (1) the low reaction rate with —SH, $—NH_2$ and, $>NH$ groups in wool; (2) the tendency for reactive groups to hydrolyze under acid conditions; (3) the behavior of hydrolyzed in dye acting as an ordinary acid dye, which unlike the cellulose reactive dyes, has high affinity for the fiber and resists removal during washing off; (4) the instability of the reactive group, which can lead to hydrolysis even during manufacture; and (5) the low diffusion rates of these dyes in wool. In addition, the wool fiber itself can accentuate unlevelness due to differential dye uptake by its tip and root portions.

One approach to the improvement of the level-dyeing properties of reactive dyes on wool has been to modify the structure of the reactive group so that it forms only during dyeing. Particularly suited to this modification are the vinylsulfone precursors, typified by the Hostalan (FH) dyes.[60] The early Remalan (FH) range of reactive dyes for wool

[58] E. Bellhouse, *J. Soc. Dyers Colour.* **91**, 33 (1975).

[59] D. Hildebrand and G. Meier, *Farben Rev.* (*USA*) **20**, 12 (1971).

[60] F. Osterloh, *Text.-Prax.* **26**, 164 (1971).

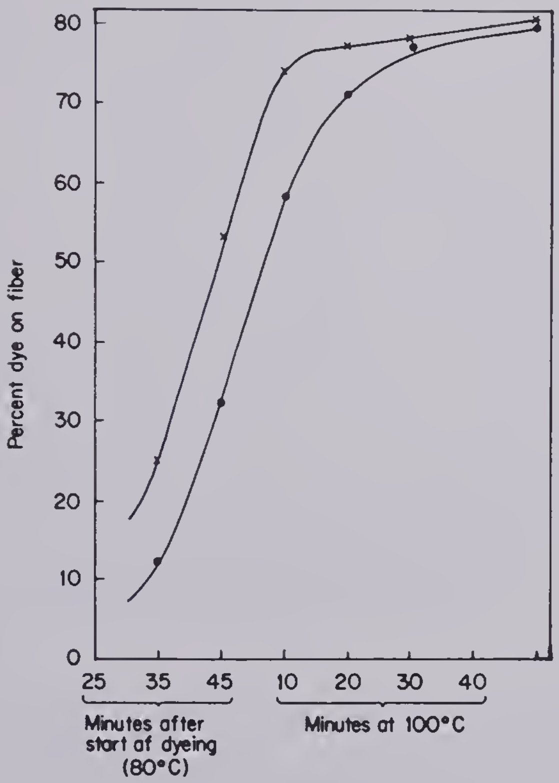


FIG. 16. The dependence of the rate of dyeing on the functional group of a reactive dye (2% Remazolan Red R);[61] (×) D—SO_2—CH=CH_2, (●) D—SO_2—CH_2—CH_2—OSO_3H.

contained the β-sulfatoethylsulfonyl group as precursor, and though the rate of dyeing is slowed down at pH 6 by the precursor compared with the active vinylsulfone group (Fig. 16), the Remalan dyes still did not give acceptable levelness.[61]

However, it was found that the reactive vinylsulfone group can be formed in a controlled manner during dyeing from a β-N-methyltaurine ethylsulfone precursor, D—SO_2—CH_2CH_2—$N(CH_3)$—$CH_2CH_2SO_3H$. The equilibrium between the reactive form and the methyltaurine addition product is rapidly changed in favor of the reactive form under boiling acid conditions, while the migrating power of the dyes can be maintained during the early stages of dyeing without the reactivity being affected. Figure 17 shows the effect of pH on the conversion of the methyltaurine precursor to the reactive vinylsulfone and the hydrolyzed form of the dye. By dyeing at pH 5, the Hostalan dye is slowly converted to the reactive vinylsulfone at the boil. Other manufacturers have concentrated on producing dyes having a high degree

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[61] H.-U. von der Eltz, *Textilveredlung* 7, 297 (1972).

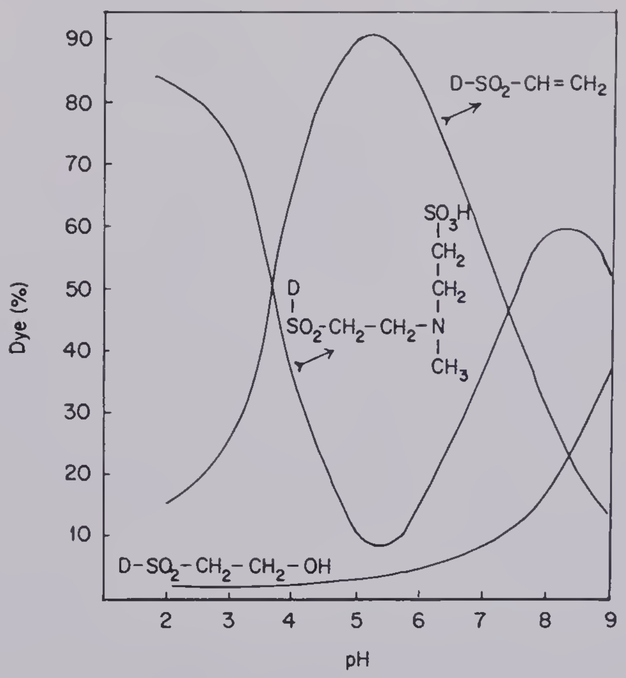


FIG. 17. Conversion of a reactive red to vinyl and hydroxyl dye in the absence of wool.[61]

of fixation due to the relatively high substantivity of unreacted and hydrolyzed dyes for wool, and a number of groups of high reactivity have been introduced. Some examples are:

1. 2,4-Difluoro-5-chloropyrimidine group. The Verofix (FBy), Drimalan F (S) and Reactolan (CGY) ranges are all based on this system, and compared with the corresponding wholly chlorinated pyrimidines, the fluorine atom is about one-hundred times more reactive than chlorine as an exchangeable radical.[18]
2. α-Bromoacrylamide group (D—NH—CO—CBr═CH_2), as in the Lanasol dyes (CGY).
3. Acrylamido group (D—NH—CO—CH═CH_2), as in the Procilan dyes (ICI), which are metal complexes.

These unsaturated types have the advantage of being less prone to acid hydrolysis under dyeing conditions than dyes based on the halogeno-heterocyclic systems, which undergo nucleophilic substitution. Relative reactivities are also influenced, however, by the chromogen, as shown in Fig. 18 for dyes A, B, C, and D[62] of related structures. Thus, the dyes differ in reactivity, and this is influenced markedly by the chromogen structure, even small differences (as in dyes B and C) having a significant effect.

[62] A. N. Derbyshire and G. R. Tristram, *J. Soc. Dyers Colour.* 81, 584 (1965).

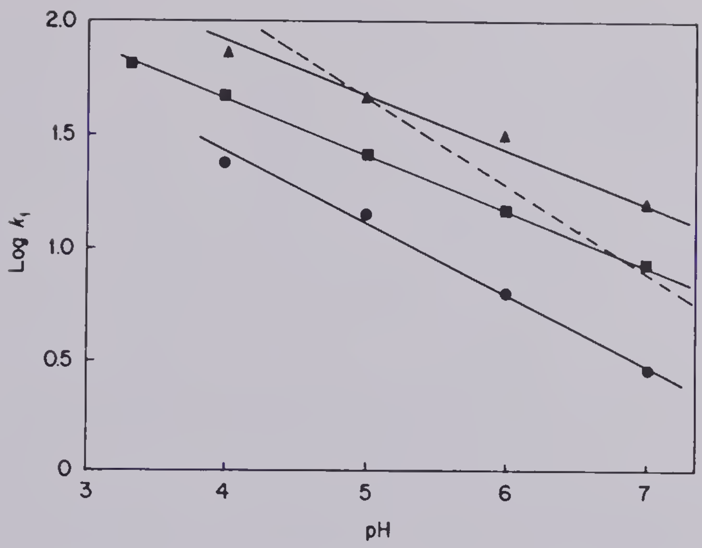


FIG. 18. Variation of reactivity of acrylamido dyes with pH[62]; (– – –) dye A (metal complex), (▲) dye B, (■) dye C, (●) dye D.

B. ACID DYES

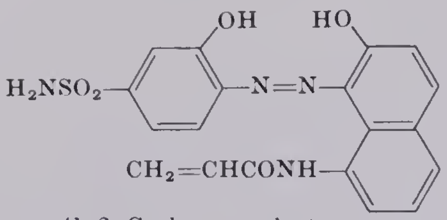
1. *General Remarks*

The wool acid dye system has been fairly widely studied in so far as the success of the finished dyeing is related to the molecular structure of the dyes. The hydrophobic nature of the wool fiber highlights the importance of the hydrophobic/hydrophilic ratio of the dye, and in addition to the importance of the number of sulfonate groups per dye molecule, their disposition is also critical. Thus of the two dyes (naphthionic acid → Schaeffer acid) and (1-naphthylamine → R-acid) of identical hydrophobic/hydrophilic ratios, the former is by far the more level dyeing.

To satisfy the requirements of a high level of wetfastness while retaining the brightness of shade associated with this class of dye, it is necessary to increase the molecular weight of the dye without increasing the number of azo groups. This is achieved in a number of ways: thus, the fastness of many yellows is slightly improved by using 1-phenyl-pyrazolones, e.g., CI Acid Yellow 17 (CI 18965).

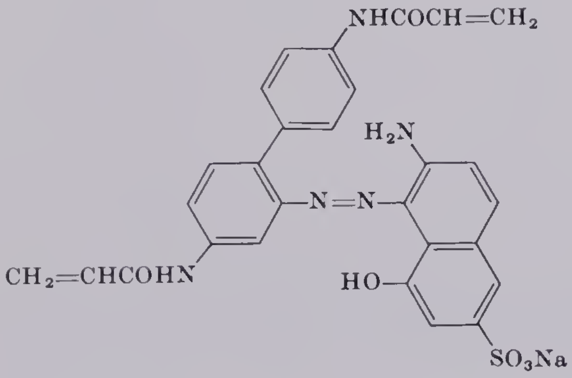
A more effective method for increasing wetfastness properties is to couple the *N*-acyl or *N*-aryl derivatives of naphthalamido acids such as H-, γ-, and J-acids with diazo components of higher molecular weight. Dyes of this type (e.g., CI Acid Red 172; CI 18135) have properties associated with the milling acid dyes.

The Carbolan (ICI) range of dyes (*CSD II*, p. 491) has high wetfastness properties due to the use of diazonium components containing heavy alkyl groups. An example is CI Acid Red 138 (*p*-dodecylaniline → *N*-acetyl H-acid). Besides being surface active, these dyes have high

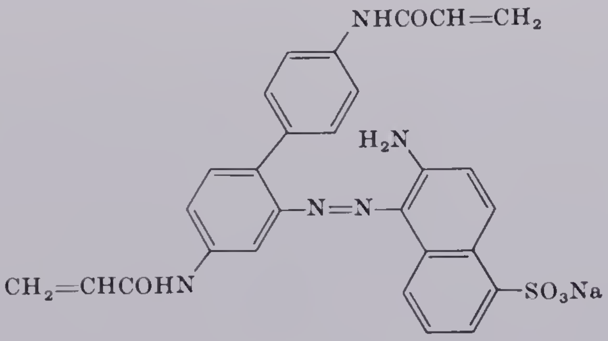


(1:2, Cr-dye complex)

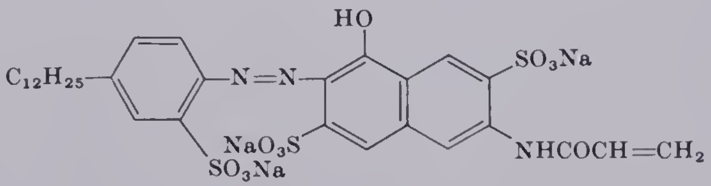
A



B



C



D

wetfastness properties, are applied as super-milling dyes, yet still retain the brightness associated with the low molecular weight acid dyes.

Increasing the molecular weight in these ways alters the solubility, the diffusion properties, and the tendency to aggregate in water of the dye; the number and positions of the solubilizing sulfonate groups are again of importance.

2. *Relationship between Structure and Dyeing Properties*

Many workers have drawn attention to the relationships existing between the degree of sulfonation of acid dyes and dyeing properties.

There is a general tendency for an increase in the number of sulfonate groups to produce the following effects: (1) a reduction in rate of dye absorption,[63] (2) an increasing contrast between untreated and chlorinated wool when dyed with acid dyes,[64] (3) an increase in "tippy" dyeing,[65] and (4) a reduced ability to cover abrasion damage.[66] It has been pointed out[65] that while such general relationships exist for acid equalizing dyes, with milling dyes the situation is more complex. With the latter, which vary widely in molecular weight, the dyeing properties on uneven-dyeing wools depend both on the degree of sulfonation and the molecular weight. An increase in the former will produce more uneven dyeing, while an increase in molecular weight will have two effects: (1) an increased hydrophobic character, which will enhance the coverage properties; and (2) a lowering of the diffusion rate due to steric effects above a critical molecular size. As a consequence, there is no simple relation between dyeing properties and degree of sulfonation with acid milling dyes.

3. *Dyeing of Polyamides with Acid Dyes*

One of the main problems arising in the dyeing of polyamide fabrics is the appearance of barré, resulting from chemical, and more particularly physical, differences between yarns. The mechanism of the dyeing of nylon with acid dyes has been fairly widely studied,[67,68] and the levelness attained is determined by a combination of the processes of dye absorption at the fiber surface and subsequent diffusion into the fiber. Thus, the two important properties of the dye molecule—adsorption behavior (determined by the concentration and thermodynamic affinity of the dye) and the diffusion coefficient—have been combined in a function known as the *K* index of the dye.[69] The effect of one of its components, the diffusion coefficient, on so-called barry dyeing has been investigated[70] and is shown in Fig. 19. Thus, the difference in depth, as measured by the ratios of the degree of saturation on normally (θ_n) and highly (θ_h) drawn nylon 66, is shown for a dye with a small diffusion coefficient (Nylosan Blue F-GBL) (CI Acid Blue 127) and one with a higher value (Nylosan Blue N-GL) (CI Acid Blue 251). After similar dyeing times, the former dyeing shows a

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[63] D. R. Lemin and I. D. Rattee, *J. Soc. Dyers Colour.* **65**, 217 (1949).

[64] F. Townend, *J. Soc. Dyers Colour.* **61**, 144 (1945).

[65] H. R. Hadfield and D. R. Lemin, *J. Soc. Dyers Colour.* **77**, 97 (1961).

[66] H. R. Hadfield and D. R. Lemin, *J. Soc. Dyers Colour.* **77**, 715 (1961).

[67] A. B. Meggy, *J. Soc. Dyers Colour.* **66**, 510 (1950).

[68] E. Atherton, D. A. Downey, and R. H. Peters, *J. Soc. Dyers Colour.* **74**, 242 (1958).

[69] H. G. Otten, *Farben Rev.* (*USA*) **21**, 32 (1972).

[70] K. Greider, *J. Soc. Dyers Colour.* **90**, 435 (1974).

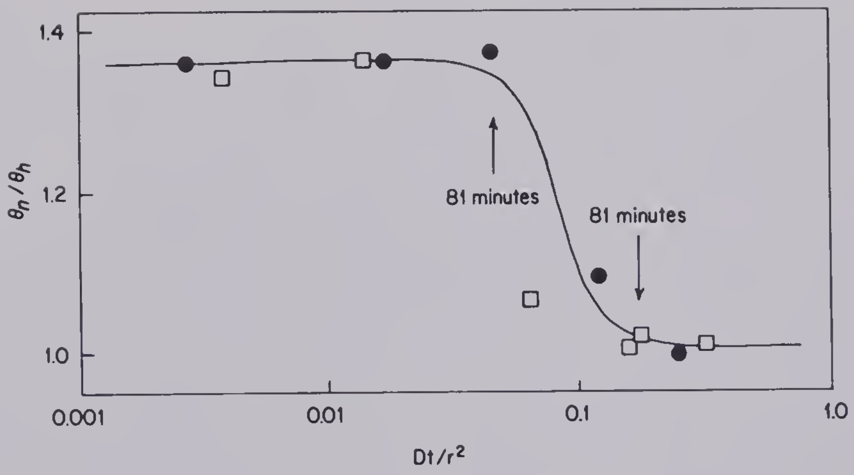

FIG. 19. Ratio of degree of saturation of differently drawn nylon 6.6 filaments as a function of mean time parameter (finite dyebath)[70]; (□), Nylosan Blue N—GL; (●) Nylosan Blue F—GBL. The differences obtained with both dyes after 81-minute dyeing times are indicated by arrows. Maximum bath exhaustion, 70%.

difference of about 34% in degree of saturation, while with Nylosan N-GL, both highly and normally drawn fibers are dyed to a similar depth. The figure also shows the general behavior of dyes in the dyeing of barry nylon materials when the depth difference remains constant for a length of time determined by the diffusion coefficient of the dye and then rapidly decreases.

The K indices have been developed, therefore, in an attempt to assess the compatibility of acid dyes in admixture when applied to polyamide fibers under conditions such that (1) dyeing times are as short as possible; (2) optimum levelness, as judged by tone-in-tone appearance, is achieved; (3) optimum color yield is attained. This has successfully been exploited in the Telon S process[71,72] and has resulted in the grouping of acid dyes into suitable compatible ranges, based not only on physicochemical measurements of compatibility, but also on the end use of the dyed material. Thus, one group consists of dyes having the following properties, as well as compatibility: (1) high light fastness, (2) low molecular weight, (3) monofunctionality, and (4) good coverage of physical differences in fibers. These dyes are recommended for the dyeing of carpets and furnishings.

The second group consists of higher molecular weight monosulfonated dyes, still possessing good leveling properties coupled with better wet fastness, making them suitable for outer garments. The third group are disulfonated dyes, combining excellent wet fastness with only a limited

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[71] W. Beckmann, F. Hoffmann, and K. J. Rohr, *Melliand Textilber.* **55**, 51 (1974).

[72] F. Lesszinsky, *Farben Rev.* (*USA*) **25**, 24 (1975).

ability to cover fiber differences. Combinations from different groups, e.g., of mono- and disulfonated dyes, lead to blocking effects in medium to heavy depths of shade.

By comparison with the development of the above process, earlier selections of acid dyes for nylon had been made more arbitrarily from existing acid wool dyes. As rough guidelines, the best compromise between level-dyeing and wetfastness properties was achieved using monosulfonated dyes with molecular weights of 400–500 or disulfonated dyes with molecular weights around 800.[73] In addition to differences in molecular weight, the introduction of polar substituents such as hydroxyl or acylamino groups generally increases wet fastness at the expense of level dyeing behavior. For both wool and nylon, relationships have been established between molecular weight and standard affinity and hence washfastness.[74,75] The following points may be made regarding such relationships:

1. The increase in molecular weight that gives rise to an increased standard affinity does not, in the case of wool, require being associated with continuing planarity of the molecule, as happens in the case of direct cotton dyes. If by increasing the molecular weight of an acid dye a planar configuration does result, then such a dye may also dye cotton. This is exemplified by the dyes CI Direct Red 2 and 61 (CI 23500; CI 23040; naphthionic acid ← *o*-tolidine or 3,3′-dichlorobenzidine → naphthionic acid), which dye solid (or practically solid) shades on wool–cotton union fabrics.
2. Replacement of a benzene by a naphthalene residue results in a fairly uniform increase in affinity.[76]
3. With a substituted *n*-alkyl group, the standard affinity increases uniformly with addition of each methylene group up to $n\text{-}C_4H_9$, beyond which further lengthening of the chain leads to relatively small increases.[77]
4. The addition of a sulfonate group causes a decrease in affinity for nylon, other factors remaining constant, and within a series of disulfonates, the affinity increases with the distance between sulfonate groups.[78]

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[73] C. V. Stead, *Rev. Prog. Color.* **6**, 1 (1975).

[74] T. Shimiza, S. Ohya, and K. Ito, *J. Soc. Fiber Sci. Technol. Jpn.* **21**, 213 (1965); through *J. Soc. Dyers Colour.* **81**, 382 (1965).

[75] T. Vickerstaff, "The Physical Chemistry of Dyeing," 2nd ed., Oliver & Boyd, Edinburgh, 1954. p. 415.

[76] E. Atherton, D. A. Downey, and R. H. Peters, *Text. Res. J.* **25**, 988 (1955).

[77] K. Greider, *J. Soc. Dyers Colour.* **92**, 8 (1976).

[78] T. Iijima and M. Sekido, *J. Soc. Text. Cellulose Ind. Jpn.* **18**, 153 (1962); through *J. Soc. Dyers Colour.* **78**, 359 (1962).

5. When the addition of a sulfonate group is coupled with an increase in molecular weight (other than that due to the sulfonate group) the resulting dye may have a higher affinity on nylon, but this will be associated with a lower exhaustion.

C. Disperse Dyes

1. *General Remarks*

The growth in the use of made-made fibers and particularly polyester fiber, which is widely used both as texturized polyester material and in blends with wool and cellulose, has led to the synthesis of a large number of new disperse dyes with improved dyeing and fastness properties. With a few exceptions, the conventional acetate dyes do not build up sufficiently on polyesters, nor are they sufficiently fast to light or thermofixation. Hence, new dyes especially designed for dyeing and printing polyester fibers have had to be developed. During the 1960s increasingly stringent requirements for fastness of dyed polyester material to heat treatments led to the development of disperse dyes for polyester of low diffusion coefficient and high sublimation or heat-fastness. However, the main requirement for transfer printing (see Section IV C, 6) is that the dye must possess a comparatively high vapor pressure at the application temperature. Hence, in recent years there has been a trend toward developing special ranges of disperse dyes for different fibers and for special application conditions.[79] Numerically, the number of disperse dyes listed in the Colour Index now far exceeds any other dye application class, except acid and direct dyes.

The term "disperse dyes" has been defined as "a class of water-insoluble dyes originally introduced for dyeing cellulose acetate and usually applied from fine aqueous suspensions." Chemically, the dyes are principally simple azo and anthraquinone derivatives, which for cellulose acetate often contain β-hydroxyethylamine groups to confer a limited solubility in water. However, the physical form of the dye is also important, and early studies showed the importance of small particle size. Thus, in order to obtain maximum color yield, reproducibility, and freedom from faults, the disperse dye must be presented to the fiber as a fine, uniform, stable suspension. In practice, disperse dyes contain a dispersing agent whose main functions are[80] (1) to assist the process of reducing the size of the dye particle during manufacture, (2) to facilitate the change from powder to dispersion when the dyebath is prepared, and (3) to maintain the dispersion during dyeing.

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[79] J. F. Dawson, *Rev. Prog. Color.* **3**, 18 (1972).

[80] R. K. Fourness, *J. Soc. Dyers Colour.* **72**, 513 (1956); **90**, 15 (1974).

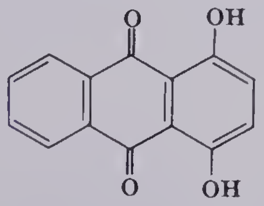
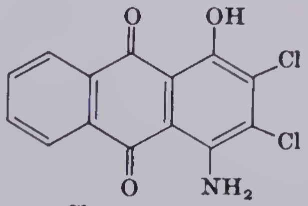
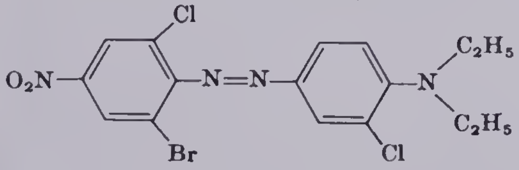
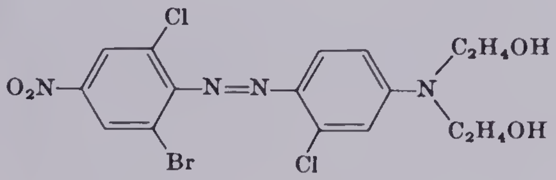
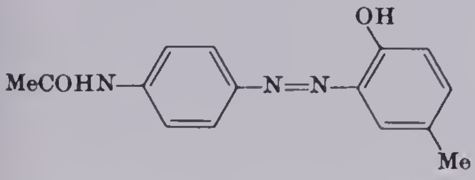
2. *Molecular Structure and Diffusion Rate in Hydrophobic Fibers*

The smaller the diffusion coefficient *D*, the lower the rate of dyeing. *D* itself decreases with increase in molecular weight or volume of the dye, but it also depends on the polarity of the substituent groups or even on the ability of the substituent groups in the dye molecule to form hydrogen bonds with the fiber (see *CSD VII*, p. 132; Fig. 8).

Glenz *et al.*[81] find that the hydrogen-bonding property of this type of

TABLE III

Diffusion and Saturation Data (100°) for Disperse Dyes on PET (without Carrier)[81]

	Dye	*Molar volume factor*	*Diffusion coefficient* *(cm^2/sec) × 10^{11}*	*Saturation adsorption* *(mmole kg fiber)*
A		900	0.6	142
B		1000	0.10(±0.01)	25
C		3200	0.26(±0.03)	23
D		4100	0.06	112
E		2500	0.06	134

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[81] O. Glenz, W. Beckmann, and W. Wunder, *J. Soc. Dyers Colour.* 75, 141 (1959).

dye is in many cases more effective in determining the value of D in such systems than the purely geometric factor or the molecular weight. This is illustrated by their results shown in Table III.

3. *Dyes on Cellulose Acetate*[82]

Disperse dyes are applied to secondary cellulose acetate at temperatures below 85°, because higher temperatures cause undesirable changes to occur in the fiber. Cellulose triacetate, however, can withstand higher temperatures, and fabrics made of this fiber can be treated by thermal finishing processes at temperatures higher than are safe for the secondary ester. This led to the demand for higher heatfastness in the dyed material. Dyes meeting this requirement necessarily have lower diffusion coefficients than those not required to withstand high temperatures, and their use in turn necessitated higher temperatures in dyeing cellulose triacetate than had been used for the secondary acetate, and for heavy shades, the use of carriers became necessary.[83] These requirements, however, are much more important in the dyeing of polyester fiber than cellulose triacetate.

4. *Dyes on Polyester*

Disperse dyes are virtually the only class of dye that can be used for coloring polyester materials, and in the early days, considerable difficulty was experienced in obtaining adequate color yield from the disperse dyes then available and used for cellulose acetate and nylon. The early pioneering work of Waters[84] demonstrated that the yield from disperse dyes was limited essentially by low rates of dyeing rather than by low substantivity for the fiber. By using sufficiently long dyeing times, it was possible to show that the saturation values of disperse dyes on polyester are comparable with those on secondary acetate and can be higher than saturation values for nylon (Table IV).[85]

The low rate of dyeing of these dyes on polyester is due to the very slow diffusion of the dye in this fiber, as is evident from dyed fiber cross-sections, which show very marked ring-dyeing effects. This supposition is confirmed by determination of relative diffusion coefficients on the three fibers (Table V).[85] This table also illustrates the considerable temperature dependence of diffusion coefficients in polyester.

The advantages of using dyeing temperatures in excess of 100° were quickly appreciated, but at first their use was limited by the lack of

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[82] C. L. Bird, *Palette* **15**, 25 (1964).

[83] C. L. Bird, F. Manchester, and D. F. Scott, *J. Soc. Dyers Colour.* **72**, 49 (1956).

[84] E. Waters, *J. Soc. Dyers Colour.* **66**, 609 (1950).

[85] A. N. Derbyshire, *J. Soc. Dyers Colour.* **90**, 273 (1974).

TABLE IV

SATURATION VALUES OF DISPERSE DYES[85]

Fiber	CI disperse dye (% on weight of fiber at 85°)			
	Orange 3	*Red* 15	*Violet* 1	*Yellow* 1
Polyester	4.1	12.0	4.4	7.1
Nylon	2.0	4.4	4.9	5.0
Cellulose acetate	5.1	11.2	8.3	16.0

TABLE V

RELATIVE DIFFUSION COEFFICIENTS OF DISPERSE DYES[85]

Fiber	CI disperse dye		
	Orange 3	*Red* 15	*Violet* 1
Polyester (85°)	1	1	1
Polyester (100°)	48	34	31
Nylon (85°)	680	1000	450
Cellulose acetate (85°)	460	286	452

suitable dyeing equipment. However, the use of reagents, termed "carriers," diphenyl and *o*-phenylphenol in the dyebath, allowed good color yields to be obtained even at the boil. This had an immediate effect on dye selection, allowing the use of slower-diffusing dyes of higher fastness.

Disperse dyes are now placed,[86] according to their heat or sublimation fastness, into an A, B, C, D classification, D having the best fastness. The trend over the years of replacing the dyes of lower fastness reflects the increased usage of polyester, the changing demands for higher heatfastness, and the increased availability of pressure-dyeing equipment.

5. *Chemical Structure and Heatfastness*

Heat- or sublimation-fastness, like rate of dyeing, depends on the diffusion coefficient of the disperse dye in the polymer substrate. Thus, in general heatfastness is increased by molecular size or increase in polarity. However, these changes tend to lower the color yield when the dyes are applied by exhaustion methods, and high temperatures

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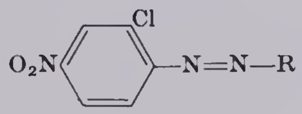
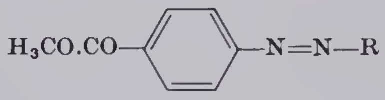
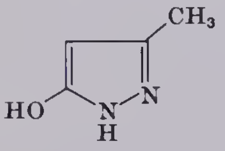
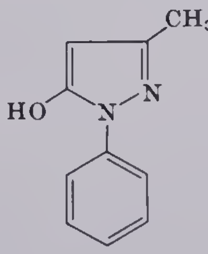
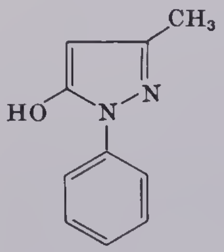
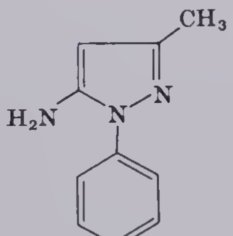
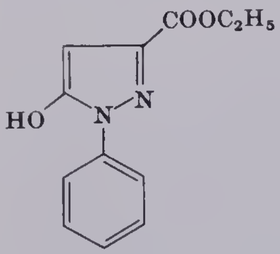
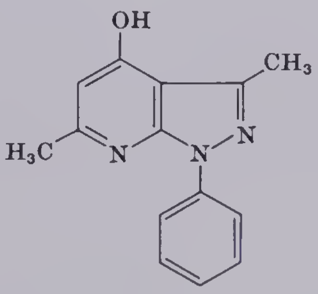
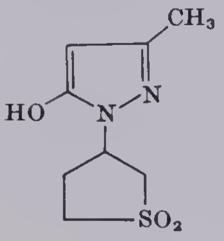
[86] ICI, Technical Information D1389 (1973).

must be used to counteract this effect. Thus, dyeing of polyester with Class D disperse dyes now involves using temperatures up to 130°.

In an excellent and comprehensive paper on the relationship between the structure of disperse dyes and their dyeing properties, Muller[87] discussed the influence of chemical structure on thermofixation-fastness for both azo and anthraquinone disperse dyes. The importance of the

TABLE VI

INFLUENCE OF COUPLING COMPONENT (R) IN AZO DISPERSE DYES ON THEIR THERMOFIXATION FASTNESS (TFF)[87]

Dye 		*Dye* 	
R	TFF	R	TFF
	1–2		2–3
	2–3		3–4
	3–4		4–5
	5		

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[87] C. Muller, *Am. Dyest. Rep.* **59**, March, 37 (1970).

nature of the coupling component of some azo dyes is illustrated by the data in Table VI.

The increases in thermofixation fastness appear to be associated with increases in molecular weight and polarity changes, although in Table VI the polarity effect of the tetramethylene sulfone group is seen to produce a significantly larger increase in heatfastness compared with the phenyl group, despite only a modest molecular weight or volume difference. In the second example, a simple polarity difference between the amino and hydroxy groups leads to an increase of one grade in the thermofixation-fastness.

Muller also compares the influence of nuclear and side-chain substituents on the thermofixation and light fastness of a series of azo disperse dyes (Figs. 20 and 21). Thus, it is clear that to obtain both

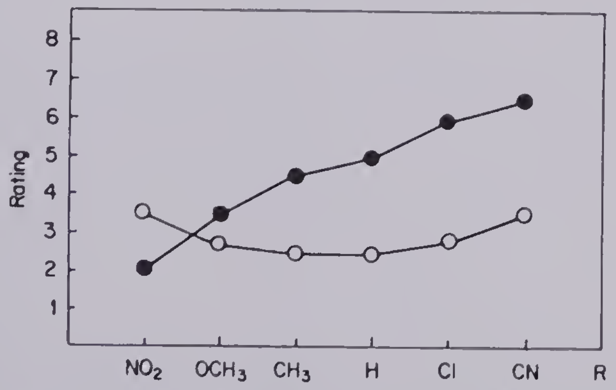

FIG. 20. Influence of various substituents on the thermofixation (210°, 30 seconds) (○) and lightfastness (●) of dyes applied to Dacron polyester fabric.[87]

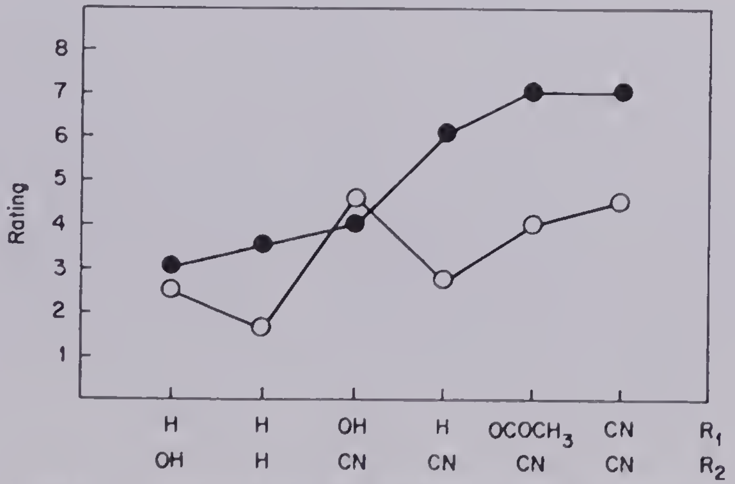

FIG. 21. Influence of various side-chain substituents on the thermofixation (210°, 30 seconds) (○) and lightfastness (●) of dyes applied to Dacron polyester fabric.[87]

satisfactory heat- and lightfastness, a judicious choice of substituent groups is required, as is also illustrated in Fig. 21 for the side-chain substituents.

The thermofixation fastness of anthraquinone disperse dyes is also appreciably influenced by the nature of the substituent, with the sulfonamide and carboxylamide groups present in a phenyl ring leading to marked improvement in both dry heat and steam fastness (Table VII).

Other factors that influence the thermal stability of disperse dyed material have also been investigated, and their relevance to the suitability of a dye for permanent press or durable-press styles discussed.[88] Factors found to influence heatfastness include dye concentration, time and temperature conditions in testing, the nature of the substrate, and the presence and nature of dyeing auxiliaries.

6. *Disperse Dyes for Transfer Printing*

Transfer printing is a relatively new process in which multicolored designs are transferred through the vapor phase from a paper support to a synthetic fiber fabric under controlled conditions of temperature and pressure (see Chapter V). The design is preprinted on the paper using inks formulated from specially selected disperse dyes that are able to sublime at the temperatures employed in the transfer process. This development has partially reversed the trend of research in disperse dye synthesis, because the properties required for efficient transfer printing are the opposite of those required for high heatfastness.

According to Moore,[89] to be suitable for transfer printing the dyes must (1) sublime at a rate suitable for the fabric; (2) sublime in a temperature range low enough to prevent melting or discoloration of the fibers (150°–220°); (3) have little or no substantivity for cellulose-based papers used as the support, but be readily absorbed by the synthetic polymer fibers to give adequate depth and sufficient color fastness to light, washing, etc. for the intended end use of the fabric; and (4) sublime in mixture with other dyes with similar rates of vaporization, especially when used for blacks, dark greens, and browns. To achieve optimum characteristics, the dye must possess a comparatively high vapor pressure at the application temperature, thus imposing an upper limit on its molecular weight. Therefore, the simple azo and anthraquinone compounds with nonpolar substituents might be expected to be the most useful. However, it has been pointed out[90] that an

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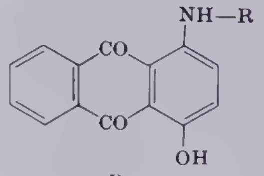
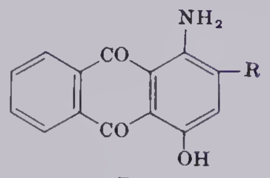
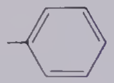
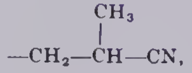
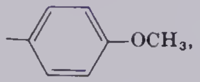
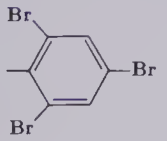
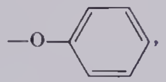
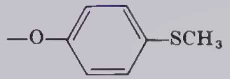
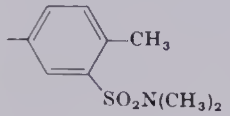
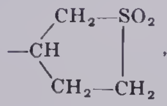
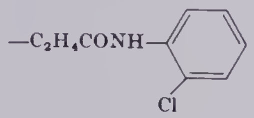
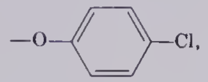
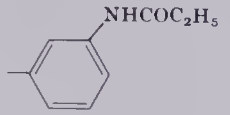
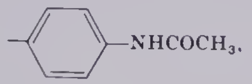
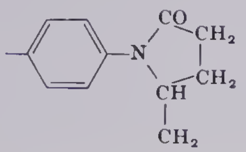
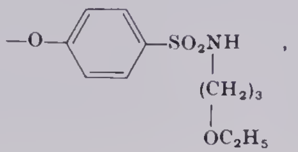
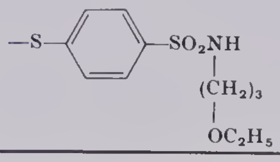
[88] H.-U. von der Eltz, H. Seifert, and W. Birke, *Chemiefasern + Text.-Anwendungstech.* **21**, 678 (1971).

[89] N. L. Moore, *J. Soc. Dyers Colour.* **90**, 318 (1974).

[90] R. Peter, Private communication, (1974).

TABLE VII

INFLUENCE OF SUBSTITUENTS ON THE THERMOFIXATION AT 215° OF 1-AMINO-4-HYDROXYANTHRAQUINONE DYES ON DACRON POLYESTER FABRIC[87]

Rating	 R	 R
1–2	—H, 	—H, —Br, —OCH$_3$
2–3	 $-CH_2-CH(CH_3)-CN$, —C$_2$H$_4$COOC$_2$H$_5$,  	 —OC$_2$H$_4$OC$_2$H$_4$OCH$_3$, 
3–4	 ,  , 	—SC$_2$H$_4$CN,  —O—(CH$_2$)$_6$—OH
4–5	  	 , 

anthraquinone derivative with a number of hydroxyl groups, which gives very low color yield on polyester by exhaustion techniques, exhibits very satisfactory transfer printing behavior.

A study involving three simple disperse dyes[91] with the properties given in Table VIII showed that the diffusional behavior of disperse dyes in the transfer printing of polyester material is similar to that shown in heat fixation and vapor dyeing under anhydrous conditions.

A high concentration of dye just within the fiber surface is rapidly achieved and is attributable to the large number of dye molecules striking the surface in unit time combined with a high partition coefficient in favor of the polymer phase. The degree of penetration into an assembly of fibers is dependent on this coefficient and on the mean free-path length of the dye molecules in the gas phase. It was shown that under atmospheric conditions the latter depends very little on the molecular weight of the dye.

TABLE VIII

VAPOR PRESSURE (VP) AND DIFFUSION COEFFICIENT (*D*) DISPERSE DYES[91]

CI disperse dye	*Formula*	*VP (cm Hg at 160°)*	*Melting point*	*D (m^2/second × 10^{13})*
Yellow 3	*p*-Aminoacetanilide → *p*-cresol	1.35×10^{-4}	193°	2.39
Red 9	1-Methylaminoanthraquinone	6.92×10^{-3}	164°	6.87
Blue 14	1,4-Di(methylamino)anthraquinone	1.01×10^{-5}	217°	~1.20

D. CATIONIC DYES

1. *General Remarks*

The realization that acrylonitrile copolymerized with anionic monomers resulted in polymeric fibers that could be dyed with basic dyes, and the subsequent development of these dyes from the mid 1950s onward, removed most of the fastness and shade problems originally associated with the dyeing of acrylic fibers. Early work on acrylic fiber–basic dye systems has been summarized by Beckmann,[92] whose name has been closely associated with subsequent theoretical and experimental studies leading to the development of the more recent rapid dyeing methods and with enunciation of the factors involved in the compatibility of basic dyes in admixture.

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[91] F. Jones and T. S. M. Leuny, *J. Soc. Dyers Colour.* **90**, 286 (1974).

[92] W. Beckmann, *J. Soc. Dyers Colour.* **77**, 616 (1961).

It is generally agreed that the mechanism of basic dye adsorption involves a form of ion exchange between metal (or H^+) cations in the fiber and dye cations, with subsequent salt formation.[93–98] As a result of their adsorption on a relatively limited number of specific fiber sites, each basic dye influences the behavior of the others present, both thermodynamically and kinetically. Thus, both the equilibrium exhaustion of a dye and its diffusion rate in the fiber are affected by other dyes in a mixture.[98]

In practice, it is important to be able to predict the behavior of a given dye in a mixture from the individual properties. A number of authors[99–101] have described methods of determining indices that allow such predictions about dyeing behavior to be made. These so-called compatibility values are products of functions of the affinity and the diffusion coefficient of the dyes, and two dyes may be considered compatible if the products of these functions are similar. In view of the importance of the affinity term, simpler parameters, such as time of half dyeing, do not give an accurate indication of the dyeing behavior of a basic dye in combination with others, and a test has been proposed[102] to evaluate the dyeing characteristics of a given dye in combination with a set of five standard dyes. This is based on a dip test as described by Beckmann,[103] in which the dye of unknown dyeing properties is compared visually for on-tone shade throughout the dyeing sequence when applied with five standard dyes. The compatibility value (CV), or K value, assigned is that of the standard with which on-tone dyeings are obtained. By this method, therefore, basic dyes can be classified as to compatibility on a 1–5 scale. In general, dyes with a high CV or K value have better migrational properties than those with low values; and these values are a useful guide to the dyeing rates of dyes in admixture. It has been pointed out,[104] however, that in

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

[94] T. Vogel, J. M. A. De Bruyne, and C. L. Zimmerman, *Am. Dyest. Rep.* **47**, 581 (1958).

[95] S. Rosenbaum, *Text. Res. J.* **33**. 899 (1963); **34**, 159 (1964).

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

[97] J. Cegarra, *J. Soc. Dyers Colour.* **87**, 149 (1971).

[98] W. Beckmann, F. Hoffmann, and H. G. Otter, *J. Soc. Dyers Colour.* **88**, 354 (1972).

[99] W. Beckmann, *Melliand Textilber.* **39**, 1121 (1958).

[100] U. Mayer, W. Ender, and A. Würz, *Melliand Textilber.* **47**, 653 and 772 (1966).

[101] N. G. Morton and M. E. Krecht, *J. Soc. Dyers Colour.* **85**, 639 (1969).

[102] D. G. Evans and C. J. Bent, *J. Soc. Dyers Colour.* **87**, 60 (1971); see also *ibid.* **88**, 220 (1972).

[103] W. Beckmann, *Int. Text. Semin. 11th* (1968).

[104] D. Blackburn, *Int. Dyer* **153**, 418 (1975).

practice certain mixtures may behave better than the individual K values suggest. However, K values are generally independent of the total amount of dye present and of the presence of a cationic retarder. It has been shown[98] that there is a consistency between the practical dip-test method and compatibility evaluations from more fundamental studies. The large amount of experimental data on basic dyes (in particular compatibility value and saturation factors, which determine the amount of the dye that can be applied to a particular fiber), together with fiber saturation factors for different acrylic fibers, which have now been accumulated, have been exploited in the successful development of the rapid-dyeing methods.

The general chemistry of basic dyes with respect to structure, wetfastness, and lightfastness has been well reviewed,[105–107] though relatively little appears to have been published on the influence of molecular structure on dyeing properties. As has been pointed out above, the theoretical compatibility value is the product of an affinity term and a diffusion term, and attempts to improve one of these properties may well adversely affect the other. Thus,[107] very bulky hydrophobic substituents, while increasing the affinity, may restrict diffusion within the fiber. It is perhaps unfortunate that the nature of the compatibility test emphasizes the importance of the rate of adsorption, i.e., dyes taken up initially are assigned a low K value and vice versa, whereas there is in fact a poor correlation between compatibility and diffusion coefficient.[103] It has been pointed out[107] that above a certain minimum dyebath concentration the rate of adsorption can be higher with dyes with a high K value than those with a lower value.

2. *Relation between Compatibility and Molecular Structure*

The following examples illustrate the effects of molecular structure in determining or altering compatibility characteristics. In general, increasing the hydrophilic character of a basic dye will decrease its affinity for the fiber. Since there is a fairly close relationship between affinity and compatibility,[103] this increase in hydrophilic character results in an increase in K value.

The solubilizing effect of the anion has been increased by the introduction of an $-SO_2R$ group, where R = alkyl, aryl or $-NH_2$ in a series of dyes of the formula[108] shown below.

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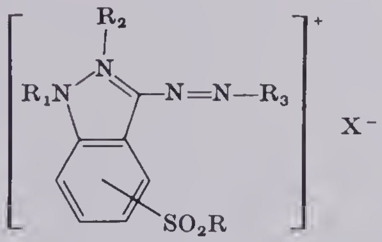
[105] D. R. Baer in *CSD IV*, p. 161.

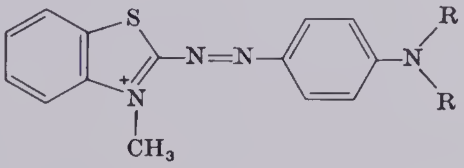
[106] D. Rao, *Colour. Annu.* 4, 25 (1974).

[107] U. Mayer and E. Siepmann, *Rev. Prog. Color.* 5, 65 (1974).

[108] BASF, *BP* 1,276,911 (1968).

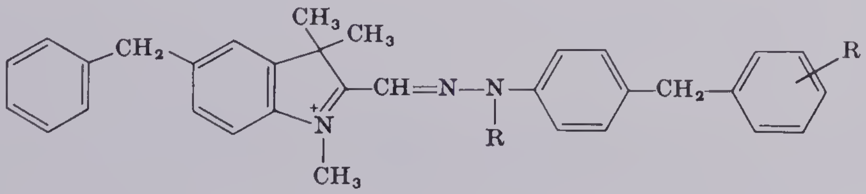


Increases in K value are obtained using other hydrophilic substituents. Thus an N-methylthiazole azo blue dye ($K = 1.5$) of general formula



has N-2-hydroxypropyl ($K = 3.5$) and N-carboxyethyl ($K = 5$) analogs.

Raue[109] has indicated that the introduction of, e.g., a phenylene group or a heteroaromatic nucleus into a dye of K value 2.5 can change the compatibility characteristics to $K = 1$. A similar effect is obtained in dyes of the type



where the presence of large aralkyl residues lowers the K values due to increased affinity.[107]

The compatibility values (K values) of basic dyes, while of practical use in suitable selection for mixtures in rapid-dyeing processes, are of less importance, however, in determining their choice in printing processes, where fixation is achieved by steaming.[110]

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[109] R. Raue, *Textilveredlung* 7, 799 (1972).

[110] W. Beal and J. J. Warwick. *J. Soc. Dyers Colour.* **90**, 425 (1972).

Chapter VIII

THE DYE DEVELOPER IN THE POLAROID COLOR PHOTOGRAPHIC PROCESS

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I. Introduction

Polaroid Corporation introduced Polacolor, the first instant color film, in 1963. Polacolor film was based on a simple but revolutionary concept, the dye developer. A dye developer is a preformed dye that is also a photographic silver halide developer. Although a simple version of such a molecule had been described by K. and L. Schinzel in 1936[1]

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[1] K. Schinzel and L. Schinzel, *Photogr. Ind.* **34**, 942 (1936); J. S. Friedman, *Am. Photogr.* **31**, 446 (1937).

and J. Friedman in 1944,[2] it remained for Rogers and the Polaroid research group to recognize the unique advantages dye developers would offer in the generation of color images by one-step photography.[3]

The discovery and use of the dye developer bypassed all the photographic chemistry that had been built up around color development,[4] the method successfully exploited in commercial color films during the 1930s. Initial efforts to produce instant color photographs by one-step photography had used color development,[5] but this approach was put aside in favor of the dye developer route.

A. ONE-STEP PHOTOGRAPHY

The principle used by Land to generate continuous-tone instant black and white photographs provided the basis for the research on instant color photography.[6] Exposure of a photosensitive element followed by development of the exposed silver halide generates a negative image in silver. In the black and white process, the undeveloped silver halide is concurrently solubilized and transferred to a superposed receiving sheet, where it is reduced to silver to form the positive black and white image. In the Polacolor process, development immobilizes the dye developer in exposed areas, while dye developer in unexposed areas is free to migrate to the receiving sheet where it is mordanted to form the positive dye image. Thus, the basic design of a one-step color process evolved directly from the earlier black and white research.

This chapter will focus on dye developers that transfer in the unoxidized state to provide the positive image. In order to make a transfer image in this manner, it is essential that the dye developer show a difference in mobility as a result of oxidation of the developer group during the photographic development process. Dye developers that cleave during photographic processing to separate the dye from the developer[7] are outside the scope of this review.

A difference in mobility is readily achieved when the developer is a hydroquinone or aminophenol. Such dyes are made soluble and transferable in the alkaline processing reagent by the presence of the ionized

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[2] J. S. Friedman, "History of Color Photography." Am. Photogr. Publ. Co., Boston, Massachusetts, 1944.

[3] H. G. Rogers and Polaroid Corp., *USP* 2,983,606.

[4] R. Fischer, *DBP* 253,335; R. Fischer and H. Siegrist, *Photogr. Korresp.* **51**, 18 (1914).

[5] E. H. Land and Polaroid Corp., *USP* 2,661,293.

[6] E. H. Land, *Photogr. J., Sect. A* **90**, 7 (1950); E. H. Land, *J. Opt. Soc. Am.* **37**, 60 (1947); E. H. Land, H. G. Rogers, and V. K. Walworth, *in* "Neblette's Handbook of Photography and Reprography" 7th Edition (J. Sturge, ed.), Chapter 12. Van-Nostrand-Reinhold, Princeton, New Jersey 1977.

[7] H. G. Rogers and Polaroid Corp., *USP* 3,245,789; S. M. Bloom, H. G. Rogers, and Polaroid Corp., *USP* 3,443,940.

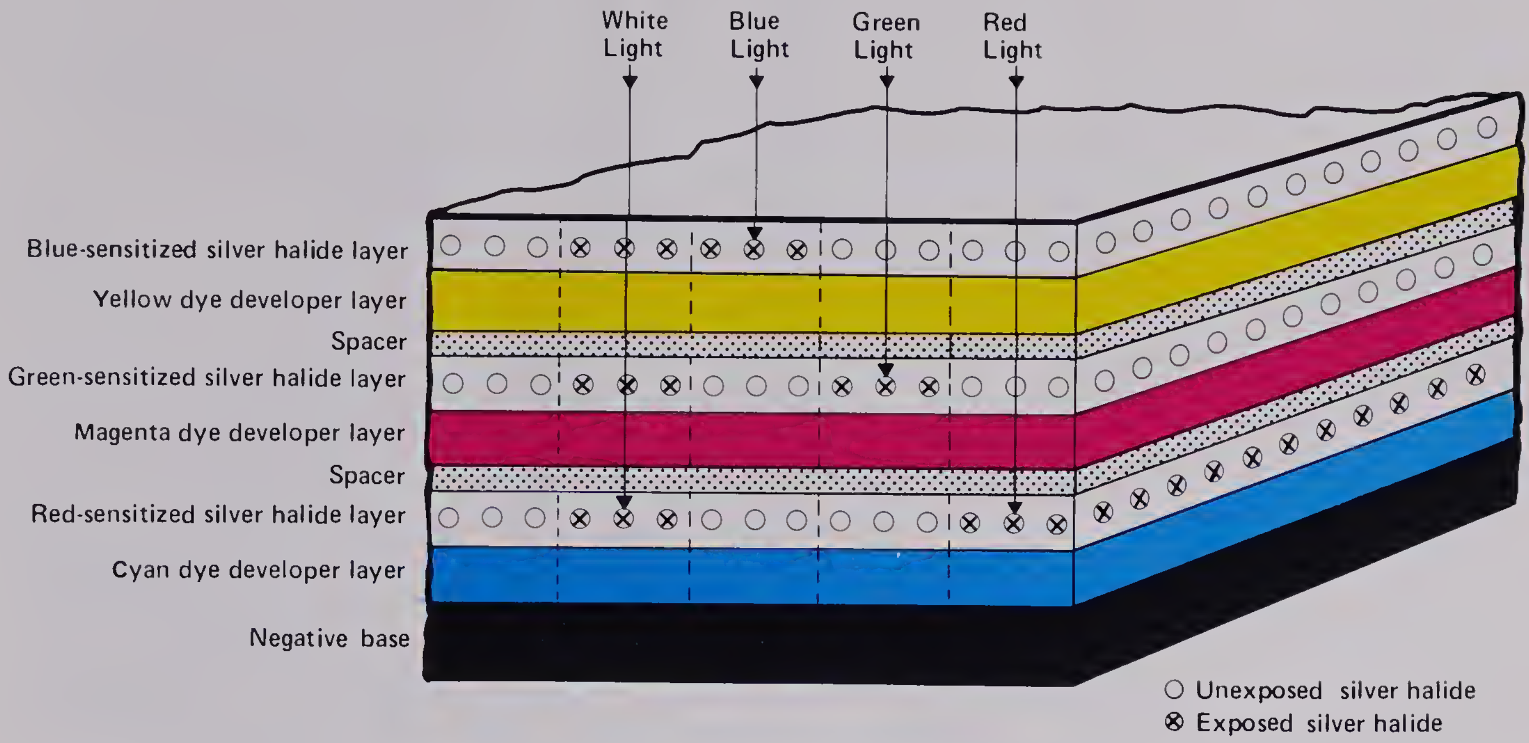


FIG. 1. Polacolor film unit during exposure.

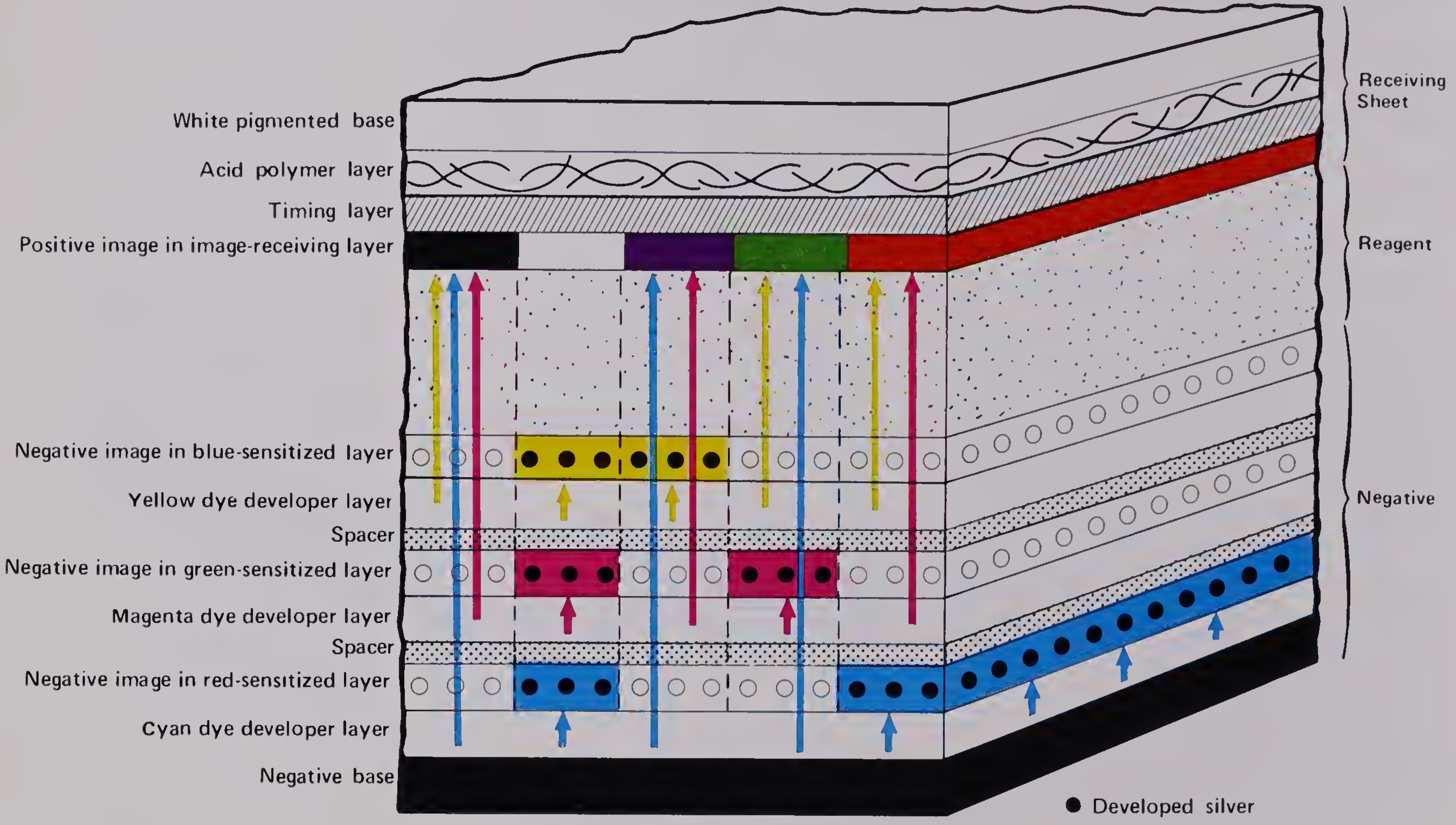
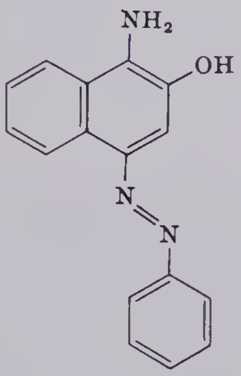


FIG. 2. Polacolor film unit during development.

phenolic substituents and are made immobile by oxidation. The very first such molecule (I) synthesized in the Polaroid laboratories gave a dye transfer image so promising that it led to the synthesis of hundreds of dye developers and ultimately, a commercially successful instant color process.



(I)

B. Polacolor

An excellent discussion of subtractive color systems in photography appears in Volume IV of this treatise.[8] A few key points may be helpful for the understanding of the subsequent description of the Polacolor process. Three dyes are used—a yellow, a magenta, and a cyan; these absorb blue, green, and red light, respectively. A blue-sensitive emulsion is used to control the formation of the yellow dye image, a green-sensitive emulsion to control the magenta, and a red-sensitive emulsion to control the cyan.

Figure 1 is a diagram of the Polacolor negative during exposure showing the three color units arranged in a tripack. Figure 2 shows the development and transfer steps. In the column that corresponds to a black area of the subject, no emulsions have been exposed to light. All dyes remain in their reduced forms and are free to travel to the receiving layer, where their combined light absorption produces black. The light coming from white areas of the subject has exposed all three emulsions, trapping all three dye developers; no dye transfers, so that this part of the image is the white of the pigmented base. Where light from a blue area of the subject has exposed only the blue-sensitive emulsion, the yellow dye developer is oxidized and trapped as a result of the development process; the magenta and cyan dye developers migrate to the receiving layer and combine to form a blue area in the image. Similar analyses explain the action of green or red light.

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[8] J. Bailey and L. A. Williams in *CSD IV*.

The receiving sheet is also illustrated in Fig. 2. In addition to the mordanting layer in which the image dyes are deposited, a timing layer and an acid polymer layer[9] are also provided. The acid polymer layer reduces the alkalinity of the system to stabilize the image, while the timing layer prevents premature pH reduction, allowing the image dyes to complete their transfer. By the time the positive receiving sheet is separated from the negative, the pH of the mordanting layer is rapidly approaching neutrality, providing a stable, almost dry photograph.

C. Dye Developers

An intensive program was undertaken in the Polaroid laboratories in the early 1950s to synthesize dye developers. It was recognized that in combining a dye with a developer in the same molecule a number of requirements must be met. As an example, early dye developers such as (I) showed undesirable spectral shifts with changes of pH and state of oxidation. This led to the decision to concentrate on dye developers in which the chromophore was separated from the developer by an insulating link (see Section II, A).[10] Other criteria for these molecules include: (1) light stability—the chromophore in the dye developer is the image dye; (2) stability in the negative—the dye developer should not adversely interact with the silver halide emulsion, nor change during storage; (3) stability to the alkaline processing reagent; (4) spectral characteristics—the chromophore should absorb one-third of the visible light efficiently while transmitting most of the other two-thirds of the light; (5) diffusibility—dye developers should transfer through the layers of the negative and the reagent without dyeing them; and (6) ability to form an image—the transfer of the dye developer should be regulated by the state of oxidation of the developer group.

The most important dye developer types investigated were azo dyes, anthraquinone dyes, and metallized dyes. The remainder of this chapter will describe the work on these dyes and others that were studied primarily for their spectral characteristics. Before discussing the dye research in detail, the dyes used in the Polacolor and SX-70 and Polacolor 2 color films will be described.

1. *Polacolor Dye Developers*

The yellow dye (II) in Polacolor was an azopyrazolone with an absorption maximum at 454 nm. The amide group in the 3-position in the pyrazolone ring is required to attain the desired color when the developer group is attached to the para position of the diazotized aniline.

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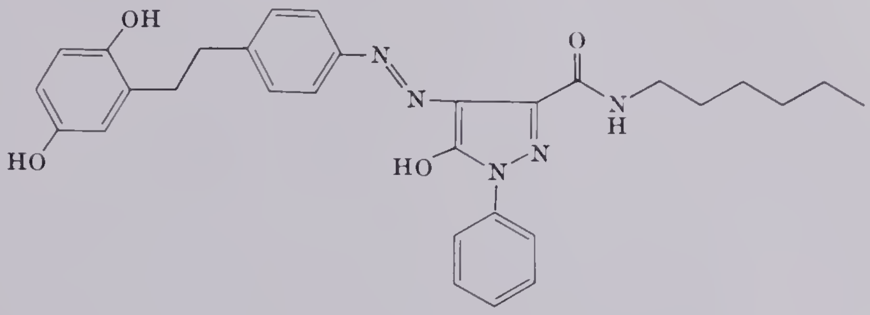
[9] E. H. Land and Polaroid Corp., *USP* 3,362,819.

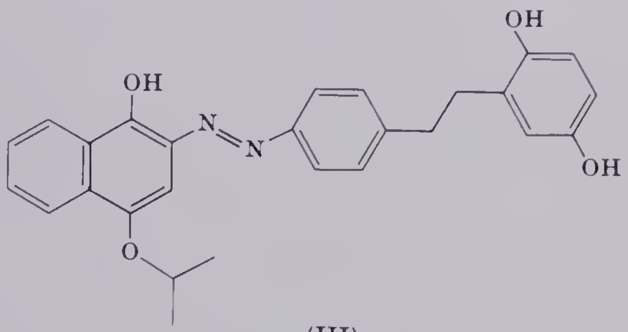
[10] E. R. Blout, H. G. Rogers, and Polaroid Corp., *USP* 3,255,001.



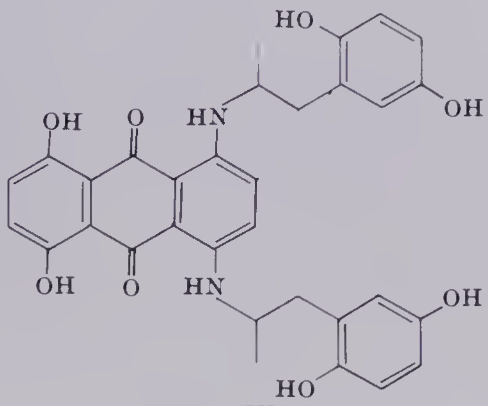
(II)

The magenta (III) was also an azo dye. The absorption maximum was adjusted to 530 nm by putting an ether substituent in the 4-position of the 2-azo-1-naphthol system.

The cyan (IV) was an anthraquinone dye. The absorption maxima at 622 and 676 nm result from the bathochromic effect of the hydroxyl groups at the 5- and 8-positions in the 1,4-bisalkylaminoanthraquinone chromophore. Use of the branched chain on the amino groups increases light stability and mobility in the photographic system. The spectra of these three dyes are shown in Fig. 3.



(III)



(IV)

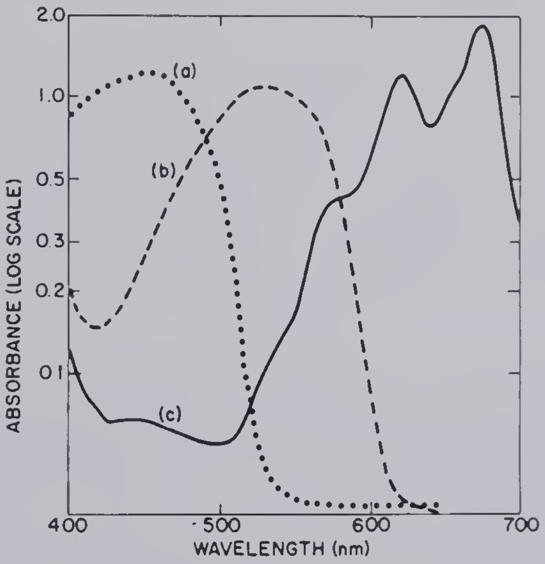
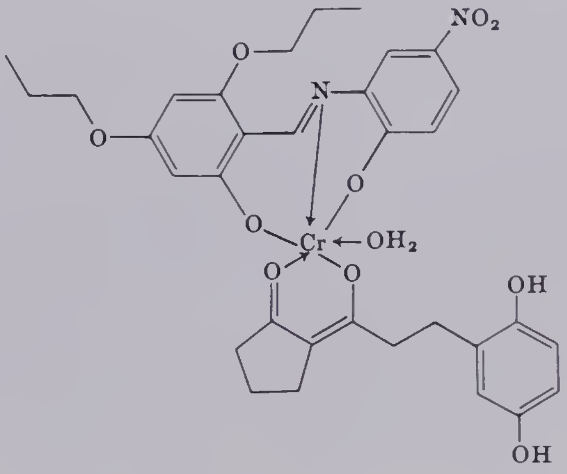


FIG. 3. Absorption spectra of (a) compound II, (b) compound III, and (c) compound IV.

2. *SX-70 and Polacolor 2 Dye Developers*

The research on dye developers continued after the introduction of Polacolor film. In 1972 Land demonstrated the SX-70 system, an entirely new camera and integral film,[11] which employed a new generation of dye developers in the negative. The yellow dye is the chromed *o,o'*-dihydroxyazomethine (V); the magenta is the chrome complex of an *o,o'*-dihydroxy azo dye (VI); and the cyan is the copper phthalo-



(V)

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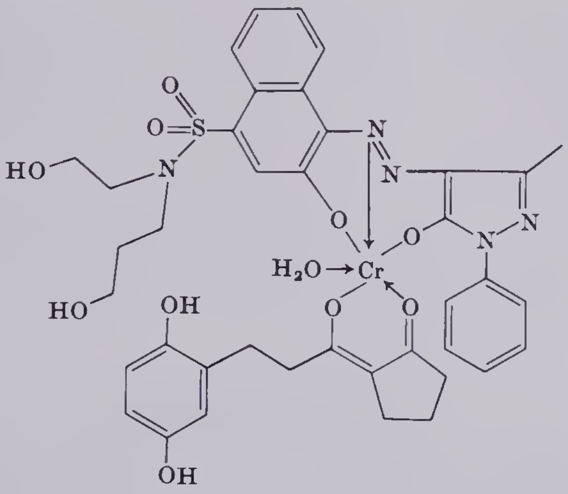
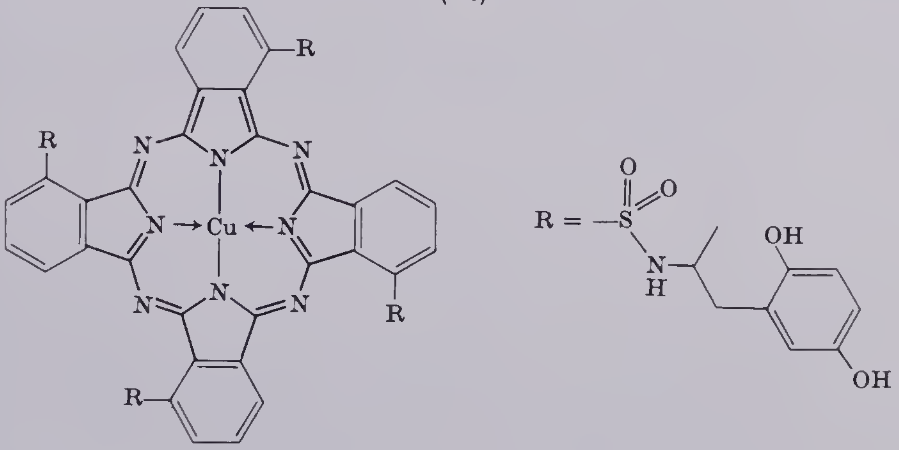
[11] E. H. Land, *Photogr. Sci. Eng.* **16**, 247–252 (1972).



(VI)



(VII)

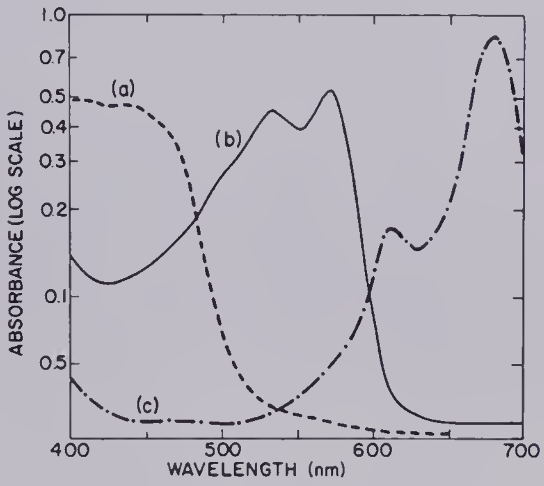


FIG. 4. Absorption spectra of (a) compound V, (b) compound VI, and (c) compound VII.

cyanine derivative (VII). Their spectra are shown in Fig. 4. These dyes are also used in Polacolor 2, the successor to Polacolor. The remarkable light stability of these new instant films has been described in a recent communication.[12]

We will now proceed to a detailed review of the dye developers synthesized for the Polacolor and SX-70 programs. The diversity of chromophores that were converted into photographic images by attachment of a developer moiety demonstrates the power and versatility of the basic invention.

II. Azo Dye Developers

The broad range of chromophores and wide variety of structures available made it inevitable that a major effort would focus on azo dyes. In addition, there are a great many possibilities for varying substituent groups in order to influence both color and light stability and a variety of means by which the developing fragment may be incorporated into the system.

A. NONINSULATED AND INSULATED DYE DEVELOPERS

The first dye developers, which established the workability of the photographic invention, were simple azo dyes in which the developer was attached through the azo group to the coupler to form the chromophore. In the earliest work, such dyes were made by coupling into a protected hydroquinone or by diazotizing aminohydroquinone monobenzoate and reacting with a suitable coupler (Chart I). Since hydroquinones can reduce diazonium salts, protection of at least one of the phenolic groups was required. 2-Naphthylazohydroquinone (VIII) and 2-hydroxy-1-naphthylazohydroquinone (IX), yellow-orange and magenta dyes, respectively, are representative of these dye developers. 2-Amino-4-phenylazo-1-naphthol (X) and 4-phenylazo-1,2-naphthalenediol (XI) are two more examples of early dye developers.[13]

Hydroquinone monobenzoate (XII) was supplanted as a coupler by hydroquinone monosulfate, since the latter, as the pyridine salt, is water soluble and more reactive than the benzoate. Even *p*-alkylbenzene diazonium salts that react poorly with (XII) give high yields of alkylphenylazohydroquinone sulfates. Dilute acid hydrolysis readily removes the protecting group.[14]

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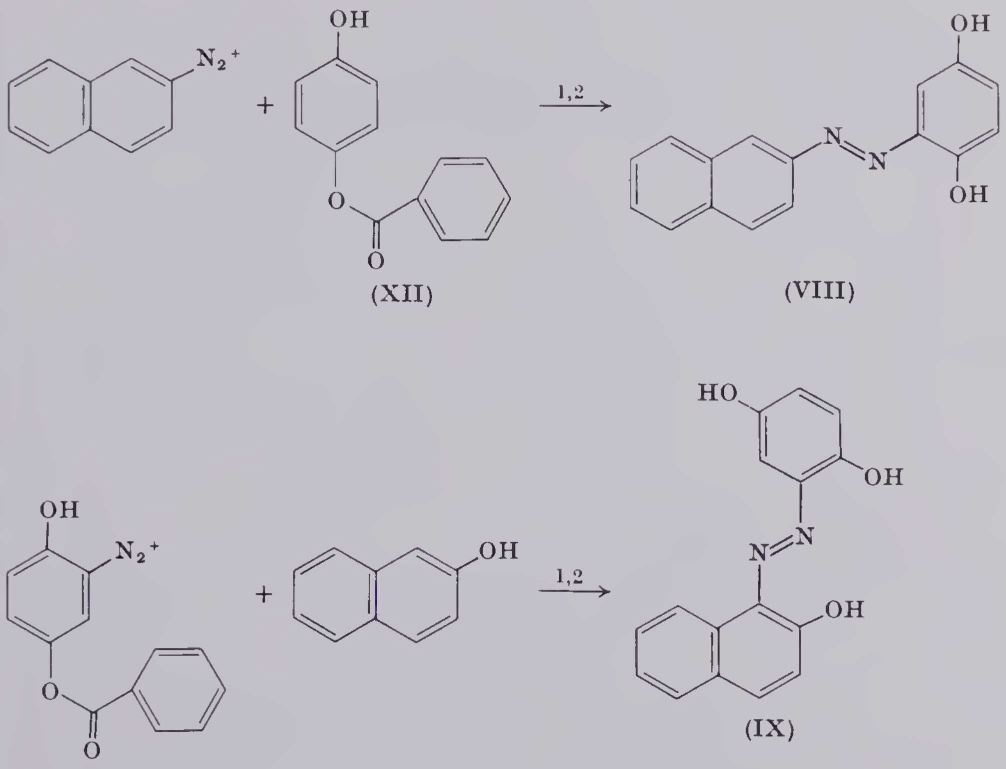
[12] H. G. Rogers, E. M. Idelson, R. F. W. Cieciuch, and S. M. Bloom, *J. Photogr. Sci.* **22**, 138 (1974).

[13] E. R. Blout, R. S. Corley, M. Green, M. S. Simon, and Polaroid Corp., *USP* 2,992, 106.

[14] Unpublished results, Polaroid Corporation.



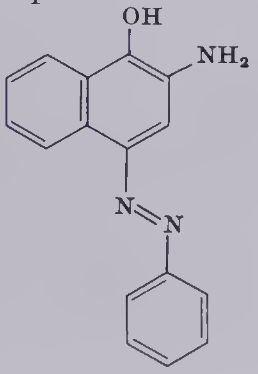
(XII)

(VIII)

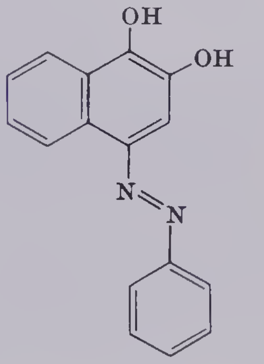
(IX)

CHART I. (1) Coupling; (2) hydrolysis.

These simple dye developers are easy to prepare, but their colors change with pH. Because the developer is an integral part of the chromophore, oxidation of the image dye will also change its color. A step of major importance was the synthesis of insulated dye developers.[10] In these systems, an insulating group, such as a chain of one or more methylene units or a benzene ring joined in the meta positions, attaches the dye to the developer and at the same time ensures that the shape and position of the absorption curve are unaffected by the oxidation state of the developer.



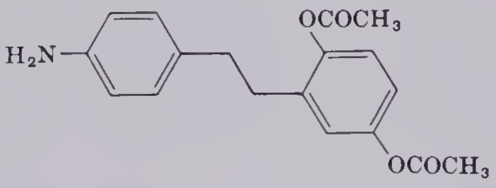
(X)



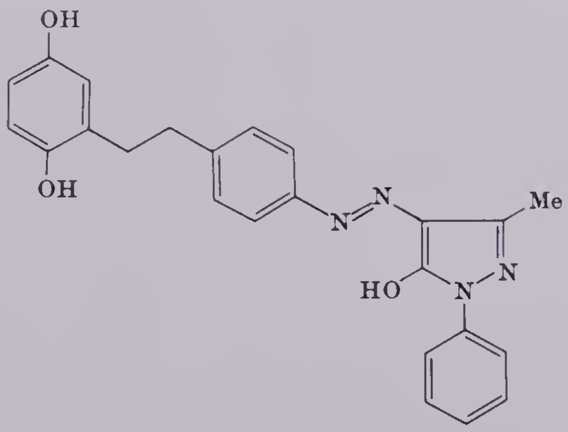
(XI)

B. ANILINE INTERMEDIATES

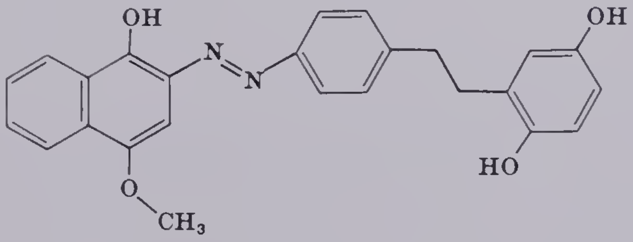
p-Aminophenethylhydroquinone O-diacetate (XIII) is a preferred aniline, which may be diazotized and coupled with a wide variety of active methylene or phenolic couplers to generate yellow and magenta dyes, e.g., (II), (III), (XIV) and (XV).[15] The preparation of (XIII) follows the sequence shown in Chart II.[16]



(XIII)



(XIV)



(XV)

A recent patent reported that the diazotization of (XVI), followed by coupling, leads directly to dye quinones that may be reduced to dye developers.[17]

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[15] E. R. Blout, M. Green, H. G. Rogers, and Polaroid Corp., *USP* 3,134,672; 3,134,764.

[16] E. R. Blout, M. Green, H. G. Rogers, M. S. Simon, R. B. Woodward, and Polaroid Corp., *USP* 3,019,107; M. Green, H. Husek, and Polaroid Corp., *USP* 3,019,254; see also M. S. Simon and Polaroid Corp., *USP* 3,406,194.

[17] Fuji Photo Film, *DOS* 2,413,223.

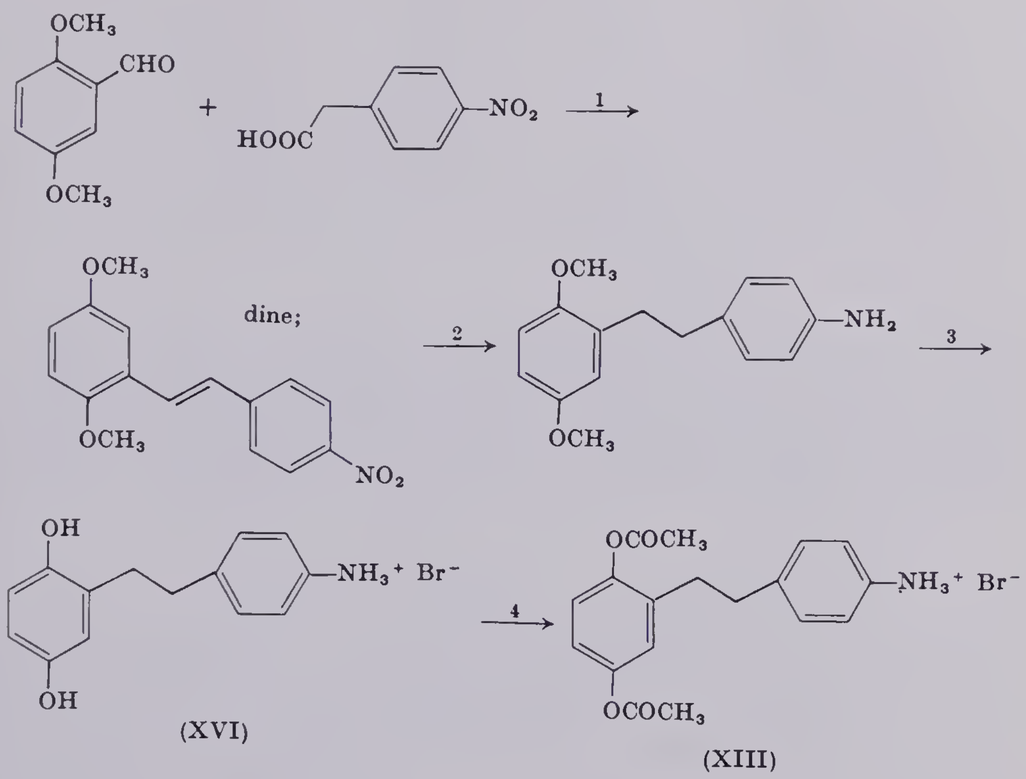
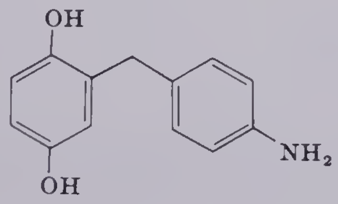
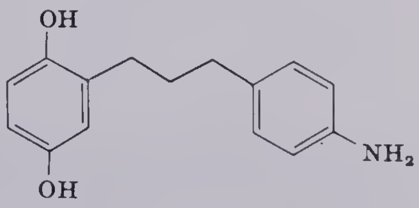


Chart II. (1) Piperidine; (2) catalytic H_2; (3) HBr; (4) Ac_2O, AcOH, HCl.

A variety of linkages may be used to join the hydroquinone to the aniline. The number of methylene groups may be varied by condensing *p*-dimethoxybenzene with *p*-nitrobenzoyl chloride, or *p*-nitrophenylalkanoyl chlorides for higher homologs, followed by reduction of the carbonyl group and demethylation to produce (XVII) or, for example, (XVIII).[15] *p*-Nitrophenylhydroquinone is prepared by the unusual



(XVII)



(XVIII)

reaction of hydroquinone with diazotized *p*-nitroaniline[18] and is then reduced to *p*-aminophenyl hydroquinone (XIX).[19] The meta analog (XX), a better insulating system, is prepared by the better known

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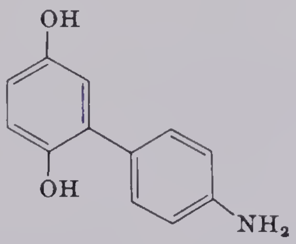
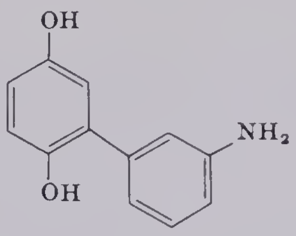
[18] J. I. Dobás, *Chem. Listy* **46**, 277 (1952); *CA* **47**, 8669d.

[19] M. S. Simon and Polaroid Corp., *USP* 3,134,765; 3,183,089.

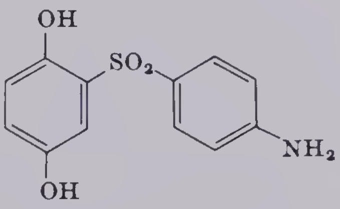


(XIX)

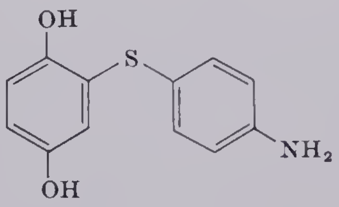


(XX)

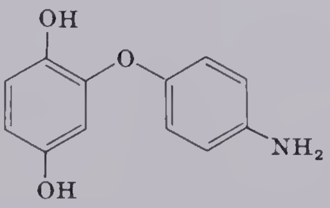
Meerwein reaction.[20] *p*-Aminobenzenesulfonylhydroquinone (XXI) results from the addition of *p*-acetamidobenzenesulfinic acid to quinone followed by hydrolysis,[21] while addition of *p*-nitrothiophenol to quinone followed by reduction gives the thiohydroquinone, (XXII).[22] Condensation of potassium 2,5-dimethoxyphenolate with *p*-fluoronitrobenzene, demethylation, and reduction gives *p*-aminophenoxyhydroquinone (XXIII).[23]



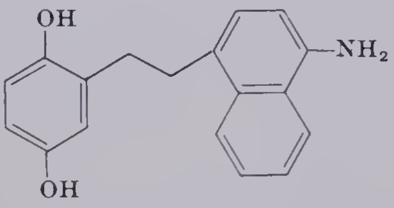
(XXI)



(XXII)



(XXIII)



(XXIV)

Carboxamido groups are particularly useful linkages between dye and developer moieties. Three representative structures are (XXV),

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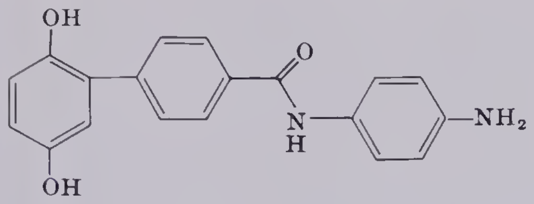
[20] D. E. Kvalnes, *J. Am. Chem. Soc.* **56**, 2478 (1934); A. D. Jarrett and Polaroid Corp., *USP* 3,183,090; 3,424,742.

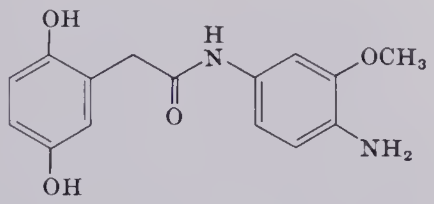
[21] H. Burton and E. Hoggarth, *J. Chem. Soc.* p. 468 (1945); M. Green and Polaroid Corp., *USP* 3,218,312.

[22] M. Green, H. G. Rogers, and Polaroid Corp., *USP* 3,009,958; 3,081,339; 3,222,169.

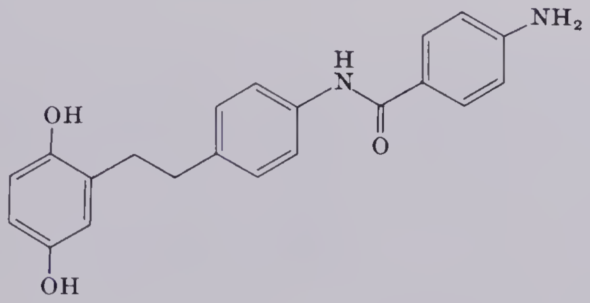
[23] M. Green and Polaroid Corp. *USP* 3,303,183; M. Green, W. Solodar, and Polaroid Corp., *USP* 3,061,434; 3,188,343; 3,419,600.



(XXV)



(XXVI)

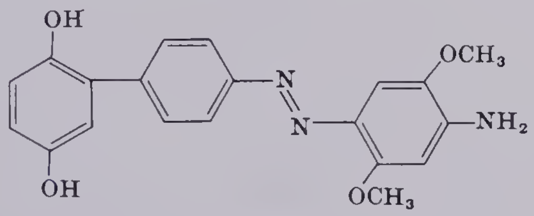


(XXVII)

(XXVI), and (XXVII), but the reaction is a general one, and many other combinations may also be employed.[24]

Acyl[25] and sulfonamido[26] groups have also been used as linkages between dyes and developers.

Substituents such as alkyl and halogen on the hydroquinone ring modify the developing characteristics or the solubility of the dye developer, while substituents such as methoxy on the aniline ring



(XXVIII)

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[24] M. Green and Polaroid Corp., *USP* 3,022,167; 3,262,924; 3,329,700; M. Green, M. S. Simon, and Polaroid Corp., *USP* 3,022,166; M. Green, H. Husek, and Polaroid Corp., *USP* 3,158,595; 3,214,469; M. Green, H. G. Rogers, and Polaroid Corp., *USP* 3,135,604; 3,135,734; 3,186,982; M. Green, T. Milligan, D. Ross, and Polaroid Corp., *USP* 3,241,963; M. Green, H. Husek, S. Kasman, and Polaroid Corp., *USP* 3,255,231; E. R. Blout, R. S. Corley, M. Green, H. G. Rogers, M. S. Simon, R. B. Woodward, and Polaroid Corp., *USP* 3,288,778.

[25] E. R. Blout, M. S. Simon, and Polaroid Corp., *USP* 3,131,219; E. R. Blout, M. Green, H. G. Rogers, M. S. Simon, and Polaroid Corp., *USP* 3,208,991.

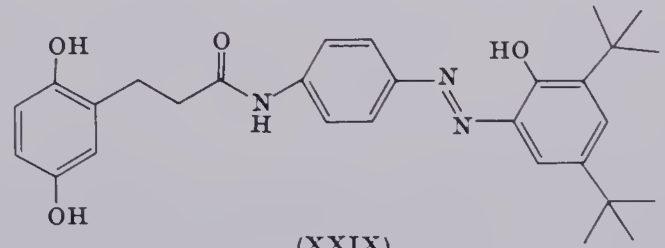
[26] E. R. Blout, M. Green, H. G. Rogers, R. B. Woodward, and Polaroid Corp., *USP* 3,252,969.

modify the color of the resulting azo dye. Aminonaphthyl developers (XXIV) were also prepared, but they broaden the absorption curve.[15,16]

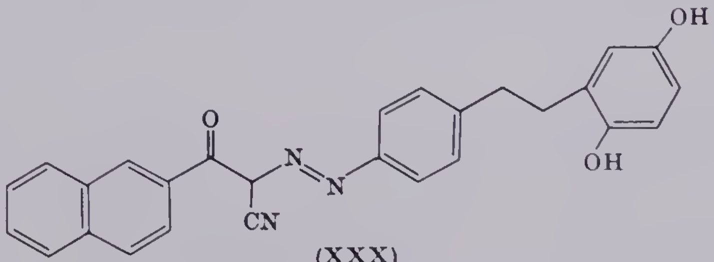
Any of the protected developers just described may be used to prepare additional aniline intermediates by diazotizing and coupling with aniline or a substituted aniline to give compounds such as (XXVIII).[27] Disazo dye developers result from the use of a component such as (XXVIII) as well as more conventional intermediates such as dianisidine.[28]

C. Yellow Dye Developers

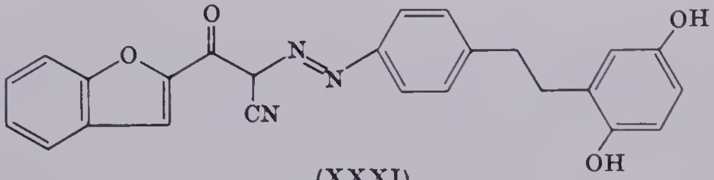
Pyrazolones are the most versatile of the yellow-forming couplers. Phenols couple poorly and give dyes of low extinction coefficient ϵ. Several open-chain methylene couplers were investigated to get yellows of higher efficiency. For example, (XXIX) has $\lambda_{\max}$ 365 nm, $\epsilon = 25{,}200$, with a shoulder at 402 nm, $\epsilon = 17{,}600$[24]; (XXX) at 390 nm, $\epsilon = 46{,}000$; and (XXXI) at 417 nm, $\epsilon = 21{,}700$; compound (XXXII) has twin peaks at 404 and 432 nm, $\epsilon = 31{,}000$.[15]



(XXIX)



(XXX)



(XXXI)

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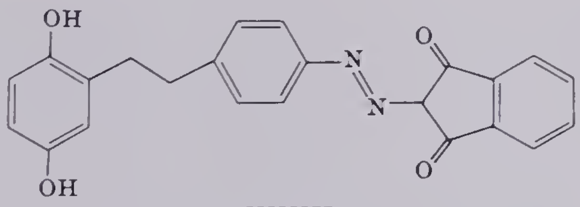
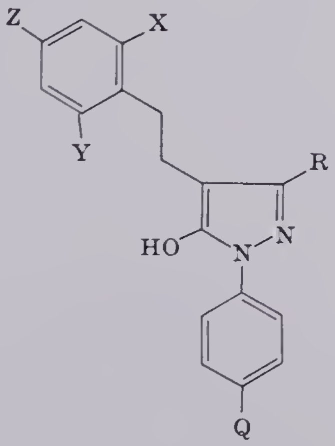
[27] H. Husek and Polaroid Corp., *USP* 3,134,762; 3,236,643; H. Husek, M. S. Simon, and Polaroid Corp., *USP* 3,134,763; 3,236,645; M. Green, H. G. Rogers, and Polaroid Corp., *USP* 3,173,906; M. S. Simon and Polaroid Corp., *USP* 3,134,765.

[28] H. Husek and Polaroid Corp., *USP* 3,134,762; 3,236,643; E. R. Blout, S. Cohen, M. Green, M. S. Simon, and Polaroid Corp., *USP* 3,077,402; H. Husek, M. S. Simon, and Polaroid Corp., *USP* 3,236,645.

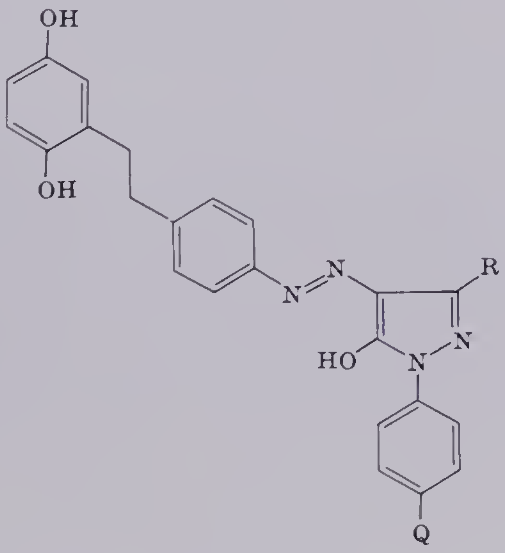


(XXXII)

The general structure of a pyrazolone yellow dye (XXXIII) shows the variations available for tailoring the dye structure to the photographic use. Many dyes were made with developing functions at positions R, Q, and Z.



(XXXIII)



(XXXIV)

One of the simplest series of yellows resulted from the diazotization of aminophenethylhydroquinone diacetate (XIII) and coupling with suitably substituted pyrazolones. These compounds (XXXIV) quickly demonstrated their photographic utility.

Absorption spectra of three representative compounds (XXXIV; Q = H) are shown in Fig. 5. The absorption peak shifts from 404 nm if R = $-CH_3$ to 422 nm if R = $-COOC_2H_5$ to 455 nm if R = $-CONHC_4H_9$.[15]

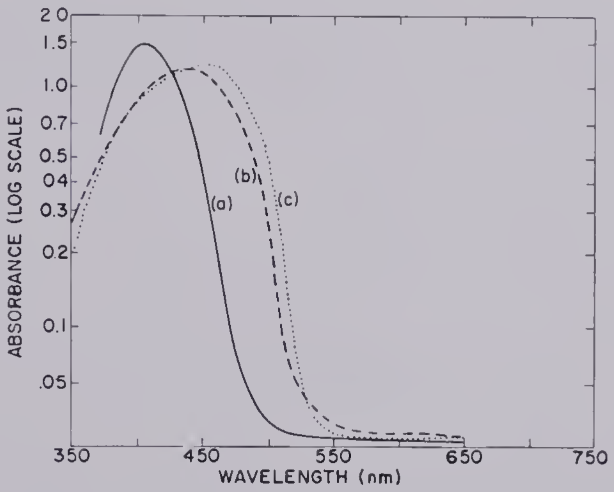
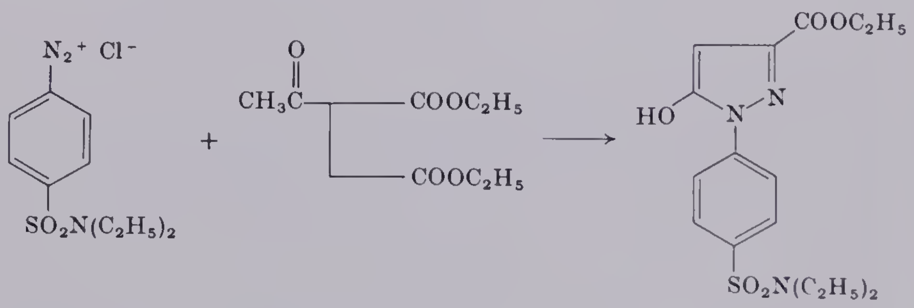


FIG. 5. Absorption spectra of (a) compound XXXIV, R = CH_3; (b) compound XXXIV, R = $COOC_2H_5$; and (c) compound XXXIV, R = $CONHC_4H_9$.

Other dyes were examined with R = $-CN$,[29] $-C_6H_5$, $-CF_3$, and dyes in which Q = $-SO_2N(C_2H_5)_2$. The coupler (XXXV) is made by the condensation of diazotized *N*,*N*-diethylsulfanilamide with diethylacetyl succinate, Chart III.[15]



(XXXV)

CHART III

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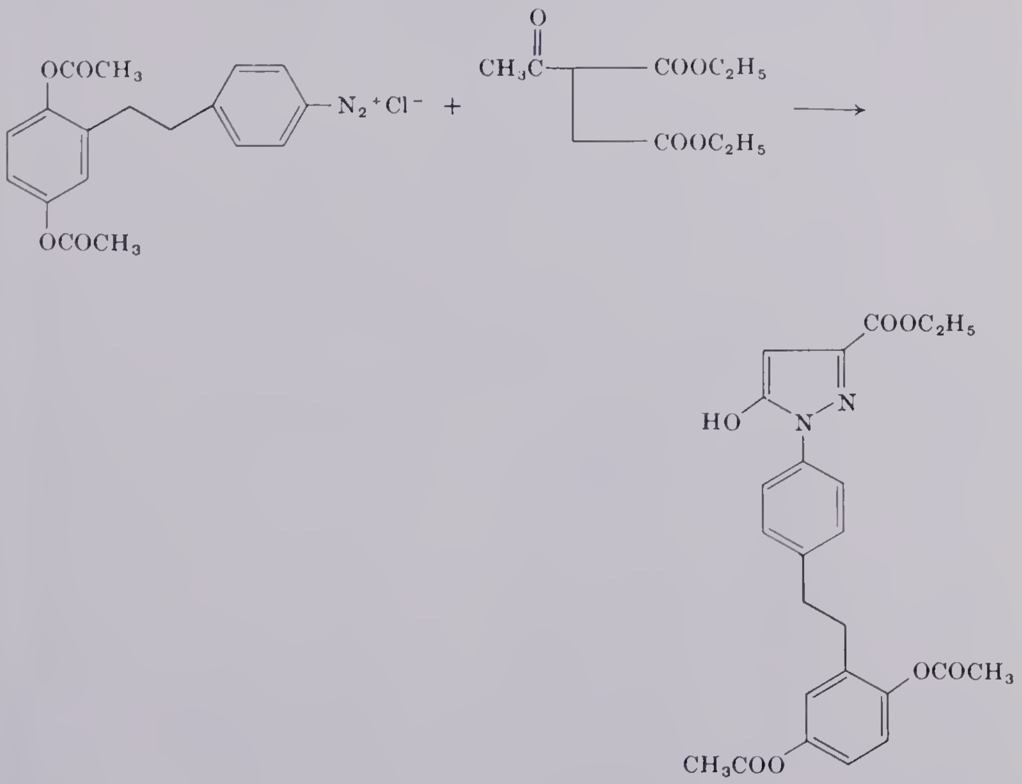
[29] D. Ross and Polaroid Corp., *USP* 3,309,199.

Incorporation of the developing function into the pyrazolone coupler (XXXVI) by the reaction in Chart IV[30] permits the preparation of a particularly interesting group of yellow dyes in which a wide selection of substituents in the diazo component becomes possible.



(XXXVI)

CHART IV

Many compounds of structure (XXXVII) were evaluated,[14,31] and Table I shows the effect on position of maximum absorption caused by some structural variations. Spectra were determined in 2-butoxyethanol. Compounds with both ortho positions blocked demonstrate a significant improvement in light stability, and the dye containing methyl groups in all three positions, X, Y, and Z, was the most stable in this series.[32]

The light stability of dyes containing ester groups in the 3-position of the pyrazolone nucleus is greater than similar dyes with 3-amido groups.[15] However, the amide group is preferred because of the color of the resulting dyes and the better opportunity it affords to adjust

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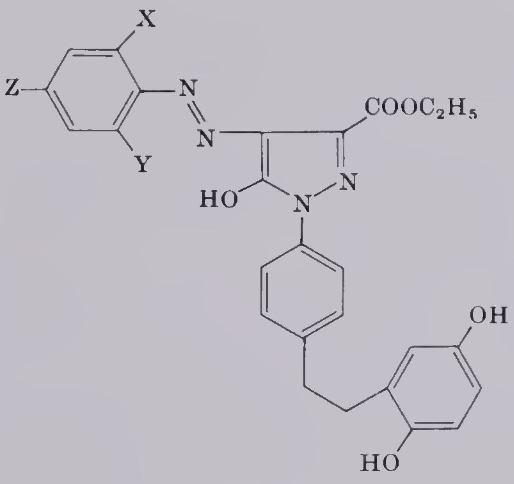
[30] M. Green, P. T. Moore, and Polaroid Corp., *USP* 3,252,990.

[31] M. Green and Polaroid Corp., *USP* 3,141,772; 3,306,891.

[32] M. Green and Polaroid Corp., *USP* 3,282,913.

TABLE I



(XXXVII)

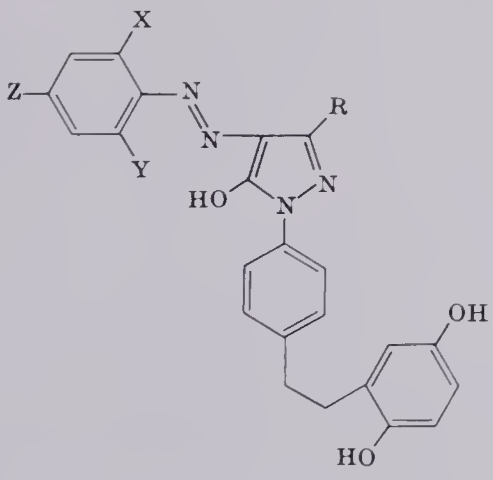
X	*Y*	*Z*	$\lambda_{\max}$ (*nm*)
CH_3	H	CH_3	440
CH_3	H	H	425
H	H	CH_3	425
CH_3	CH_3	H	415
CH_3	CH_3	CH_3	430
CF_3	H	$CH_3CONH—$	464
Cl	H	CH_3	422
CF_3	H	H	390
H	H	$—SO_2N(Et)_2$	410

solubility and diffusion characteristics by varying the length and branching of the alkyl group. Furthermore, the azo group in the 4-position of the pyrazolone ring makes the ester group in the 3-position very labile, so that some hydrolysis may take place during photographic processing. This lability can be exploited, however, since treatment of these esters with aliphatic amines under mild conditions generates the corresponding amides in high yields.[31]

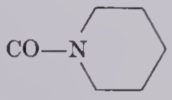
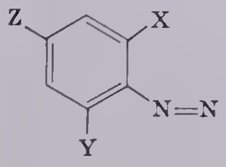
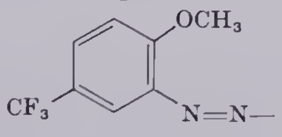
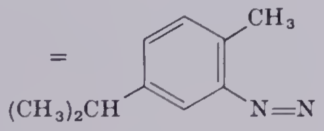
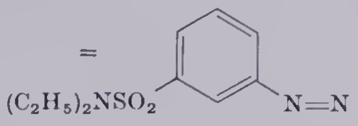
Table II shows the effect of structural variations on the absorption spectra of a series of compounds (XXXVIII), where R is a substituted amide. Note the bathochromic effect of the monoalkylamides and the hypsochromic effect of the dialkylamides when compared to the esters in Table I.[14,32] Spectra were determined in 2-butoxyethanol.

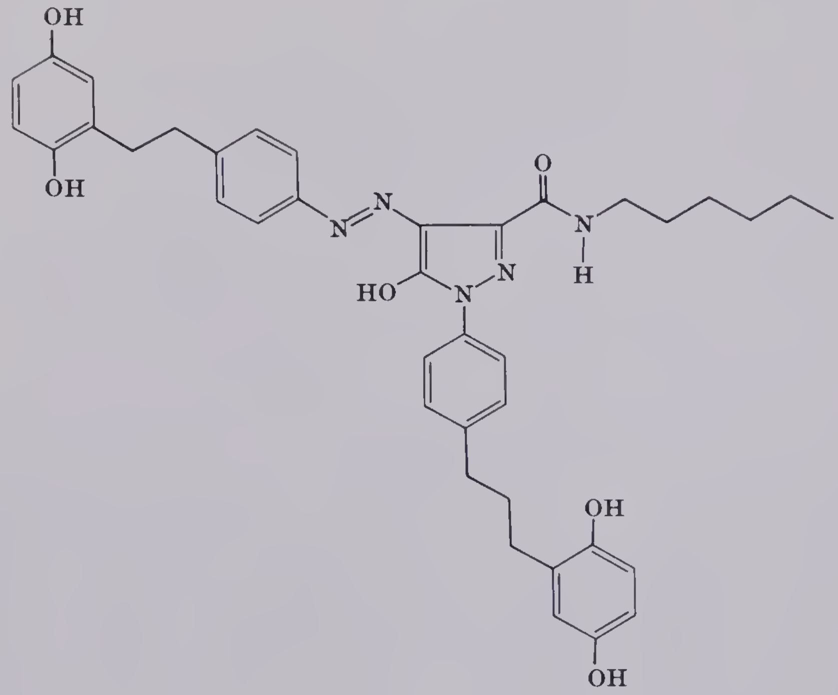
With the ready availability of the pyrazolone coupler developer (XXXVI), it was possible to synthesize dye developers containing two developing functions. Many such compounds were made and evaluated because of their significant differences in solubility, diffusion, and

TABLE II

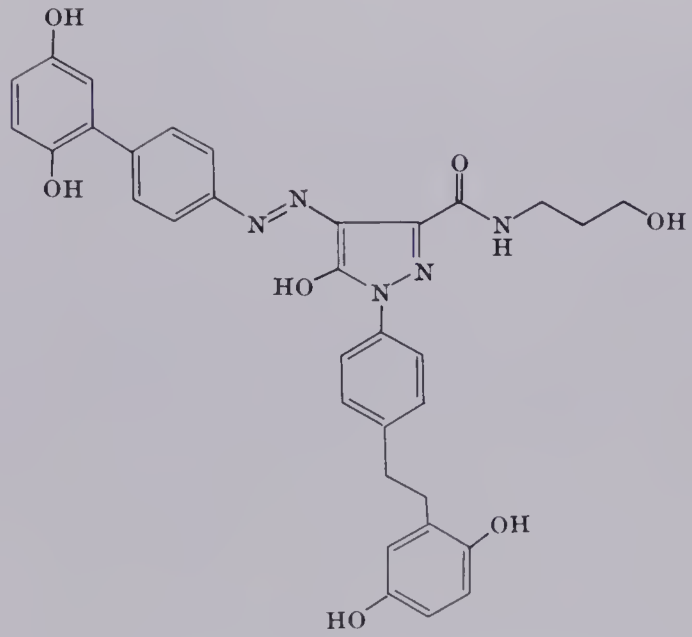


(XXXVIII)

X	Y	Z	R	λ_{max} (nm)
CH_3	CH_3	CH_3	$CONHCH_3$	438
CH_3	CH_3	CH_3	$CONH_2$	440
CH_3	CH_3	CH_3	$CON(CH_3)_2$	415
CH_3	CH_3	CH_3		412
H	H	CH_3	$CONHCH_2CH_2CH_2OH$	454
CH_3	H	CH_3	$CONHC_2H_5$	459
CF_3	H	OCH_3	$CONH(CH_2)_3OH$	431
CH_3	H	H	$CONH(CH_2)_3OH$	429
Cl	H	H	$CONH(CH_2)_3OH$	423
CF_3	H	H	$CONH(CH_2)_3OH$	408
OC_2H_5	H	H	$CONH(CH_2)_3OH$	456
$SO_2N(C_2H_5)_2$	H	H	$CONH(CH_2)_3OH$	404
H	H	CH_2CH_2OH	$CONHC_2H_5$	448
	=		$CONH(CH_2)_3OH$	439
	=		$CONH(CH_2)_3OH$	445
	=		$CONH(CH_2)_3OH$	422



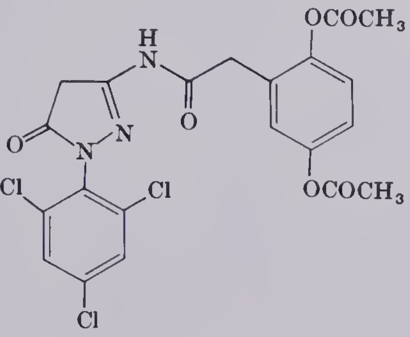
(XXXIX)



(XL)

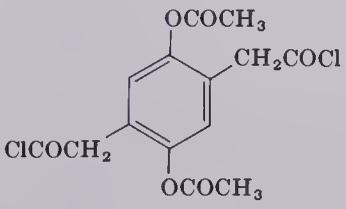
development characteristics relative to the single developer compounds. Representative dyes are (XXXIX) and (XL).[33]

Coupler developers such as (XLI) are also easily prepared and may be used to produce dyes containing either one or two developing functions.[33]



(XLI)

Two dyes may be attached to one developer by amide links using compound (XLII).[34]



(XLII)

D. MAGENTA DYE DEVELOPERS

Although a great many naphthols were examined and found to give workable magenta dye developers, four classes (XLIII)–(XLVI) were found to be particularly useful and are illustrated below. When the azo group is ortho or peri to a hydroxyl group, the resulting hydrogen bonding minimizes pH sensitivity.[14]

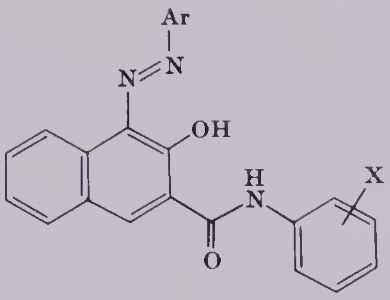
Spectra of two dyes made from 2-hydroxy-3-naphthoic acid amide derivatives (XLVII) and (XLVIII) are shown in Fig. 6. Most of the dyes in this group absorb more blue light than is desirable but demonstrate good light stability.[35]

Another large group of magenta dye developers (XLIV) was prepared

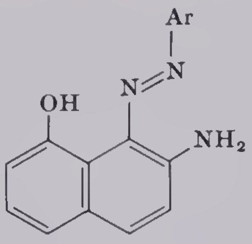
[33] M. Green, H. G. Rogers and Polaroid Corp., *USP* 3,135,604; 3,135,734; A. D. Jarrett and Polaroid Corp., *USP* 3,183,090; 3,424,742.

[34] M. Green and Polaroid Corp., *USP* 3,201,384; 3,246,985.

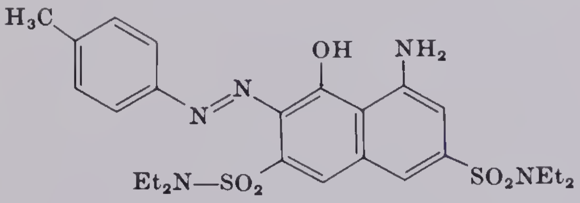
[35] M. Green, H. G. Rogers, and Polaroid Corp., *USP* 3,186,982.



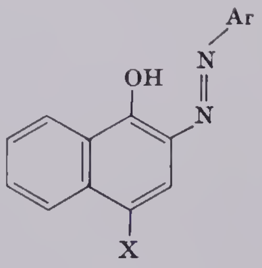
(XLIII)



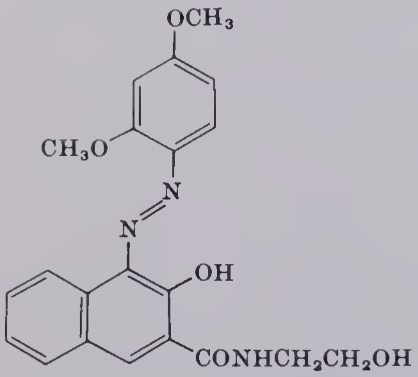
(XLIV)



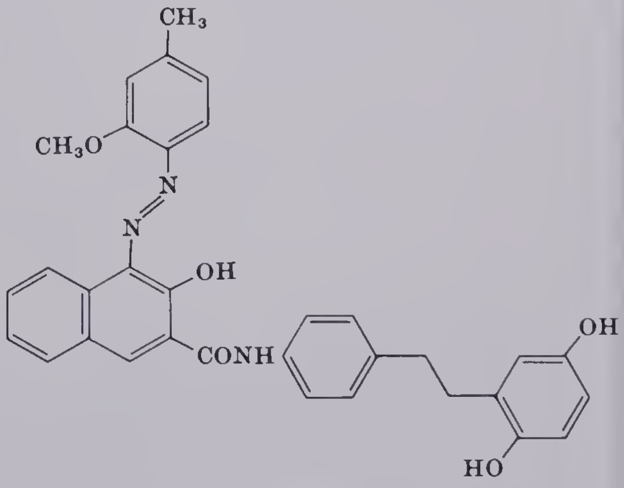
(XLV)



(XLVI)



(XLVII)



(XLVIII)

from 2-amino-8-naphthol (XLIX) and several of its *N*-alkyl derivatives.[37] The coupler was made from 2,8-naphthalenediol via the Bücherer reaction, or by the sequence in Chart V.[36] 2-Methylamino-8-naphthol may be synthesized from 2,8-naphthalenediol by a modified Bücherer reaction, and the *N*-ethyl derivative may be synthesized by acetylating (XLIX), followed by $LiAlH_4$ reduction.

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[36] A. G. Green and K. H. Vakil, *J. Chem. Soc.* **113**, 35 (1918); A. C. Mueller and C. S. Hamilton, *J. Am. Chem. Soc.* **66**, 860 (1944).

[37] D. Ross and Polaroid Corp., *USP* 3,194,838; M. Green, T. Milligan, D. Ross, and Polaroid Corp., *USP* 3,337,524.

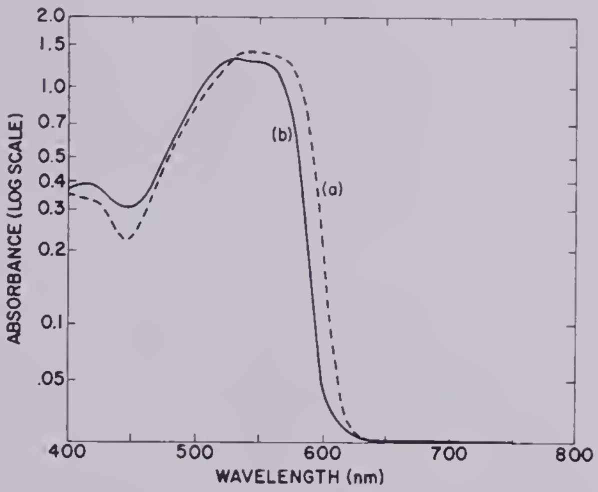
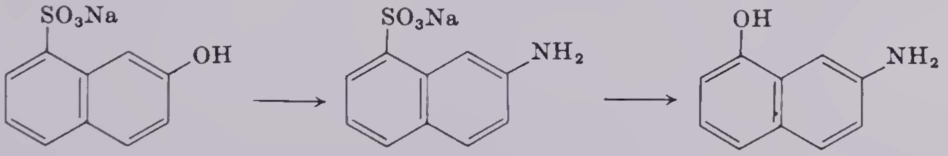


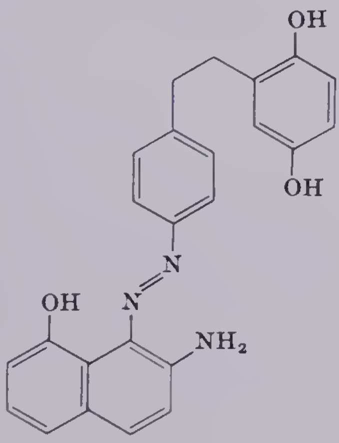
FIG. 6. Absorption spectra of (a) compound XLVII and (b) compound XLVIII.



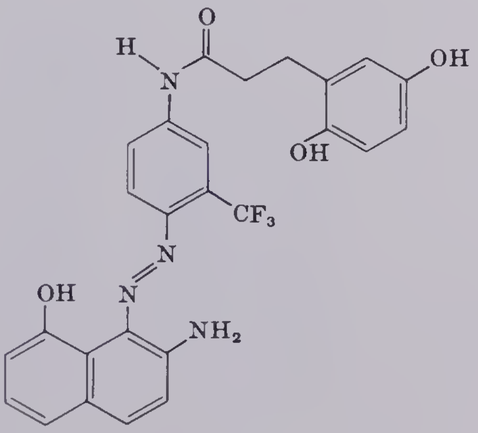
(XLIX)

CHART V

A useful magenta chromophore should have an absorption maximum longer than 525 nm to absorb green light efficiently. Although the simple dye (L) has $\lambda_{\max}$ 515 nm, its spectrum is readily modified. For

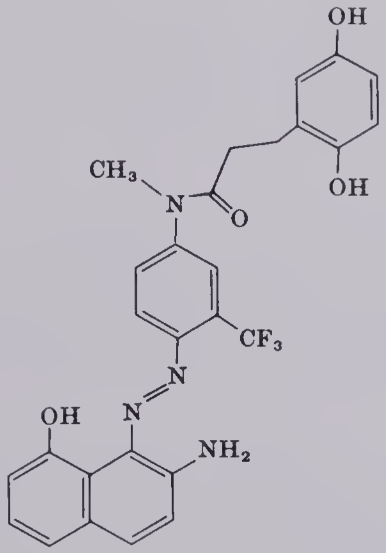


(L)



(LI)

example, coupling with *p*-acetamidobenzene diazonium chloride provides a bathochromic shift of 20–25 nm, and a chloro or trifluoromethyl substituent ortho to the azo groups adds an additional increment of up to 20 nm. The —CF_3 group confers a significant increase in light stability. Monoalkylation of the amino nitrogen of the coupler also causes a bathochromic shift of about 15 nm.[14,38] Alkylation of the amide nitrogen of (LI) to give (LII) leaves the curve substantially unchanged but results in a compound of greater light stability.[14]



(LII)

The spectrum of compound (LI), which is representative of the compounds in this series, is shown in Fig. 7. These dyes absorb more blue light than is desirable, but are superior to the dyes of structure

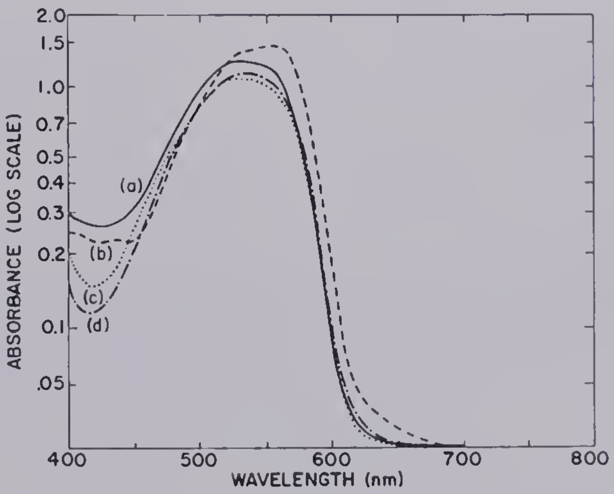


FIG. 7. Absorption spectra of (a) compound LI, (b) compound XLV, (c) compound III, and (d) compound LV.

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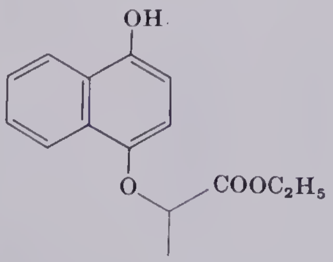
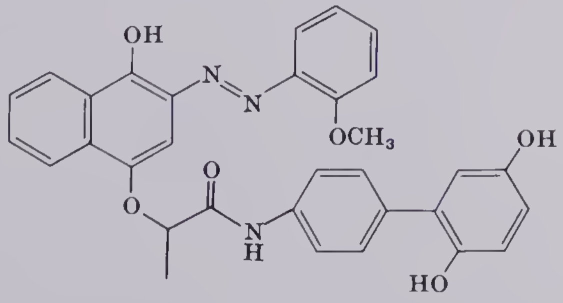
[38] M. Green, T. Milligan, D. Ross, and Polaroid Corp., *USP* 3,241,963.

(XLVII) (Fig. 6). Dyes from substituted H acid (XLV) represent a further improvement in this respect (Fig. 7).

Investigation of the azo dyes (XLVI) derived from the 4-substituted 1-naphthols led to the magenta dye (III) used in Polacolor film. The curve of compound (III) is shown in Fig. 7, and spectral data on some other representative compounds are listed in Tables III and IV.[14,15] Spectra were run in either ethanol or 2-ethoxyethanol.

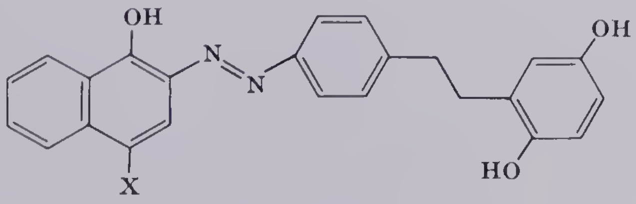


(LIII)



(LIV)

TABLE III



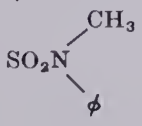
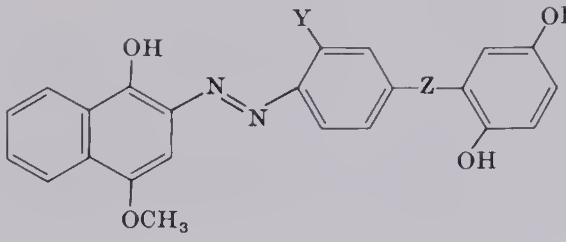
X	λ (nm)	ε
OCH_3	528	18,400
$OCH(CH_3)_2$	530	20,000
OC_4H_9	532	21,800
SCH_3	542	16,400
$NHCOCH_3$	520	14,000
CH_3	518	18,000
ϕ	511	16,000
 $SO_2N(CH_3)(\phi)$	510	19,900
Cl	509	15,400
$NHCO\phi$	508	14,600
$CO\phi$	506	19,200
$COCH_3$	504	20,000
$SO_2N(C_2H_5)_2$	498	20,000

TABLE IV



Y	Z	λ (nm)	ϵ
H	$—CH_2CH_2S—$	538	21,200
H	$—SO_2—$	520	22,100
H	—	518	20,000
$—OCH_3$	$—CH_2CH_2—$	536	23,000
H	$—NHCOCH_2CH_2—$	534	24,000
H	—O—	530	20,000

A general synthesis of 4-alkoxy-1-naphthols is to heat 1,4-naphthoquinone with an alcohol, stannous chloride, and hydrochloric acid.[39]

Ethyl lactate also reacts readily with naphthoquinone to give (LIII), which permits a developer moiety to be incorporated into the coupler fragment.[40] Many diazonium salts may be used; in (LIV), the *o*-methoxyl group gives a narrower band, less blue absorption, an increase in extinction coefficient, and a bathochromic shift; $\lambda_{max} = 535$ nm ($\epsilon = 21{,}400$) (2-methoxyethanol)[14] (Fig. 8).

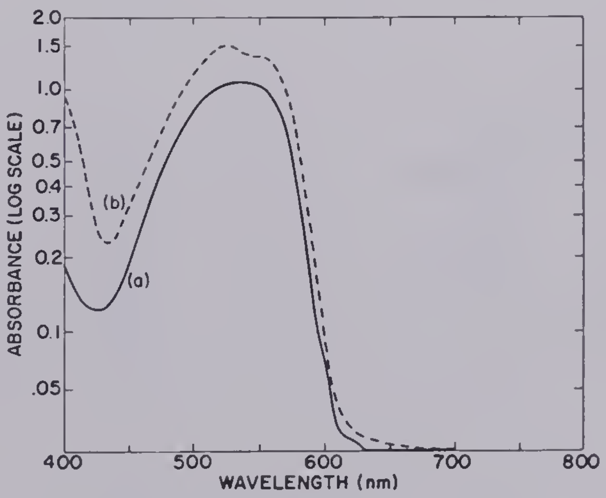


FIG. 8. Absorption spectra of (a) compound LIV and (b) compound LVI.

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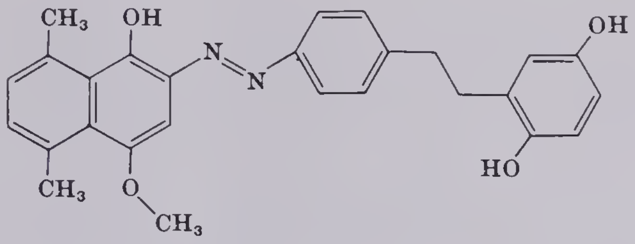
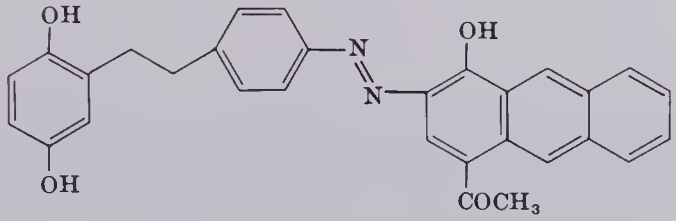
[39] C. M. Smith and G, *USP* 2,572,822.

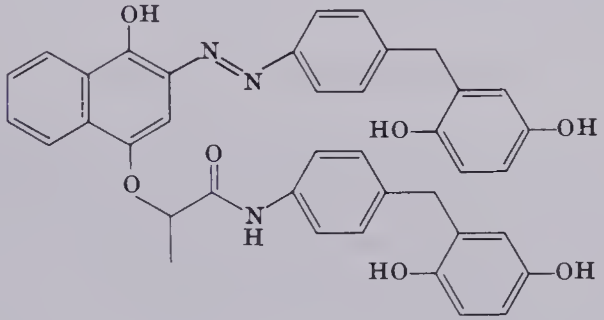
[40] M. Green and Polaroid Corp., *USP* 3,328,386; M. Green, P. T. Moore, and Polaroid Corp., *USP* 3,297,441; 3,365,441; P. T. Moore and Polaroid Corp., *USP* 3,256,269.



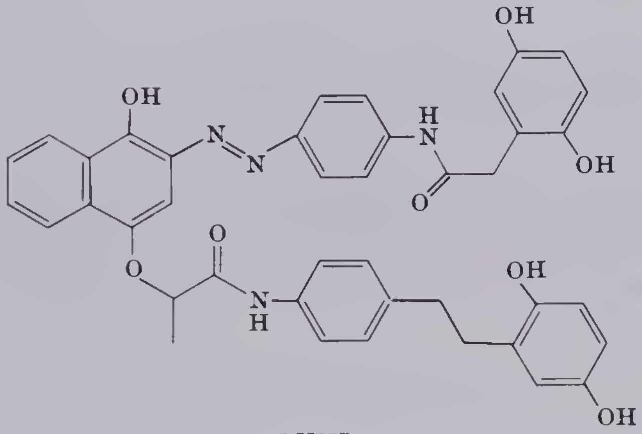
(LV)



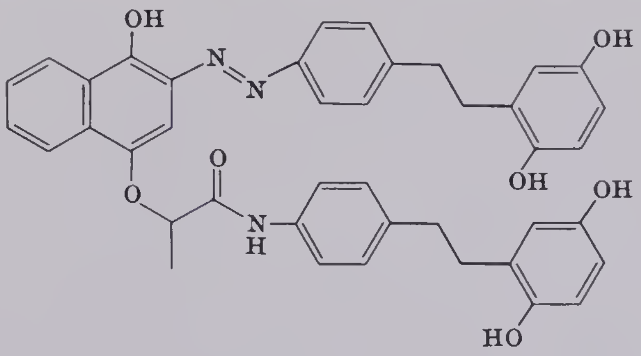
(LVI)



(LVII)



(LVIII)



(LIX)

Another compound worth noting is (LV), which has a spectrum similar to that of (LIV), with $\lambda_{\max} = 538$ nm ($\epsilon = 22{,}800$) (2-methoxyethanol), and even less absorption in the blue region (Fig. 7).

Diazotized aminophenethyl hydroquinone diacetate (XIII) coupled with 4-acetyl-1-anthrol gives a good magenta dye developer (LVI), $\lambda_{\max} = 522$ nm ($\epsilon = 30{,}000$) and $\lambda_{\max} = 546$ nm ($\epsilon = 26{,}800$) (2-methoxyethanol) (Fig. 8).[14] Compounds (LVII), (LVIII), and (LIX) are examples of the many magenta dyes with two developer groups that were synthesized.[40]

III. Anthraquinone Dye Developers

The range of colors available from anthraquinone dyes and their known chemical and photochemical stabilities[41] were recognized early in the dye developer program. Since adequate spectral curves did not appear in the literature, model compounds were synthesized to demonstrate the excellent magenta and cyan chromophores that could be obtained. Spectra of these models or the dye developers derived from them appear in Figs. 9–12.[14,42]

A. Dye Developers from Leucoquinizarin or Leuco-1,4,5,8-Tetrahydroxyanthraquinone

Once it was shown that the model anthraquinone dyes containing alkylamino groups provide satisfactory cyan and magenta chromophores, a series of aminoalkyl-substituted hydroquinones, catechols, and aminophenols were synthesized, e.g., (LX)–(LXII).[43]

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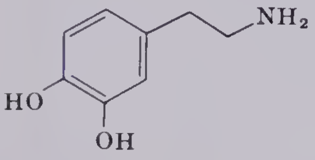
[41] *CSD II*, pp. 804ff.

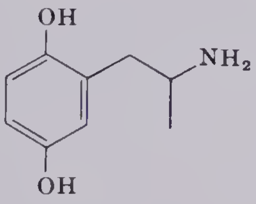
[42] *Meet. Soc. Photogr. Sci. Eng. Atlantic City, N.J., 1963.*

[43] M. Green, M. S. Simon, and Polaroid Corp., *USP* 3,002,997; M. Green and Polaroid Corp., *USP* 3,062,884; H. Curtis and Polaroid Corp., *USP* 3,187,046; M. Green and Polaroid Corp., *USP* 3,187,047; E. R. Blout, S. G. Cohen, M. S. Simon, and Polaroid Corp., *USP* 3,240,810; M. Green, H. G. Rogers, and Polaroid Corp., *USP* 3,253,001.

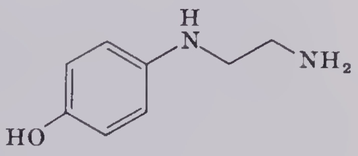
The reaction of leucoquinizarin[44] with aliphatic amines has been used frequently to make 1,4-bisalkylaminoanthraquinones,[45] but two problems prevented the simple application of this route to the preparation of dye developers. In the conventional process, liquid aliphatic amines were frequently used in large excess, a method that was impractical because of the high cost of the aminoalkyl developers. Also, the desired complex amines were frequently solids. This problem was overcome when it was found that equimolar amounts of the aminoalkyl developers and leucoquinizarin condensed successfully in pyridine with a small amount of water.[46] The solution to the second problem, the need to oxidize the leuco dye system without oxidizing the photographic developers, which are sensitive reducing agents, required the discovery of selective oxidation methods. Pyridine *N*-oxide,[47] air,[46] and especially air adsorbed on carbon black in the presence of hydrochloric acid[48] were found to be such selective oxidants. Chloranil in equivalent amount may also be used.[49]



(LX)



(LXI)



(LXII)

The condensation of aliphatic amines with quinizarin in the presence of phenols bypasses the separate oxidation step.[50] This route was used extensively in the laboratory synthesis of dye developers.

The syntheses of typical cyan dye developers (LXIII) and (LXV) are outlined in Chart VI.[46] Dyes made from quinizarins containing electron-donating substituents in the 5- and 8-positions were especially valuable because of their spectral characteristics.

By reacting leucoquinizarin with different amines in a stepwise fashion, 1,4-diaminoanthraquinone dye developers with different groups on the amino nitrogens may be prepared.[46] Alkyl, aryl, or aralkyl

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[44] K. Zahn and P. Ochwat, *Justus Liebigs Ann. Chem.* **462**, 72 (1928); S. M. Bloom and R. F. Hutton, *Tetrahedron Lett.* p. 1993 (1963).

[45] *CSD II*, p. 836.

[46] E. R. Blout, M. R. Cohler, M. Green, M. S. Simon, R. B. Woodward, and Polaroid Corp., *USP* 3,135,606; 3,209,016.

[47] S. Kasman and Polaroid Corp., *USP* 3,173,929.

[48] C. E. Jandrue, M. S. Simon, H. T. Wolosinski, and Polaroid Corp., *USP* 3,253,002.

[49] M. R. Briner, C. L. Gibson, and EK Co., *USP* 3,405,145.

[50] J. A. McSheehy and CCC, *USP* 2,727,045.

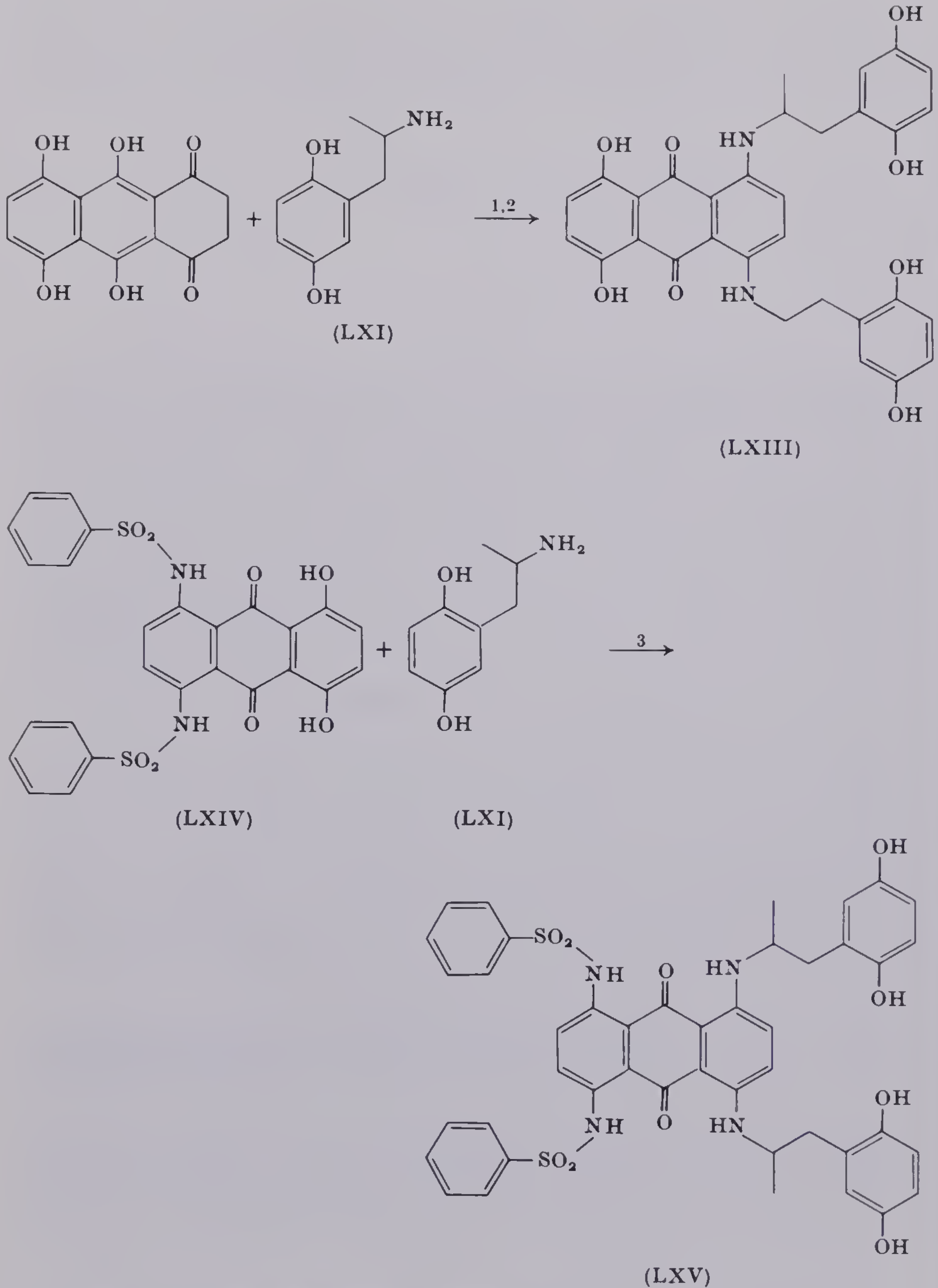
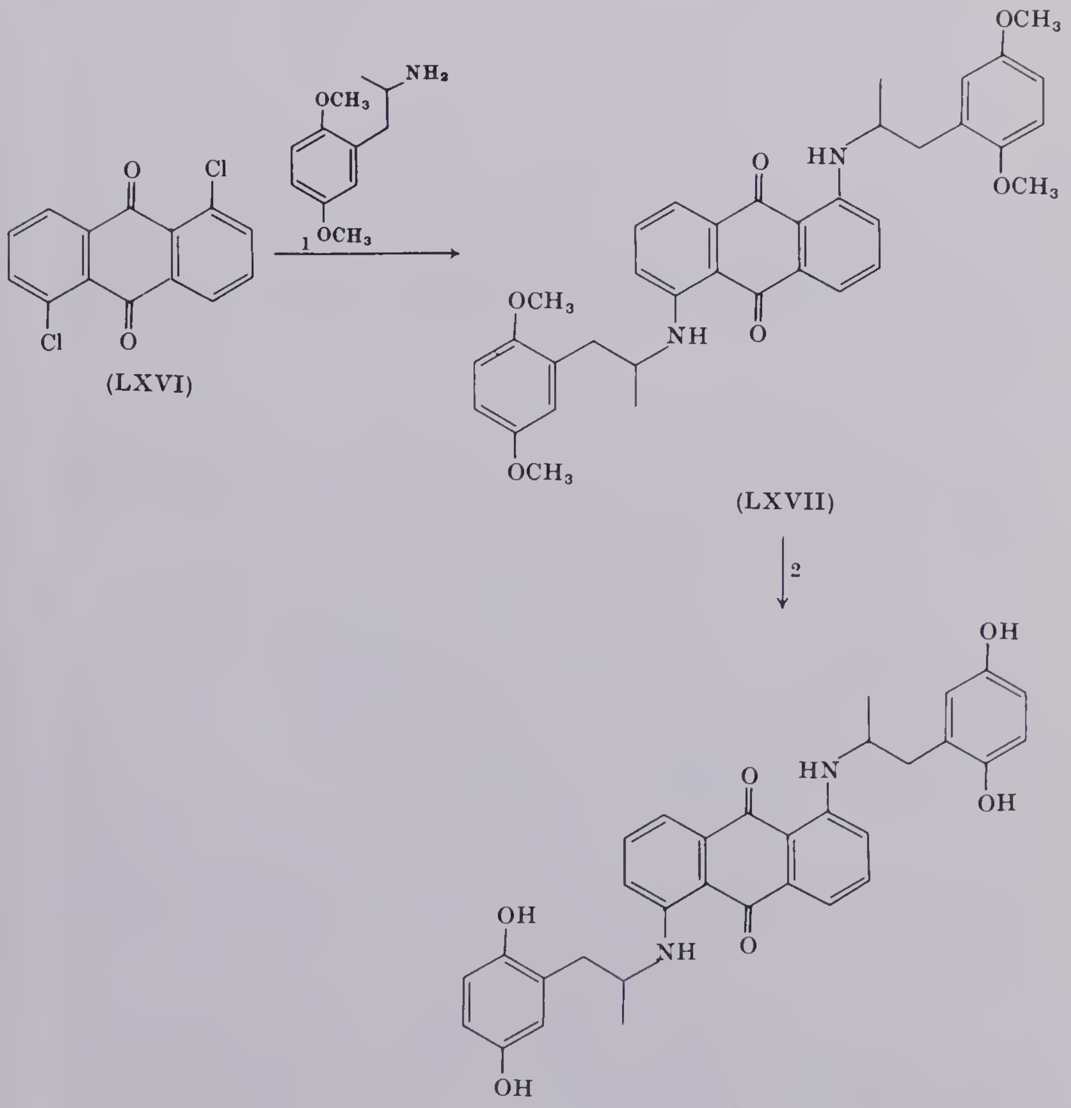


Chart VI. (1) $NaHCO_3$, pyridine, water, refluxed under N_2; (2) air; (3) Na_2CO_3, $NaHCO_3$, phenol, ethanol–water, refluxed under N_2.

bridges between dye and developer can be used,[51] and dyes can be made with only one developing group.[46]

B. 1,5-BISALKYLAMINOANTHRAQUINONES

1,5-Dichloroanthraquinone (LXVI) has frequently been reacted with aliphatic or aromatic amines to generate the corresponding magenta 1,5-diamino derivatives.[52] The method usually calls for a large excess of



(LXVI)

(LXVII)

(LXVIII)

CHART VII. (1) Cu^+; (2) BBr_3, CH_2Cl_2.

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[51] E. R. Blout, S. Kasman, M. S. Simon, and Polaroid Corp., *USP* 3,076,808; 3,126,280.

[52] E. Gutzwiller and S, *USP* 2,848,462.

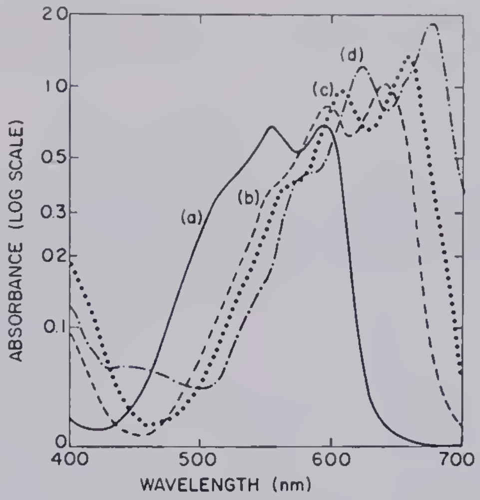


Fig. 9. Absorption spectra of (a) 1,4-diaminoanthraquinone, 2-methoxyethanol; (b) 1,4-bis(3′,4′-dihydroxyphenylethylamino)anthraquinone, ethanol; (c) 5-Hydroxy-1,4-bis(β-2′,5′-dihydroxyphenyl-α-methylethylamino)anthraquinone, ethanol; (d) 5,8-Dihydroxy-1,4-bis(β-2′,5′-dihydroxyphenyl-α-methylethylamino)anthraquinone(LXIII), 2-methoxyethanol.

the liquid amine along with copper salt catalysts to obtain complete conversion, conditions that lead to very low yields with the labile aminoalkyl catechol (LX) or hydroquinone (LXI) intermediates. One route to bypass this problem is described in Section E.[53]

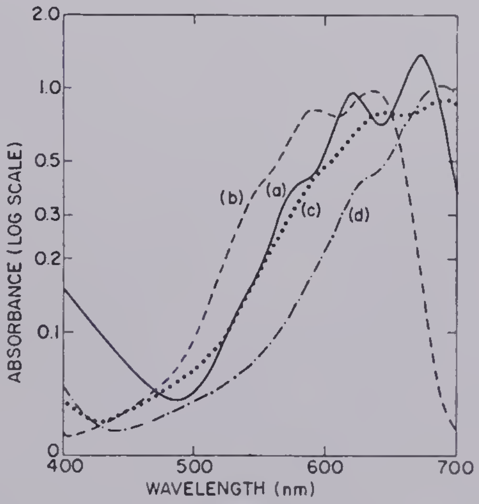
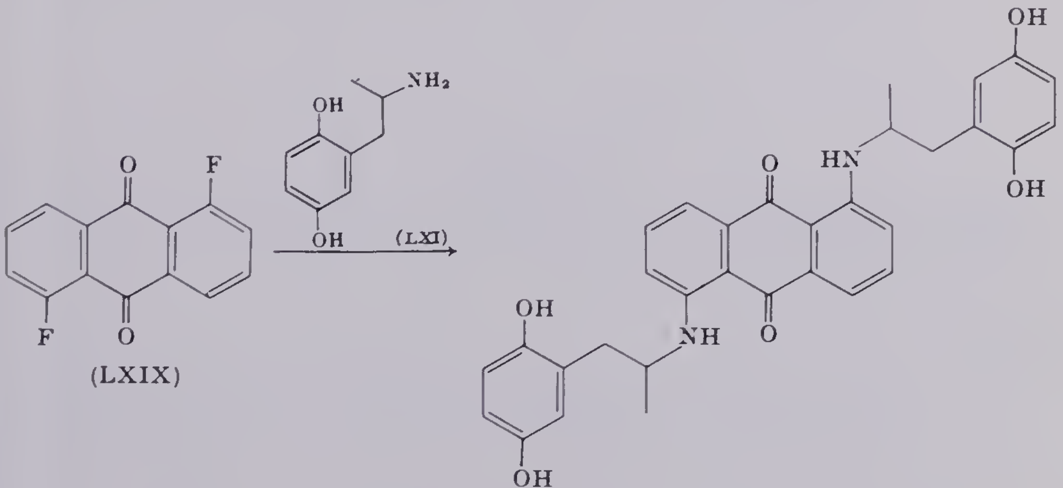


Fig. 10. Absorption spectra of (a) 5,8-bisbenzenesulfonamido-1,4-bis(β-2′,5′-dihydroxyphenyl-α-methylethylamino)anthraquinone (LXV), 2-methoxyethanol; (b) 1,4,5,8-tetraaminoanthraquinone, acetone; (c) 5,8-diamino-1,4-bis(β-hydroxyethylamino)anthraquinone, pyridine; (d) 1,4,5,8-tetrakismethylaminoanthraquinone, dimethylformamide.

[53] E. R. Blout, S. G. Cohen, M. Green, H. G. Rogers, M. S. Simon, R. B. Woodward, and Polaroid Corp., *USP* 3,288,778.

Boron tribromide and, less generally, pyridine hydrochloride were found to cleave alkyl aryl ethers without attacking the anthraquinone chromophore, permitting the use of methyl ethers to protect the developers in the dye syntheses[54] (Chart VII).

A reaction mild enough to allow the use of unprotected aminoalkyl hydroquinones was found. α-Fluoro substituents on anthraquinones, e.g., (LXIX), can be successfully displaced by aminoalkyl developers to prepare the dye developers directly[55] (Chart VIII).



(LXIX)

(LXVIII)

Chart VIII

C. 2- or 2,3-Substituted 1,4-Diaminoanthraquinones

Examination of published spectral data[56] and of spectral data obtained from model compounds[14,42] led to a simple relationship between 2- or 2,3-substitution and absorption in the 1,4-diaminoanthraquinone series; electron donating groups, e.g., amino or alkoxy, are hypsochromic, while electron withdrawing groups, e.g., cyano or carbonyl, are bathochromic substituents.

Magenta dye developers may be obtained from the 1,4-diamino-2-alkoxyanthraquinone chromophore[57] or from the 1-amino-2-alkyl-

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[54] J. F. W. McOmie, M. L. Watts, and D. E. West, *Tetrahedron* **24**, 2289 (1968); V. Prey, *Ber. Dtsch. Chem. Ges.* **74**, 1219 (1941).

[55] W. E. Solodar and M. S. Simon, *J. Org. Chem.* **27**, 689 (1962).

[56] R. A. Morton and W. T. Earlam, *J. Chem. Soc.* p. 159 (1941); C. F. H. Allen, C. V. Wilson, G. F. Frame, *J. Org. Chem.* **7**, 169 (1942), and earlier references cited therein; C. J. P. Spruit, "*Rec*". *Trav. Chim. Pays-Bas* **68**, 325 (1949); A. M. Lukin and K. K. Mozgova, *Zh. Obshch. Khim.* **20**, 1504 (1950); R. H. Peters and H. H. Sumner, *J. Chem. Soc.* p. 2101 (1953); K. Naiki and S. Tsuruoka, *J. Soc. Org. Synth. Chem. Tokyo* **11**, 113 (1953); N. S. Dokunikhin and T. N. Kurdyumova, *Zh. Obshch. Khim.* **25**, 617 (1955); H. Labhart, *Helv. Chim. Acta* **40**, 1410 (1957).

[57] J. F. Downey, M. S. Simon, and Polaroid Corp., *USP* 3,245,790; 3,246,016.

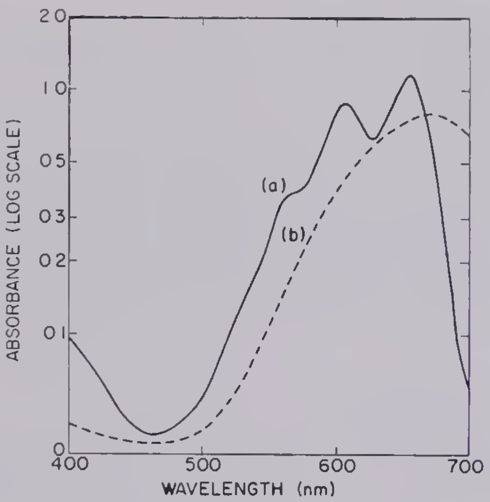

FIG. 11. Absorption spectra of (a) 6,7-dichloro-1,4-bis(β-2′,5′-dihydroxyphenyl-α-methylethylamino)anthraquinone, 2-methoxyethanol; (b) 1,4-Diaminoanthraquinone-2,3-dicarboximide (LXXIII), pyridine.

amino-4-hydroxyanthraquinone chromophore by the scheme in Chart IX.[58,59]

An interesting cyan chromophore (Fig. 11) is 1,4-diaminoanthraquinone 2,3-dicarboximide (LXXIII).[60] Higher blue and green light transmission makes this a particularly attractive dye for subtractive color photography. Reaction of (LXXIII) with 2-aminopropyl hydroquinone (LVIII) produces the dye developer (LXXIV) (Chart X).[61]

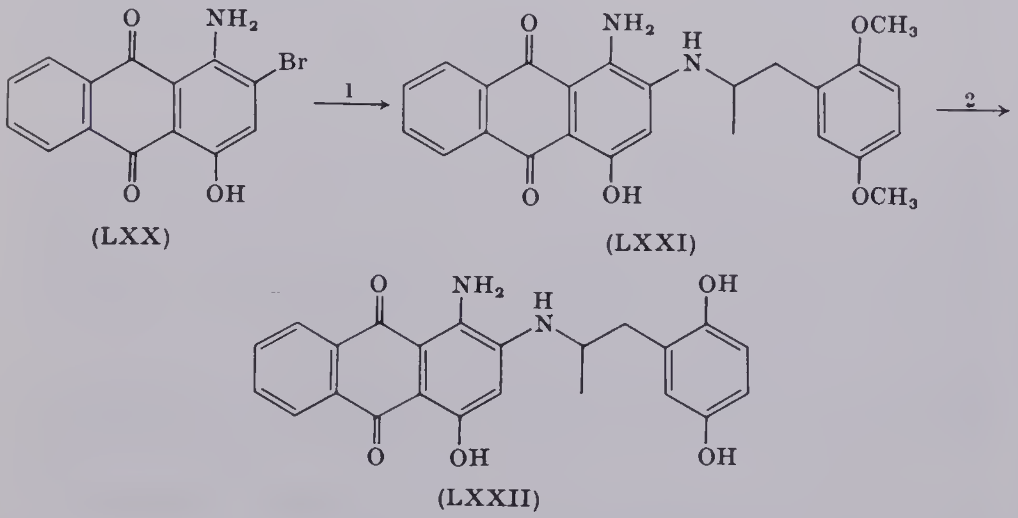

CHART IX. (1) K_2CO_3, 100°, 2(β-aminopropyl)-1,4-dimethoxy benzene; (2) pyridine hydrochloride, 225°

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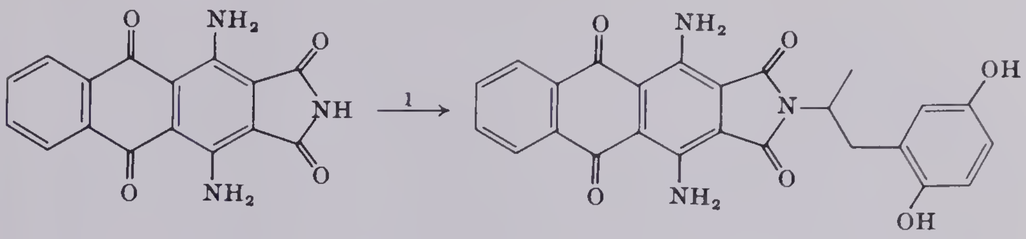
[58] J. F. Downey, M. S. Simon, and Polaroid Corp., *USP* 3,347,672; 3,491,127.

[59] J. F. Downey and Polaroid Corp., *USP* 3,347,673.

[60] J. F. Laucius, S. B. Speck, and DuP, *USP* 2,628,963; 2,753,356.

[61] M. S. Simon and Polaroid Corp., *USP* 3,131,061; 3,255,206.



(LXXIII) (LXXIV)

CHART X. (1) 2(β-aminopropyl) hydroquinone (LXI), 2-methoxyethanol.

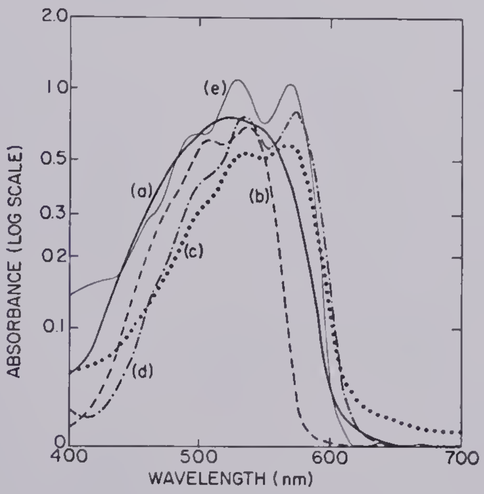


FIG. 12. Absorption spectra of (a) 1,5-bis(β-2′,5′-dihydroxyphenyl-α-methylethylamino)-anthraquinone (LXVIII), 2-methoxyethanol; (b) 3(β-2′,5′-dihydroxyphenyl-α-methylethyl)-6(β-2′,5′-dihydroxyphenyl-α-methylethylamino)anthrapyridone (LXXVIII), ethanol; (c) 3(β-2′,5′-dihydroxyphenyl-α-methylethyl)-6(β-2′,5′-dihydroxyphenyl-α-methylethylamino)anthrapyrimidone (LXXIX), 2-methoxyethanol; (d) 1,4-diamino-2(ϵ[β-2′,5′-dihydroxyphenyl-α-methylpropionamido]pentoxy)anthraquinone (LXXXII), 2-methoxyethanol; (e) 1-amino-2-*n*-butylamino-4-hydroxyanthraquinone, isopropanol.

D. ANTHRAPYRIDONES AND ANTHRAPYRIMIDONES

The use of anthrapyridones as magenta chromophores was well known.[62] Dye developers were readily synthesized with hydroquinonyl groups linked to the 1-, 3- or 6-positions.[51] Two such dye developers, (LXXVI) and (LXXVIII), may be made by the schemes shown in Chart XI. The 1,4-bisalkylaminoanthraquinones can also be converted into anthrapyrimidones (Chart XII).[63]

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[62] *CSD II*, p. 999; R. M. Evans, W. T. Hanson, W. L. Brewer, "Principles of Color Photography," p. 376ff. Wiley, New York, 1953; C. F. H. Allen, J. V. Crawford, R. H. Sprague, E. R. Webster, and C. V. Wilson, *J. Am. Chem. Soc.* **72**, 585 (1950); M. S. Simon and J. B. Rogers, *J. Org. Chem.* **26**, 4352 (1961).

[63] S. Dershowitz and Polaroid Corp., *USP* 3,239,339.

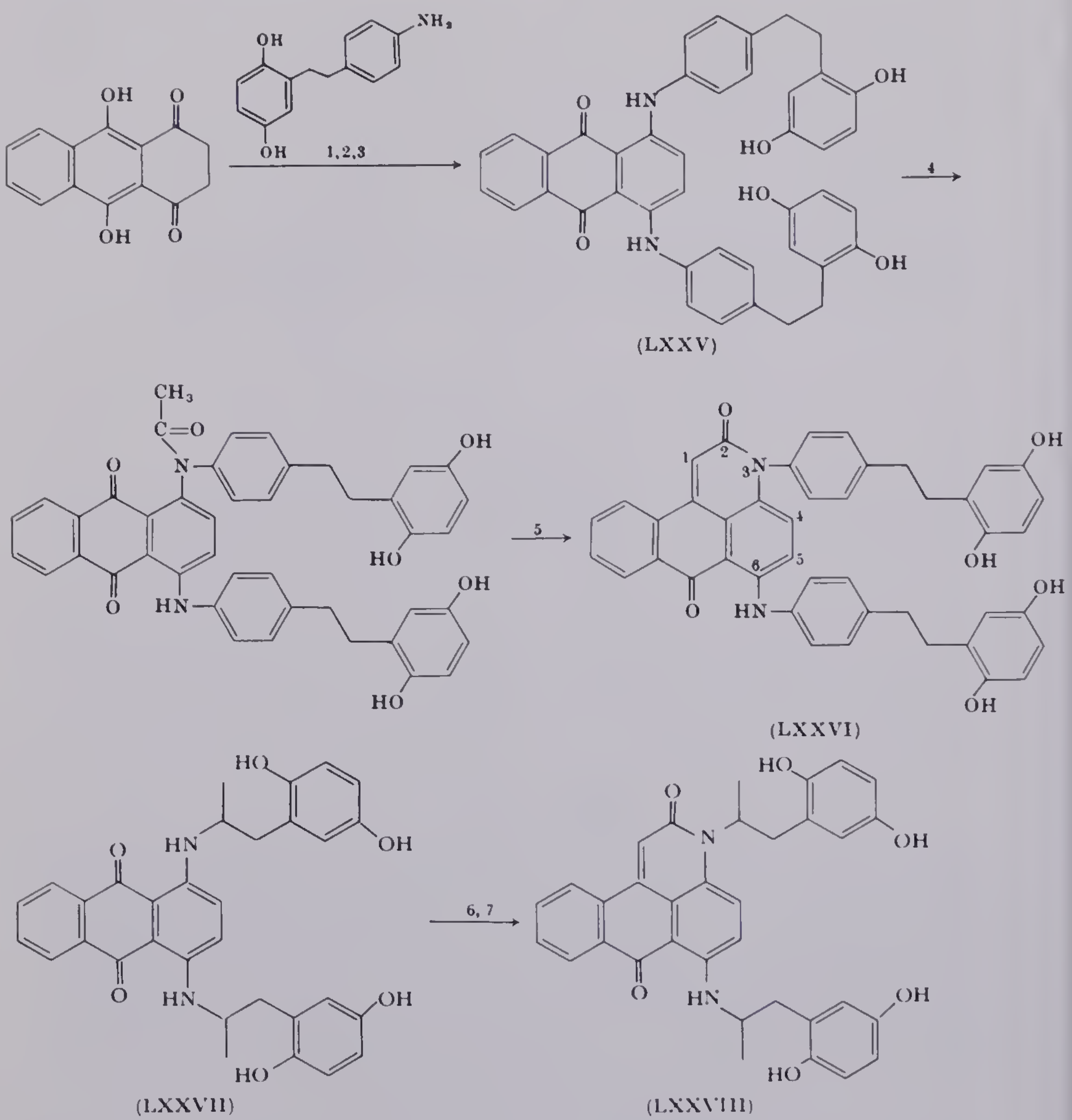

Chart XI. (1) H_3BO_3, $CH_3OCH_2CH_2OH$; (2) chloranil; (3) HCl, H_2O; (4) acetyl chloride, pyridine; (5) KOH, $CH_3OCH_2CH_2OH$; (6) acetyl chloride; (7) KOH, $CH_3OCH_2CH_2OH$.

E. Dye Developers in Which the Developer Is Attached to the Dye by an Amide Link

An invaluable method used for synthesizing many dye developers starts from preformed dyes containing carboxylic acid[64] or amino

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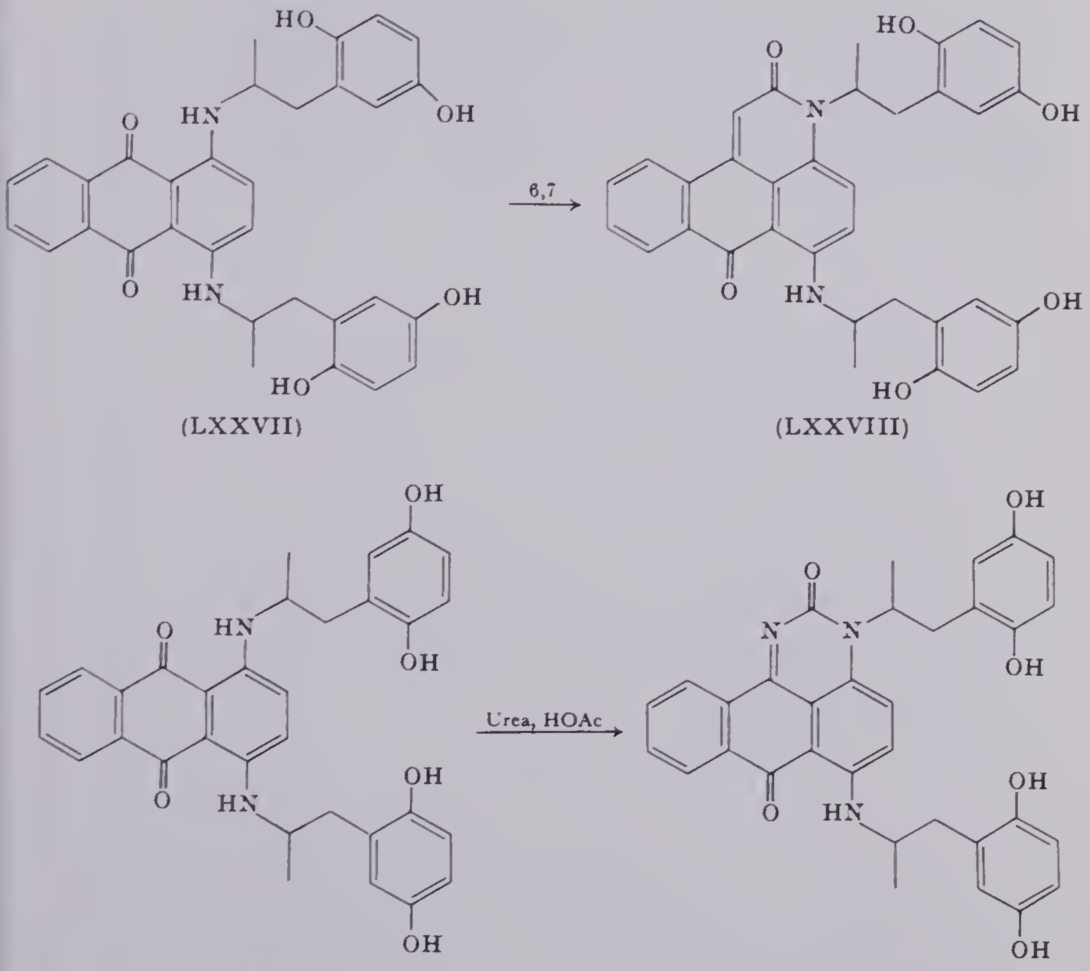
[64] E. R. Blout, M. Green, H. G. Rogers, M. S. Simon, and Polaroid Corp., *USP* 820. 3,076,

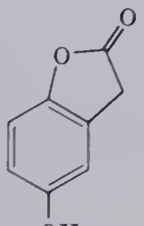


(LXXVII) (LXXVIII)

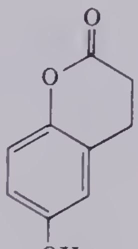
(LXXVII) (LXXIX)

Chart XII

groups.[53,65] The developers can be introduced by condensation steps to produce amide bonds. A particularly successful route employs the facile condensation of the readily prepared lactones of homogentisic



(LXXX)



(LXXXI)

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[65] E. R. Blout, R. S. Corley and Polaroid Corp., *USP* 3,236,864; A. D. Jarrett and Polaroid Corp., *USP* 3,135,605; 3,236,865.

acid and 2,5-dihydroxydihydrocinnamic acid [(LXXX) and (LXXXI)] with dyes containing aliphatic amino groups (Chart XIII).

While studying these dyes, a new reaction of the anthraquinone nucleus was discovered. Condensation of leucoquinizarin with ethylenediamine gives an unusual product (LXXXV), in addition to the expec-

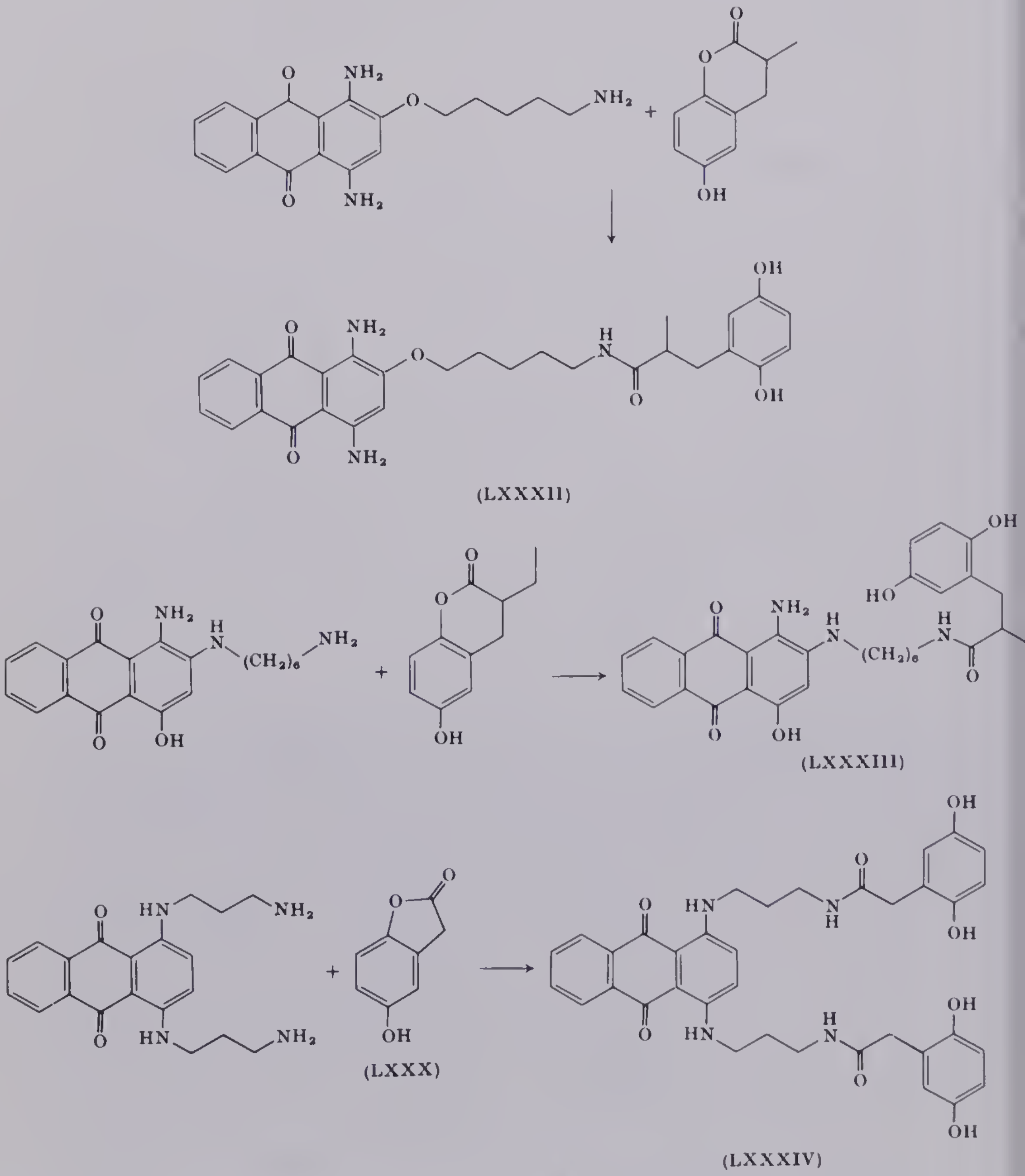


Chart XIII

ted product (LXXXVI).[66] A plausible mechanism is shown in Chart XIV.

Another unexpected reaction was encountered in the 1,4-diamino-2-alkoxyanthraquinone studies.[67] The reaction of β-methylaminoethanol

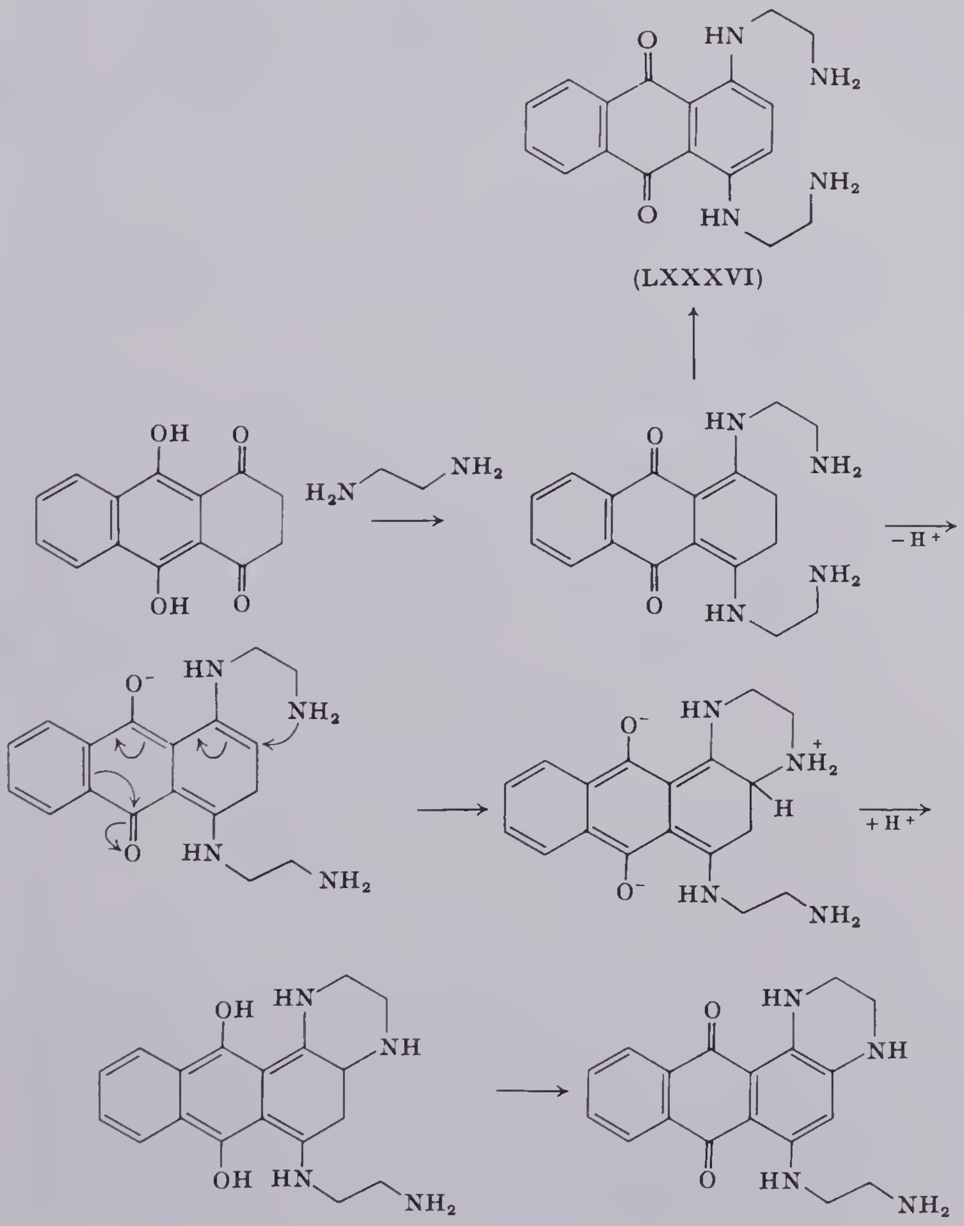


CHART XIV

[66] M. S. Simon, *J. Am. Chem. Soc.* 85, 1974 (1963); M. S. Simon and D. P. Waller, *Tetrahedron Lett.* No. 16, p. 1527 (1967); C. W. Greenhalgh and N. Hughes, *J. Chem. Soc. C* p. 1284 (1968).

[67] M. S. Simon and J. F. Downey, *Tetrahedron Lett.* No. 35, p. 3019 (1974).

with 1,4-diamino-2-phenoxyanthraquinone gave a purple dye (LXXXVIIa) rather than the anticipated magenta dye (LXXXVII). By running the reaction under milder conditions and following its course spectrophotometrically, it can be shown that the expected (LXXXVII) is indeed formed but is unstable under the reaction conditions. A Smiles rearrangement ensues leading to (LXXXVIIa), because the alkoxide group is a better leaving group than the amino group in the strongly

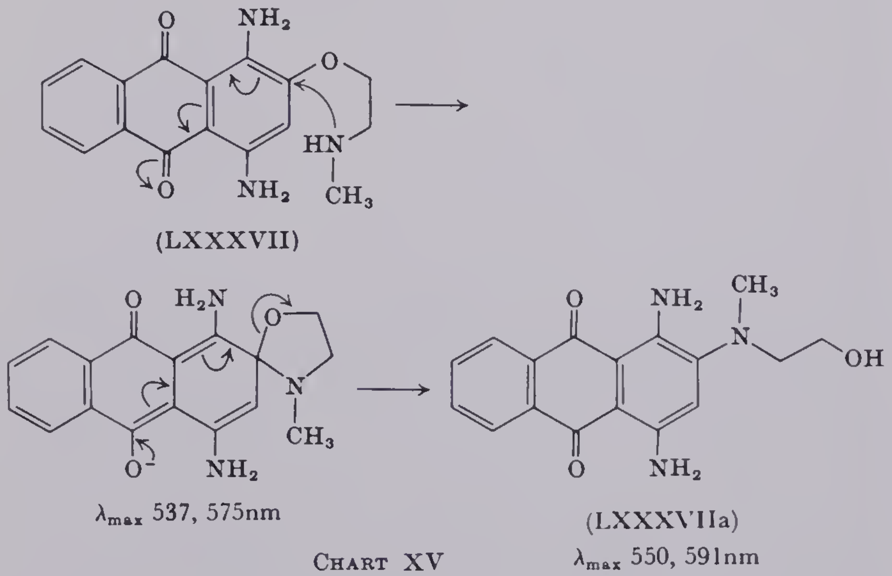


Chart XV

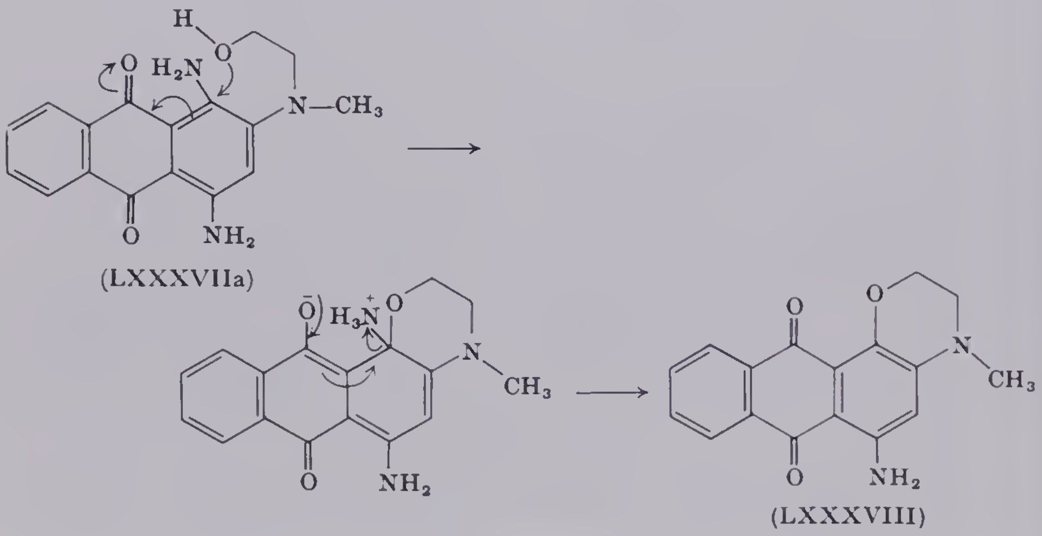


Chart XVI

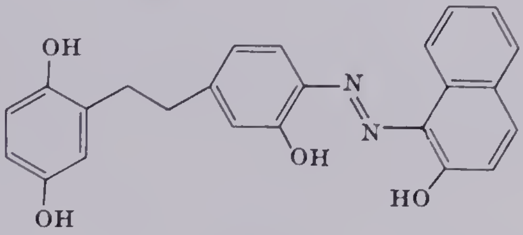
basic medium (Chart XV). Mild acid treatment generates a new dye chromophore (LXXXVIII), by loss of ammonia (Chart XVI).[68]

IV. Metallized Dye Developers

Transition metal complexes of chelatable dyes comprise some of the most light-stable dyes. A recent review in this treatise discusses the complexes of azo and azomethine dyes.[69] Because of their well-known high stability to light, attention was directed toward dyes of this type very early in the dye developer program.[70] In this review, the dye developers based on metal complexes of azo and azomethine dyes will be discussed first, followed by dye developers based on metal phthalocyanines.

A. AZO AND AZOMETHINE DYE DEVELOPERS

One technique used for providing metallized image dyes employed the imagewise transfer of chelatable dye developers to a receiving layer that contained or was swabbed with copper or nickel compounds, thereby generating the metallized dye *in situ*.[71] The dye developer (LXXXIX) is an example of the type of compound that may be used in this postmetallization process.[72]



(LXXXIX)

The preferred technique, which will be discussed in detail, uses premetallized dye developers. In addition to the requirements listed in Section I,C premetallized dye developers should meet the following: (1) The metal ion must not be reduced by the developer. (2) The complex must be sufficiently stable to prevent precipitation of the metal hydroxide in the alkaline processing medium. (3) Most of the coordination sites

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[68] M. S. Simon and J. F. Downey, *Tetrahedron Lett.* No. 38, p. 3471 (1974).

[69] R. Price in *CSD III*.

[70] M. Green, L. E. Rubin, and Polaroid Corp., *USP* 3,218,164.

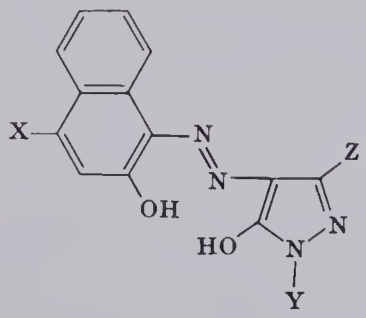
[71] A. B. Goulston, M. S. Simon, and Polaroid Corp., *USP* 3,081,167; H. G. Rogers and Polaroid Corp., *USP* 3,196,014.

[72] M. Green, M. S. Simon, and Polaroid Corp., *USP* 3,299,041.

of the metal ion should be occupied by the ligands of the complex to minimize metal–gelatin interactions.

Copper, nickel, cobalt, and chromium are the metal ions most frequently used in metallized dyes. After preliminary studies of the chemical and spectral properties of dyes containing these metals, chromium complexes were selected for exhaustive examination, as they appeared most likely to meet the above requirements.

The commercial dye CI 18760 (XC, X = SO_3Na, Y = C_6H_5, Z = CH_3) forms complexes having a dye:chromium ratio of 2:1 or 1:1. The 2:1 complex exhibits a rather broad absorption spectrum and is dull in color. This property is generally observed for the 2:1 complexes of *o,o′*-dihydroxy azo dyes.[14] The 1:1 complexes show narrower absorption spectra, and the dyes appear bright magenta in color (Fig. 13). The remaining problem was to render the other three coordination sites of the Cr(III) unreactive to gelatin.



(XC)

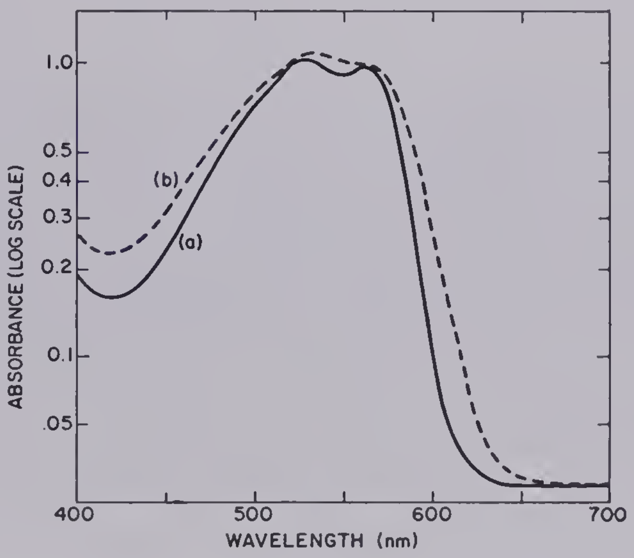


FIG. 13. Absorption spectra of (a) 1:1 complex and (b) 2:1 complex.

Transition metals, especially Cr(III), coordinate with a wide variety of inorganic and organic ligands. By reacting the 1:1 complex of the dye or dye developer with colorless polydentate ligands, a stable mixed complex such as (XCII) is formed,[73] thereby preventing metathesis to 2:1 complexes and minimizing interaction with gelatin.

An advantage of this approach is the wide degree of flexibility available for altering the spectral curve, attachment of developer groups, and otherwise adjusting the subtle parameters that affect the photographic behavior of the dye developer. In 1:1 Cr complexes of (XC), substituents at X, Y, and Z and the ligand may be varied (see Table V and Fig. 14). Choice of the ligand affects the net charge on the metal complex, and, since neutral dyes were desired, the ligand chosen was usually monoprotic, e.g., 2,4-pentanedione (acac). One route to neutral dye developers (XCII) employs the cationic diethylenetriamine (dien) complex (XCI), while in a second route, acac may react directly with the chrome complex, preferably in the presence of a base such as triethylamine[73] (Chart XVII). Dyes with a developer group incorporated in positions X, Y, or Z of (XCII) were photographically useful.[74]

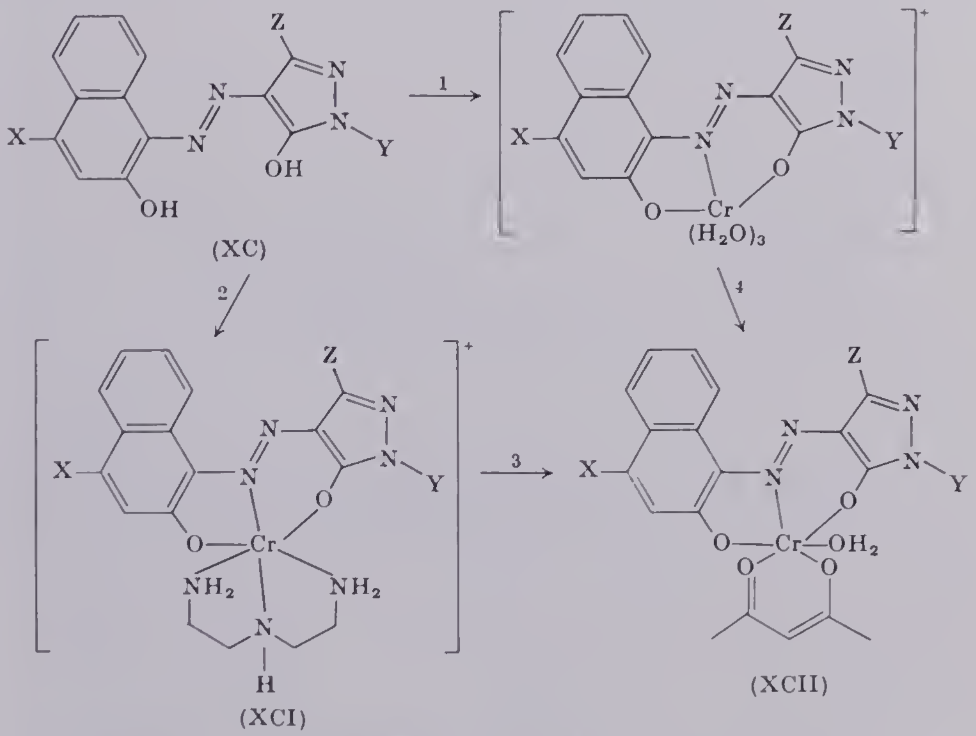


CHART XVII. (1) $CrCl_3 \cdot 6H_2O$; (2) dien; (3) $CH_3COCH_2COCH_3$, H_2O; (4) $CH_3COCH_2COCH_3$, $(C_2H_5)_3N$.

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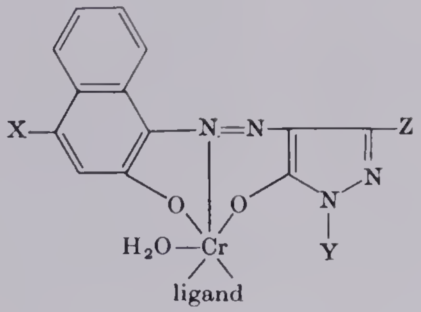
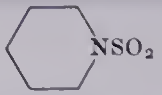
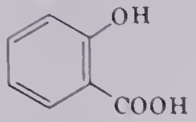
[73] E. M. Idelson and Polaroid Corp., *USP* 3,453,107; 3,544,545; E. M. Idelson, I. Karady, B. Mark, D. O. Rickter, and V. H. Hooper, *Inorg. Chem.* 6, 450 (1967).

[74] E. M. Idelson and Polaroid Corp., *USP* 3,780,105.

TABLE V



X	*Y*	*Z*	*Ligand*	λ_{max} 1 (*nm*)	$\epsilon_1 \times 10^{-3}$	λ_{max} 2 (*nm*)	$\epsilon_2 \times 10^{-3}$
CN	H	CH_3	acac	528	14.8	568	16.4
H	C_6H_5	$CO_2C_2H_5$	acac	520	16.8	556	20.4
H	C_6H_5	$CONHCH_3$	acac	520	16.9	555	20.4
 NSO_2	C_6H_5	$CO_2C_2H_5$	acac	532	17.2	570	20.0
 NSO_2	C_6H_5	$CONHCH_3$	acac	533	19.4	570	23.4
$CH_3(n\text{-}C_4H_9)NSO_2$	$m\text{-}C_6H_4NO_2$	CH_3	acac	530	20.0	567	21.6
$CH_3(n\text{-}C_4H_9)NSO_2$	$p\text{-}C_6H_4NO_2$	CH_3	acac	534	23.2	571	24.8
$CH_3(n\text{-}C_4H_9)NSO_2$	$p\text{-}C_6H_4NH_2$	CH_3	acac	533	20.7	568	20.9
CN	C_6H_5	CH_3	Tropolone	535	20.4	575	22.0

	C_6H_5	CH_3	L-Proline	527	21.0	562	21.2
$(CH_3)_2NSO_2$	C_6H_5	CH_3	Gentisaldehyde	531	21.9	566	20.4
	C_6H_5	CH_3	Acetoacetanilide	527	17.4	563	18.0
	C_6H_5	CH_3	acac	524	21.4	556	22.0
$COCH_3$	C_6H_5	CH_3	acac	527	—	560	—
H	C_6H_5	CH_3	acac	516	18.0	553	19.7
SO_3H	C_6H_5	CH_3	$2H_2O$	522	17.6	555	18.5
SO_3Na	C_6H_5	CH_3	$2H_2O$	514	15.0	539	13.9
SO_3Na	C_6H_5	CH_3	acac	525	18.2	562	21.4
SO_3Na	C_6H_5	CH_3	8-Quinoline	536	13.8	569	15.6
$(CH_3)_2NSO_2$	C_6H_5	CH_3	acac	530	21.4	567	23.2
$(CH_3)_2NSO_2$	C_6H_5	CH_3	Dien [a]	545	24.0	586	28.4
$(CH_3)_2NSO_2$	C_6H_5	CH_3	$H_2NCH_2CH_2NHCH_2COOH$ [a]	537	23.2	577	26.4
CN	C_6H_5	CH_3	acac	537	22.0	575	24.6
CN	C_6H_5	CH_3	Dien [a]	549	20.6	591	25.4
CN	C_6H_5	CH_3		539	22.4	576	23.0
CN	C_6H_5	$CO_2C_2H_5$	acac	537	19.2	576	24.0
CN	C_6H_5	$CONHCH_3$	acac	535	20.6	573	25.4
CN	C_6H_5	$NHCOCH_3$	acac	546	21.4	585	22.6
CN	CH_3	CH_3	acac	531	18.8	569	20.6

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[a] No H_2O in structure; ligand is tridentate.

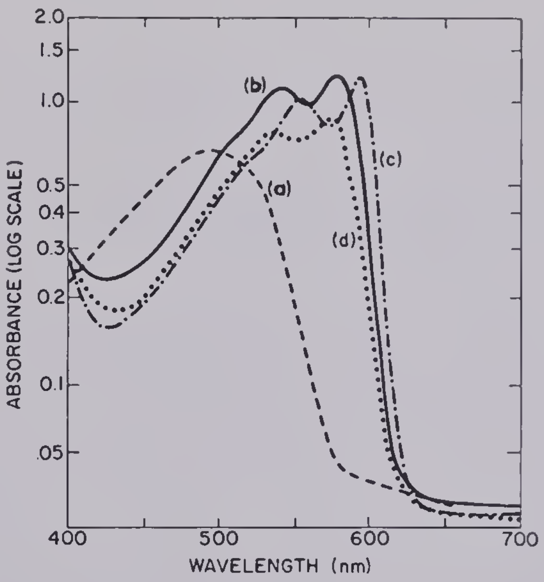
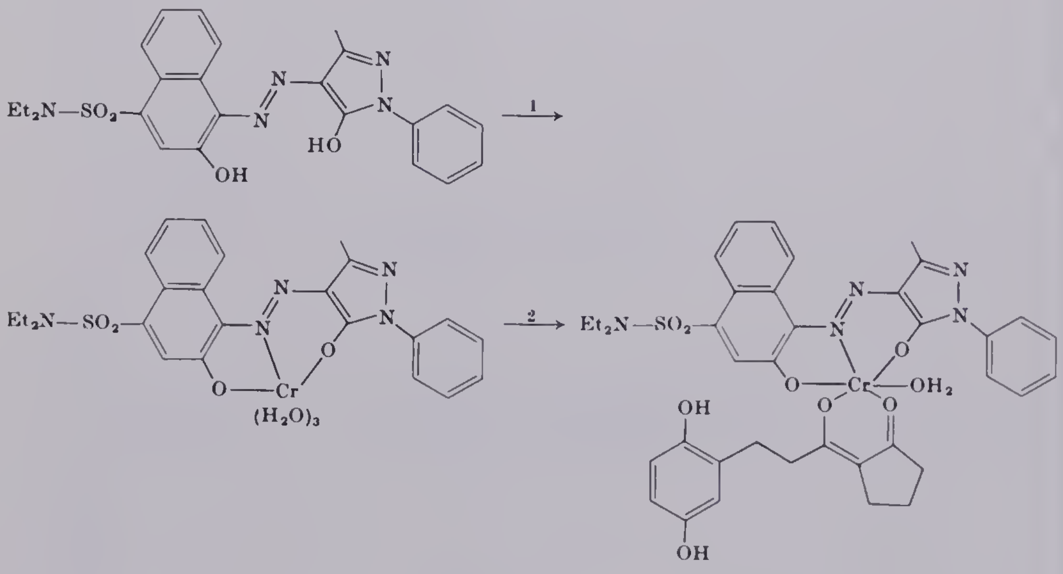
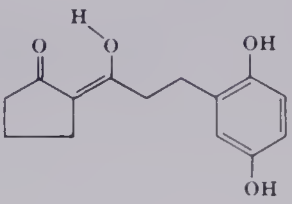


FIG. 14. Absorption spectra of (a) compound XC, X = SO_3Na, Y = C_6H_5, Z = CH_3; (b) chromed XC, ligand = $3H_2O$; (c) chromed XC, ligand = dien; (d) chromed XC, ligand = acac, H_2O.



(XCIII)

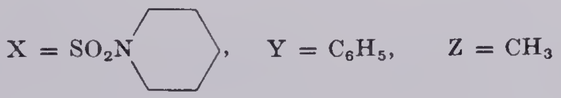
CHART XVIII. (1) $CrCl_3 \cdot 6H_2O$; (2)



Many other types of ligands are useful in coordinating with 1:1 dye–Cr(III) complexes.[73] They include amines such as triethylenetetramine, ethylenediamine, 9,10-phenanthroline, 8-hydroxyquinoline, and 2,2′,2″-triaminotriethylamine; acids such as citric acid and salicylic acid; amino acids such as ethylenediaminetetracetic acid and proline; *o*-hydroxy-aldehydes and ketones, and tropolones.

A versatile route to chromed dye developers incorporates the developing function as part of a β-diketone ligand, e.g., (XCIII).[75] In this way, virtually any 1:1 dye–Cr(III) complex can be converted into a dye developer.[76] The sequence is outlined in Chart XVIII.

The stereochemical configuration of these chromium complexes has been elucidated by an X-ray crystallographic analysis of (XCII)[77]:



$X = SO_2N$, $Y = C_6H_5$, $Z = CH_3$

In agreement with the work of Schetty on 2:1 chromium complexes of *o,o*′-dihydroxyazo dyes,[78] the dye coordinates in the meridial positions of the chromium ion (Fig. 15). It exists in the ketohydrazone

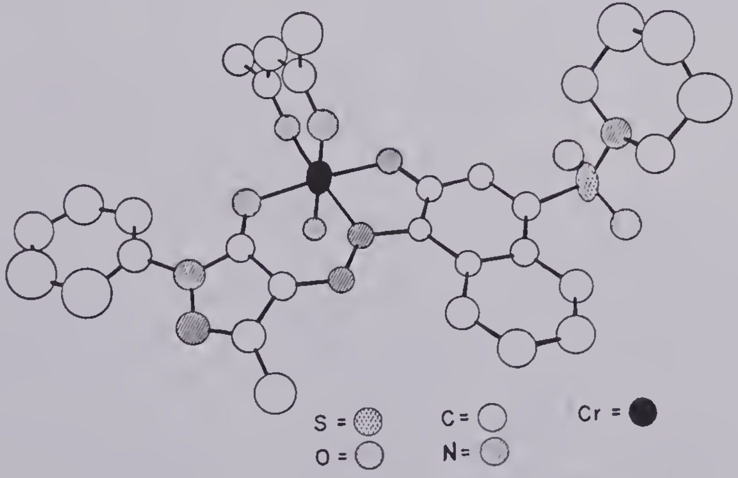
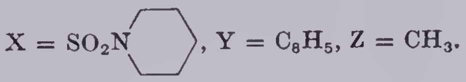


Fig. 15. X-Ray analysis of compound XCII.



$X = SO_2N$, $Y = C_8H_5$, $Z = CH_3$.

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[75] E. M. Idelson and Polaroid Corp., *USP* 3,629,336.

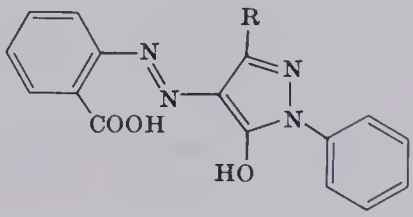
[76] E. M. Idelson and Polaroid Corp., *USP* 3,551,406; 3,563,739.

[77] Molecular Structures Corp., P.O. Box DF, College Station, Texas.

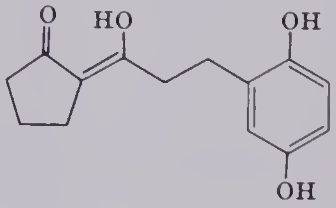
[78] G. Schetty and F. Beffa, *Helv. Chim. Acta* 50, 15 (1967); G. Schetty and W. Kuster, *ibid.* 46, 2193 (1961); R. Grieb and A. Niggli. *ibid.* 48, 317 (1965).

form, and the chromium is coordinated to the nitrogen atom attached to the naphthalene ring. This finding disproves an earlier conclusion.[79]

Similar mixed complexes can be prepared from other dyes capable of forming 1:1 complexes with Cr(III). Yellow dye developers, for example, may be synthesized from *o*-carboxy-*o′*-hydroxyazo dyes (XCIV) and the ligand-developer (XCV).[14]

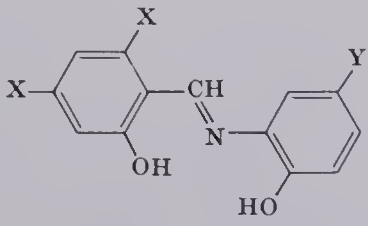


(XCIV)



(XCV)

The 1:1 chrome complexes of *o,o′*-dihydroxyazomethines, a dye class formally analogous to the azo dyes, are also capable of forming stable mixed complexes with colorless ligands such as β-diketones.[80] Although their extinction coefficients are lower than those of azo complexes, useful yellow chromophores may be obtained from (XCVI). Dyes in which X = alkoxy and Y = NO_2 possess satisfactory tinctorial strength with good color and light and chemical stability.[81] Dye developers are formed by coordination of compounds represented by (XCVI) with Cr(III) and the ligand developer (XCV).[14] Another method of attaching the developer is through the ether linkages at X, instead of on the ligand, as in (XCVII).[14]



(XCVI)

Combining these methods, it is possible to prepare a wide variety of dye developers. For example, by coordinating dye (XCVII) and ligand developer (XCV) with Cr(III), a dye developer bearing two developers is obtained.[14] In contrast with the unsatisfactory magenta dyes from 2:1 complexes of *o,o′*-dihydroxyazo dyes, 2:1 complexes of *o*-carboxy-*o′*-

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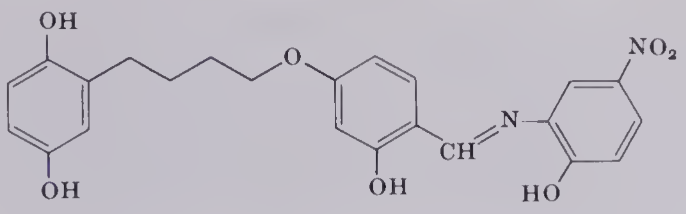
[79] E. M. Idelson and I. Karady, *J. Am. Chem. Soc.* 88, 186 (1966); R. Price in *CSD III*, p. 331.

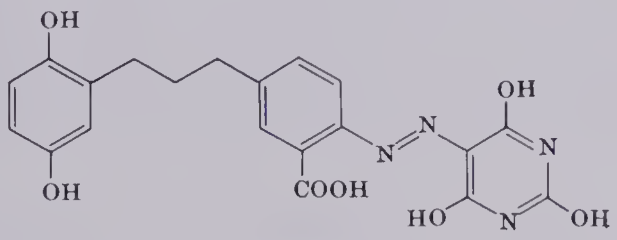
[80] E. M. Idelson and Polaroid Corp., *USP* 3,752,836.

[81] A. B. Goulston, P. S. Huyffer, and Polaroid Corp., *USP* 3,705,184.



(XCVII)

hydroxyazo dyes or of *o,o′*-dihydroxyazomethine dyes (XCVI) produce yellow dyes with satisfactory color and better stability toward light than the 1:1 mixed complexes.[14] The dye developer (XCVIII) reacts with the 1:1 complex of XCVI or *vice versa* to form a mixed 2:1 complex with one developer group.[14] Compound (XCVIII) can also form a symmetrical 2:1 complex with two developer groups.[14] Alternatively, reaction of the 1:1 complexes of (XCVII) or (XCVIII) with simple colorless ligands like acac or salicylaldehyde produces 1:1 mixed complexes having the developer moiety on the dye ligand.[14]

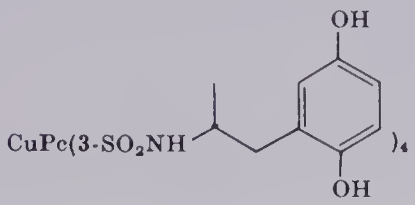


(XCVIII)

B. Phthalocyanine Dye Developers

The metal phthalocyanines, especially copper phthalocyanine, are among the finest and most light-stable cyan dyes known, and they are frequently used in four-color printing inks. They display high transmission in the blue and green regions of the visible spectrum and absorb strongly in the red region (Fig. 4).

Two routes were used for attaching developer groups to metal phthalocyanines. In one, copper phthalocyanine is chlorosulfonated to the tetrasulfonyl chloride. Reaction with the aminoalkylhydroquinone



(XCIX)

dimethyl ether and demethylation with boron tribromide gives the dye developer (XCIX).[82]

The second method starts with suitably substituted phthalic acids or their derivatives, which are converted to the corresponding phthalocyanines. Thus, 4-sulfophthalic acid ultimately leads to the 4-isomer of (XCIX).[82]

V. Miscellaneous Chromophores

The ability to select the chromophore from virtually any dye class may be demonstrated by describing a few of the other systems studied. Rhodamine dyes are noted for their brilliant magenta colors (Fig. 16). Chart XIX outlines the preparation from 3,6-dichlorofluoran (C) of rhodamines containing aryl- or alkyl-linked developers blocked with methyl ether groups.[14] Boron tribromide removes the blocking groups.

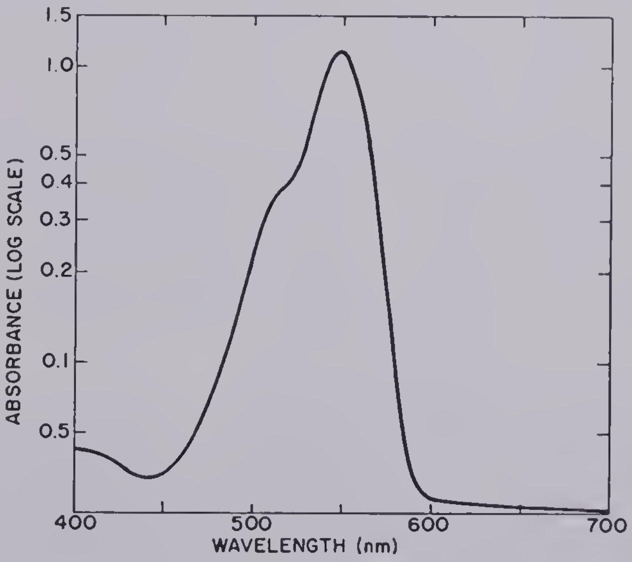


FIG. 16. Absorption spectrum of rhodamine.

Azamethines, such as (CI) from naphthostyril, are yellow[83] dyes with a sharp cut-off on the long-wavelength side of the absorption envelope (Fig. 17). The synthesis of dye developer (CII) is shown in Chart XX.[14]

Although cyanine dyes may not possess all the necessary requirements for use as image dyes, some have been converted into dye developers, e.g., (CIII).[84]

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[82] E. M. Idelson and Polaroid Corp., *USP* 3,857,855.

[83] A. Brack, H. Gleinig, R. Raue, H. Kleiner, and FBy, *USP* 3,287,465.

[84] D. D. Chapman, L. G. S. Brooker, and EK Co., *USP* 3,649,266; D. D. Chapman and EK Co., *USP* 3,653,897.

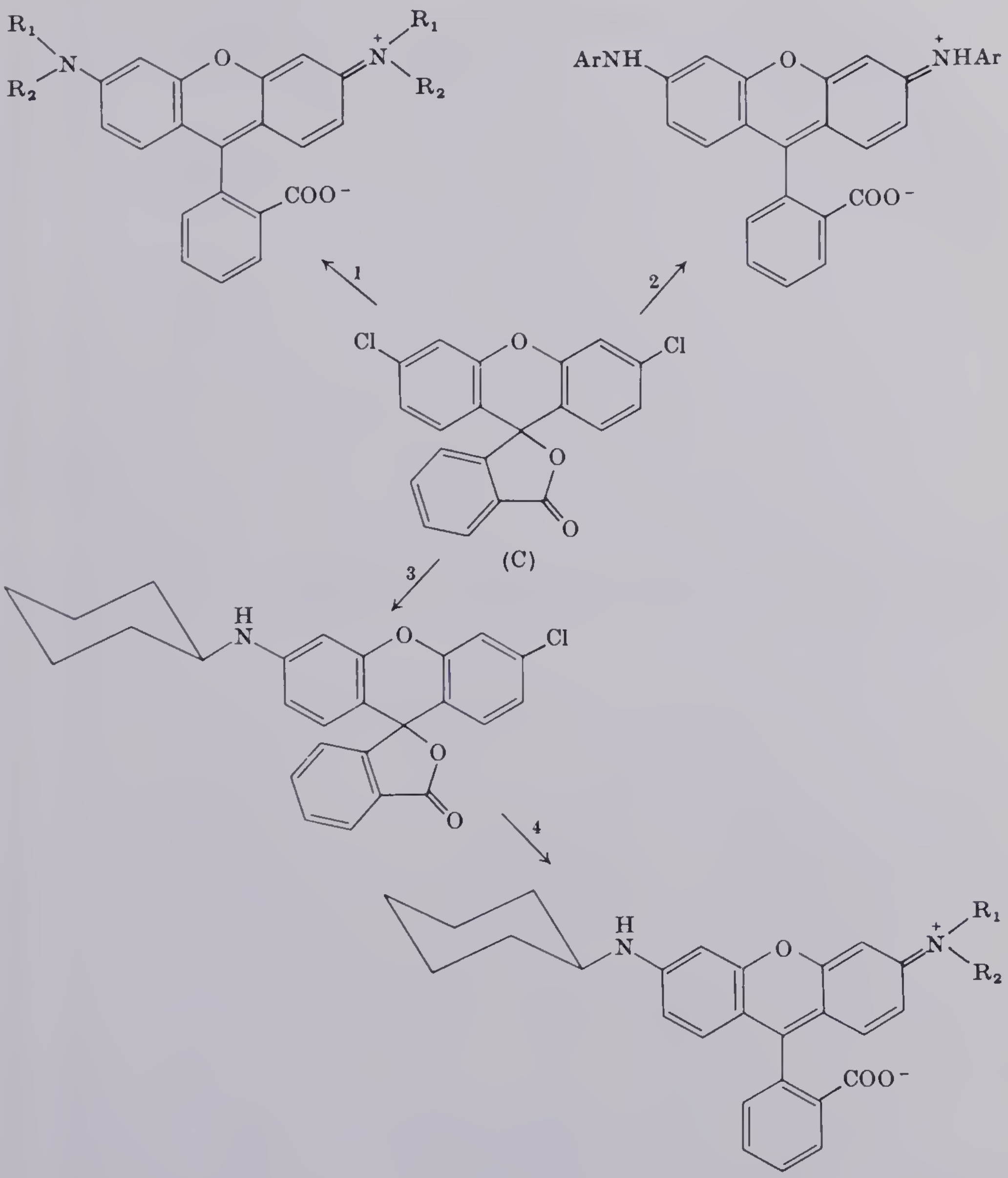
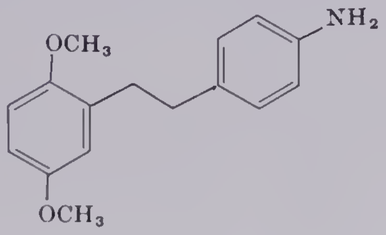
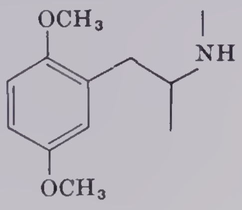


CHART XIX. (1) R_1R_2NH; (2) $ArNH_2$; (3) cyclohexylamine; (4) R_1R_2NH.

$ArNH_2$ =



R_1R_2NH =



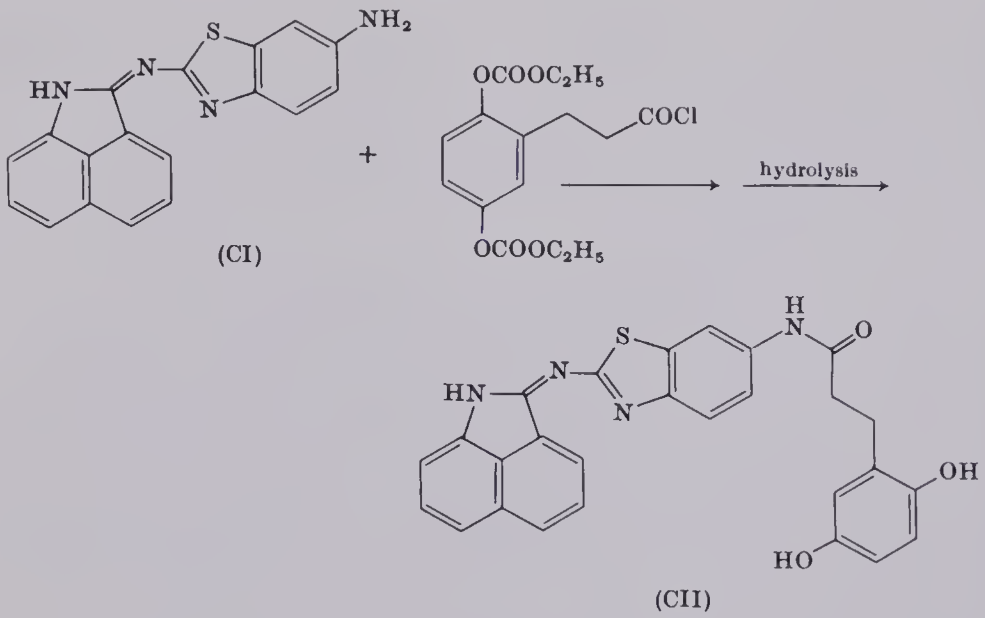


Chart XX

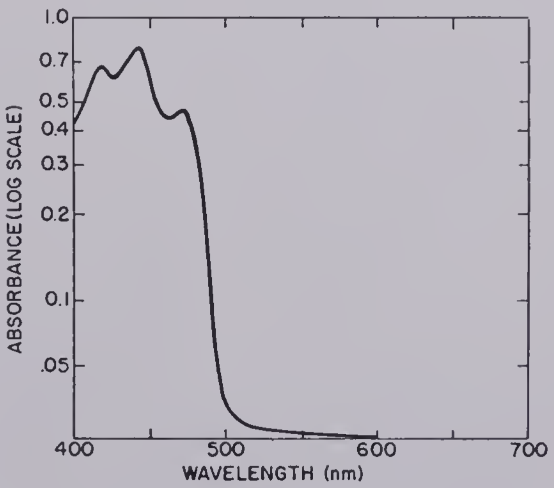
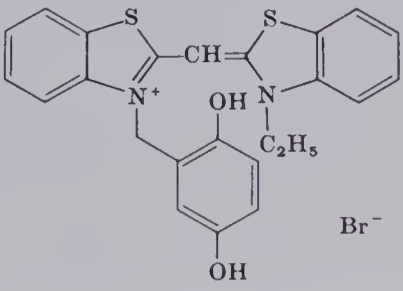
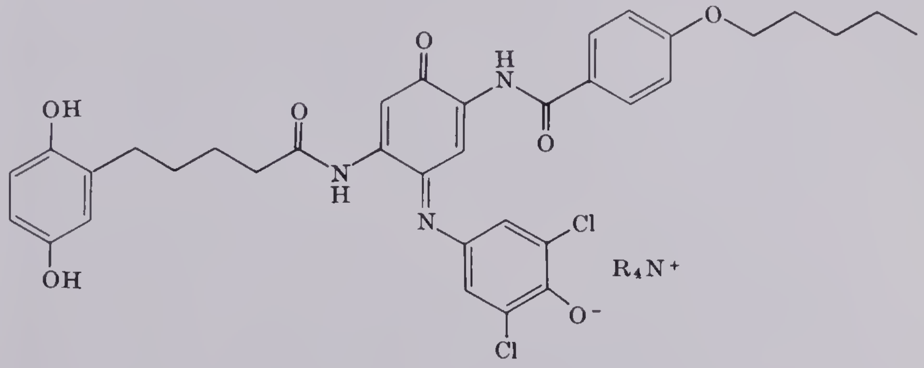


Fig. 17. Absorption spectrum of compound CI.



(CIII)

Indophenol dyes have been converted into dye developers (e.g., CIV). The use of quarternary mordants keeps the dyes of the image in the phenoxide form.[85]



(CIV)

Cyan dyes may be prepared from naphthazarin[86] (Fig. 18). The corresponding dye developers were made from leuconaphthazarin and aminoalkyl developers.[14]

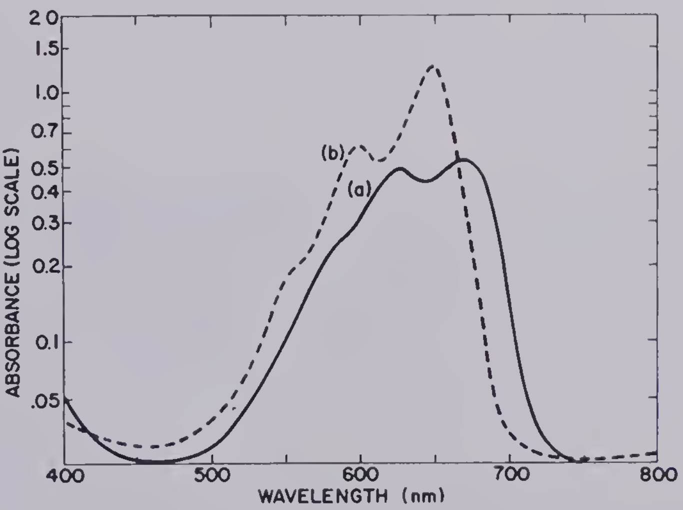


Fig. 18. Absorption spectrum of (a) 1,4-bismethylamino-5,8-naphthoquinone and (b) 1,4-bisisopropylamino-5,8-naphthoquinone (ethanol).

The naphthazarin dye developer (CV) can be prepared by the addition of the appropriate amine to 4,8-di-*p*-phenetidino-1,5-naphthoquinone.[87]

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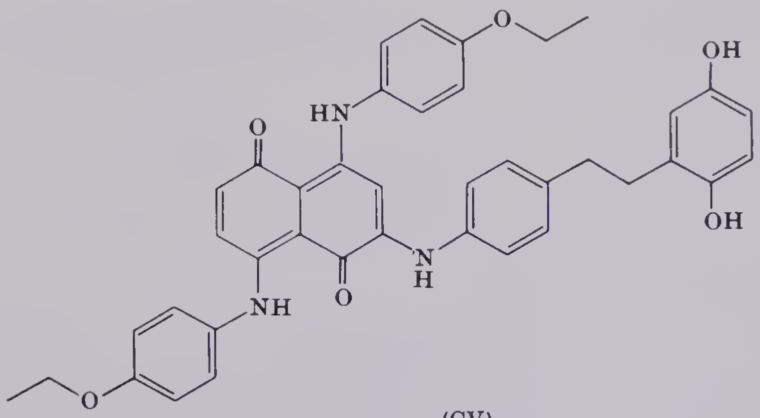
[85] G. J. Lestina, W. M. Bush, and EK Co., *USP* 3,854,945.

[86] S. M. Bloom and G. O. Dudek, *Tetrahedron* **26**, 1267 (1970); P. Nawiasky, A. Krause, and IG, *USP* 1,759,273.

[87] S. M. Bloom and Polaroid Corp., *USP* 3,666,469.



(CV)

VI. Color-Shifted Dye Developers

In the usual film unit, dye developers are placed beneath the emulsions sensitized to the complementary color of the dye (Fig. 1). If a dye developer is incorporated within its silver halide layer, a desirable location for photographic image making, it will absorb light to which the silver halide is sensitive. The sensitivity of the film is reduced because less actinic radiation strikes the silver halide grains.[2] Temporarily shifting the color of the dye developer to shorter wavelengths overcomes this problem.

A number of techniques may be used to shift the color of dyes. The yellow dye developer (CVI) reacts with trifluoroacetic anhydride to produce the bistrifluoroacetate lactone (CVII) (Chart XXI). Methanolysis removes the trifluoroacetyl groups to form the now-colorless "dye" developer (CVIII)[88] (Fig. 19). During photographic processing, the

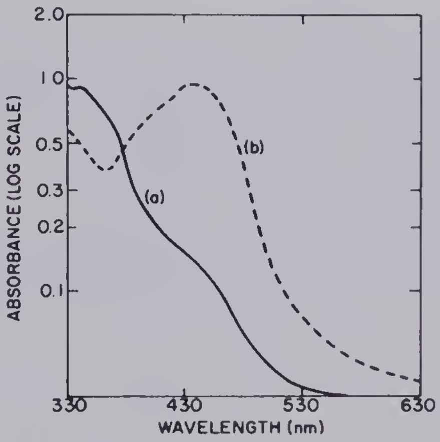


Fig. 19. Absorption spectra of (a) compound (CVIII) and (b) compound CVI.

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[88] S. Dershowitz, R. B. Woodward, and Polaroid Corp., *USP* 3,230,085; 3,329,670.

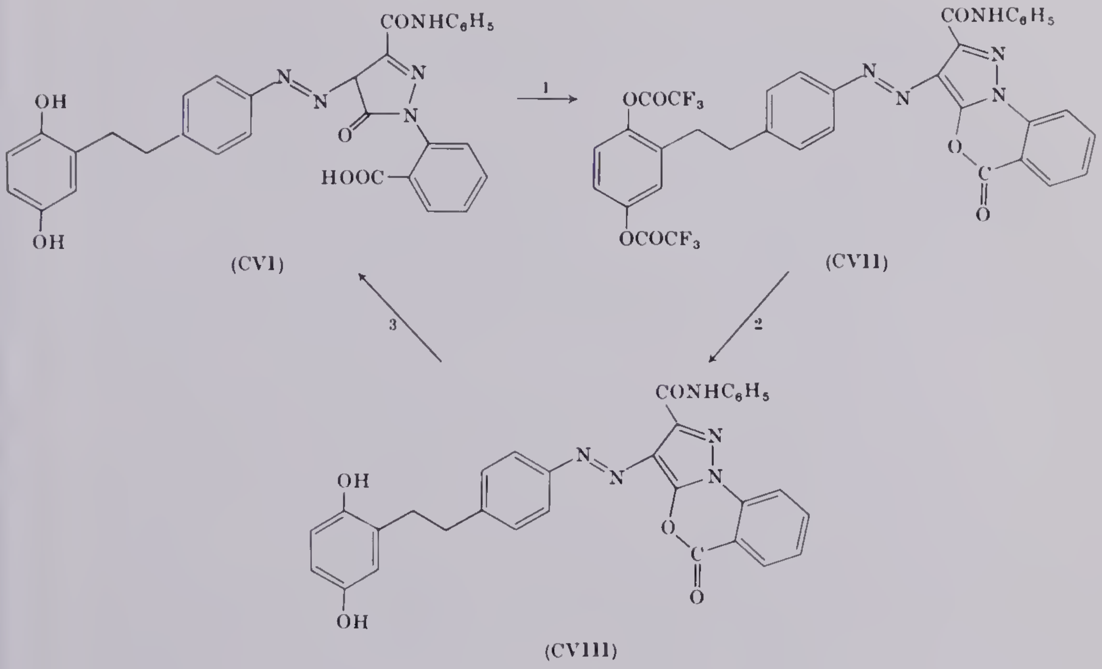

CHART XXI. (1) Trifluoroacetic anhydride; (2) methanol; (3) alkali (photographic processing).

alkaline reagent hydrolyzes the lactone to regenerate the yellow dye developer.

The magenta dye developer (CIX) was converted to the weakly absorbing yellow dye developer (CX) as outlined in Chart XXII.[89] In order to selectively acylate the naphthol, the hydroquinone group is first oxidized to the quinone.[90] After acylation, catalytic hydrogenation regenerates the hydroquinone.

More recently, a disazo dye developer was color-shifted in the same manner.[91] In addition to isopropenyl acetate, acyl chlorides were also successful acylating agents,[92] and hydrazobenzene was a particularly good reagent for the reduction step.[93]

Acylation of α-amino groups in anthraquinone dye developers likewise shifts the absorption maxima to lower wavelengths.[94] Thus 1,4-bisalkylaminoanthraquinone cyans may be converted to magentas by monoacylation or to orange-yellows by bisacylation. Use of readily

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[89] E. M. Idelson and Polaroid Corp., *USP* 3,086,005; E. M. Idelson, H. G. Rogers, and Polaroid Corp., *USP* 3,307,947; 3,336,287.

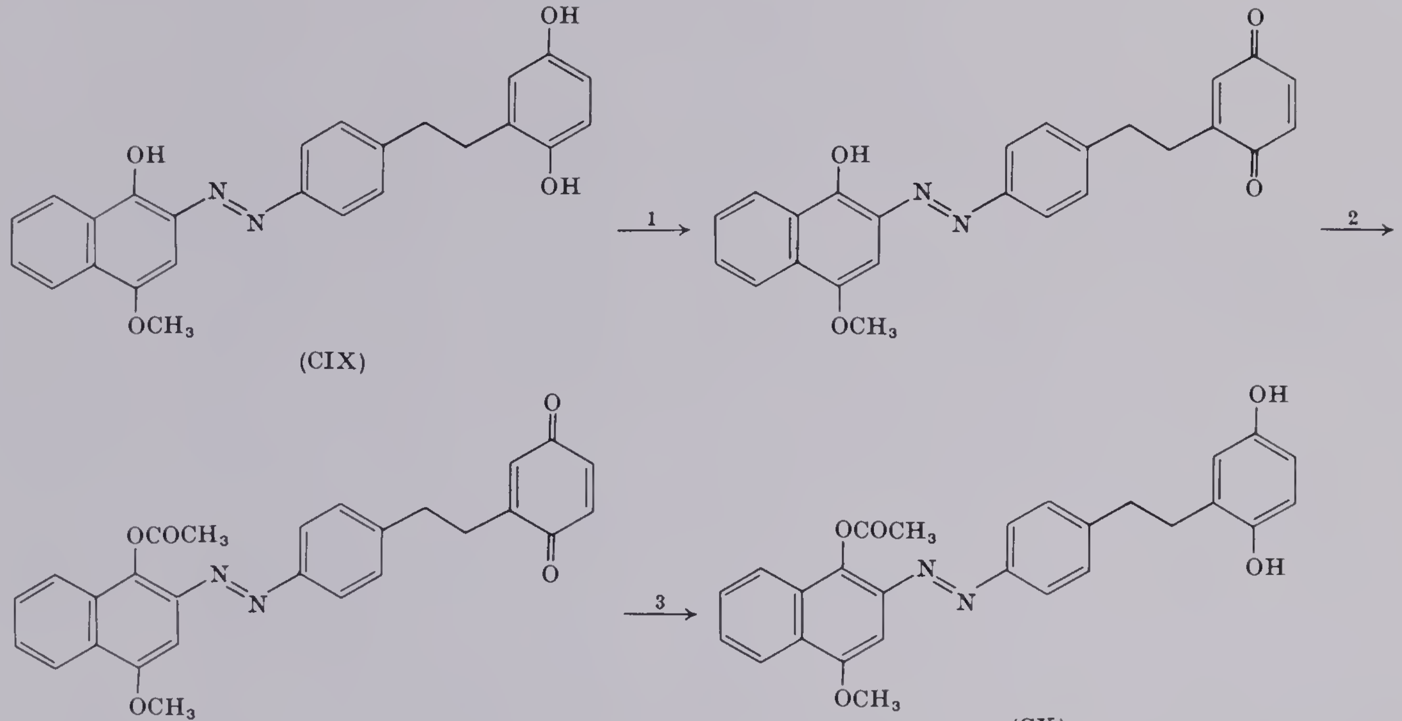
[90] R. S. Corley and Polaroid Corp., *USP* 3,116,279.

[91] Y. Maekawa, S. Sakonoue, and Fuji Phot Film, *DOS* 25 05 284.

[92] R. F. W. Cieciuch, M. S. Simon, and Polaroid Corp., *USP* 3,579,334; 3,826,801.

[93] A. E. Anderson, K. K. Lum, and EK Co., *USP* 3,725,062.

[94] R. S. Corley and Polaroid Corp., *USP* 2,983,605.



(CIX)

(CX)

Chart XXII. (1) Mercuric acetate; (2) isopropenyl acetate; (3) catalytic hydrogenation.

hydrolyzable acyl groups, such as the trifluoroacetyl groups, produces a temporary shift of color that may be reversed by the alkaline photographic processing medium.[95] Leuco forms of dye developers may also be used.[43]

Acylation of the hydroxyl groups on the hydroquinone provides a dye–"developer" whose developing activity is temporarily masked.[96]

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[95] E. H. Land, H. G. Rogers, and Polaroid Corp., USP 3,230,082.

[96] M. S. Simon and Polaroid Corp., *USP* 3,230,083; M. S. Simon, S. H. Mervis, and Polaroid Corp., *USP* 3,230,084.

Chapter IX

SYNTHETIC CAROTENOIDS AS COLORANTS FOR FOOD AND FEED

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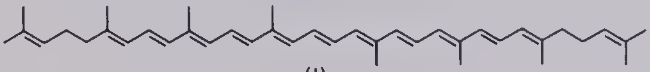
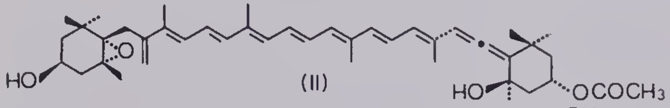
I. Introduction

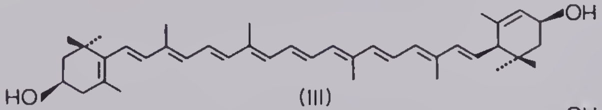
The term "carotenoid" refers to a class of compounds composed of eight isoprene units linked in such a manner that the two methyl groups nearest the center of the molecule are separated by six carbon atoms and all the other methyl groups by five carbon atoms. A series of conjugated C—C double bonds constitutes the chromophoric system. This is illustrated by the structural formula of the tomato pigment lycopene (I), from which almost all other carotenoids can be formally derived by hydrogenation, dehydrogenation, cyclization, oxidation, or any combination of these processes.

Carotenoid pigments are extremely abundant in the vegetable and animal kingdoms. In plants, their presence is often masked by chlorophyll. It has been estimated that nature produces over 100 million tons of carotenoid pigments per year. Most of this output is in the form of four major carotenoids—fucoxanthin (II), the characteristic pigment of many marine algae and without question the most abundant natural carotenoid, and the three main pigments in green leaves, lutein (III), violaxanthin (IV), and neoxanthin (V). By comparison, all other carotenoids, the structures of about 400 of which are known, are produced in quite small amounts, though some, like β-carotene (VII) zeaxanthin (VIII) occur widely.

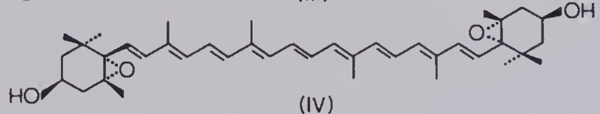

(I)



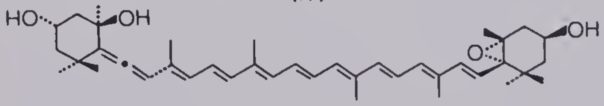
(II)



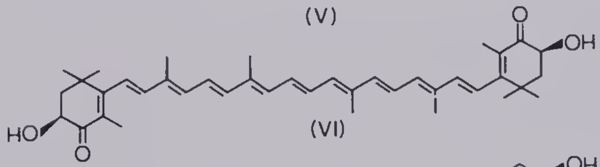
(III)



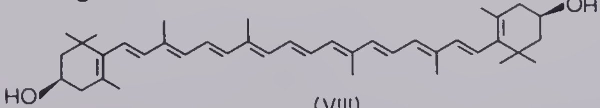
(IV)



(V)



(VI)



(VIII)

The carotenoids are responsible for many brilliant yellow and red colors in fruits, vegetables, roots, flowers, and autumn leaves; they produce the colors of egg yolk, of many algae, of mushrooms, of crustaceans, of feathers and skins of birds, and of fish.

The vital role of colors in plants and animals as attractants or deterrents is obvious. Less obvious but equally important are other physiological functions; carotenoids may act as photoprotective agents by absorbing the potentially harmful light energy or by quenching singlet oxygen. Carotenoids may also function as accessory pigments in photosynthesis as sensitizer and oxygen transporters. Some carotenoids possess vitamin A activity. As a matter of fact, β-carotene is the most important source of vitamin A for man.

Bacteria, the algae, and the higher plants possess the ability to produce carotenoids. The animals depend for their carotenoids on those present in the diet. However, subsequent transformation of carotenoids from the diet may lead to characteristic animal pigments, e.g., astaxanthin (VI), not normally found in plants.

From a practical point of view many carotenoids are responsible for color in plants, animals, or animal products used as human food. For instance in fruit juices; in broilers; in fish like salmon and trout; in dairy products such as milk, butter, and cheese; and in egg yolk. Since man has been familiar with the visual appearance of these products for thousands of years, their expected characteristic color is considered as a sign of quality.

In these days of growing populations, one relies more and more on fast and economic mass productions of food. As a result, however, the natural pigments and vitamins are often not present or only in small amounts. To produce not only quantity but also a high standard in quality, food lacking pigments and vitamins has to be supplemented. This may be achieved by direct addition of the lacking substance to the finished product, as it is done for fruit juices, soft drinks, margarine, dairy products, or by an indirect method, i.e., addition of a pigment to the feed. Of course, natural sources alone would never fill the need. Although carotenoid-containing natural products, such as extracts of annatto, carrots, palm oil, tomato, and saffron, have been used for generations, they are being more and more replaced by the crystalline carotenoids produced by chemical synthesis. The advantage of their high purity and uniformity is obvious. For a survey of the use of carotenoids, see Bauernfeind *et al.*[1]

Structural elucidation and total syntheses of these relatively complicated molecules have been challenging problems for many organic chemists. Most noted among them are the research groups around Karrer, Kuhn, Heilbron, Zechmeister, Milas, Inhoffen, Isler, Weedon, and Liaaen-Jensen. An excellent review of the art of carotenoid synthesis is given in Mayer and Isler.[2] The outstanding results often achieved without the help of modern spectroscopic and analytical tools found their culmination in economic technical syntheses of vitamin A and several carotenoids.

The purpose of this chapter is to review all the technical processes currently employed for the synthesis of carotenoids. This will necessarily include a description of the technical vitamin A syntheses, since

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[1] J. C. Bauernfeind, G. B. Brubacher, H. M. Kläui, and W. L. Marusich, *in* "Carotenoids" (O. Isler, ed.), p. 743. Birkhaeuser, Basel, 1971.

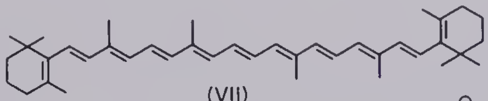
[2] H. Mayer and O. Isler, *in* "Carotenoids" (O. Isler, ed.), p. 325, Birkhaeuser, Basel, 1971.

most of the carotenoid syntheses use vitamin A as an intermediate. In this discussion, special attention will be given to a critical evaluation of the various key condensation reactions, emphasizing thereby industrial requirements and conditions. At the end, some promising new developments in this area of chemistry will be mentioned briefly.

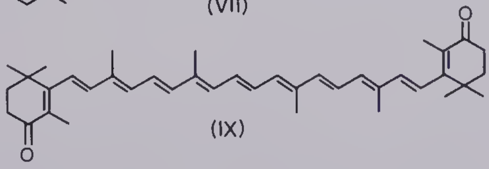
II. Discussion of Synthetic Methods

Of the more than three hundred naturally occurring carotenoids, only the following five are at present produced on an industrial scale: β-carotene (VII), canthaxanthin (IX), ethyl β-apo-8′-carotenoate (X), β-apo-8′-carotenal (XI), and citranaxanthin (XII). The annual production of all these compounds is well below 500 tons. Of the structurally closely related vitamin A acetate (XIII), however, the production reaches several thousand tons per year. The carotenoids (VII, IX–XI) are being manufactured by Hoffmann-La Roche, (VII) and (XII) by BASF. For vitamin A we have several producers.

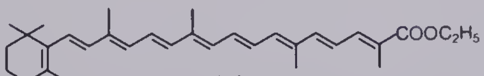
A comparison of the structures of these compounds shows that they differ only with respect to one end group. The exception, canthaxanthin (IX), is not obtained by an independent total synthesis, but by oxidation of (VII). One would therefore expect the various commercial



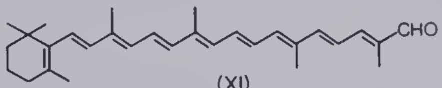
(VII)



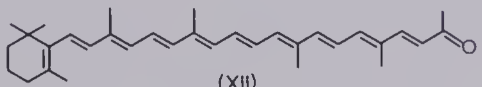
(IX)



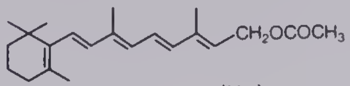
(X)



(XI)



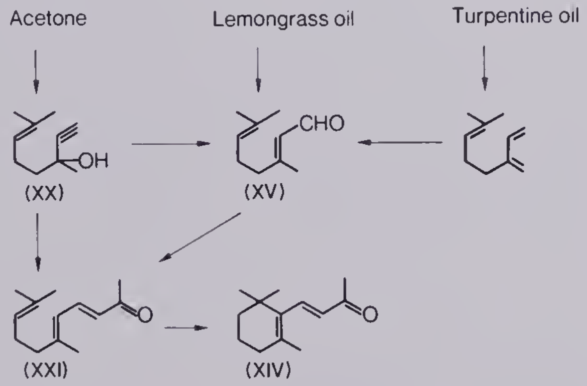
(XII)



(XIII)

syntheses to be rather similar with regard to intermediate compounds. And indeed, in all industrial carotenoid and vitamin A syntheses the first key intermediate is β-ionone (XIV).

Until recently, β-ionone (XIV) was synthesized from citral (XV), which in turn had to be obtained from natural sources such as lemongrass oil or turpentine oil. Today, most of (XIV) is manufactured from acetone.



Several processes have been developed for the synthesis of (XIV). Addition of sodium acetylide in liquid ammonia to acetone gives methylbutynol (XVI).[3,4] Partial hydrogenation over Lindlar catalyst gives methylbutenol (XVII), which is reacted with diketene to form the corresponding acetoacetate (XVIII). Thermal rearrangement will then yield methylheptenone (XIX).[3,4] Alternatively, heating (XVII) with ethyl acetoacetate[5] at 170°–190° or acid-catalyzed reaction of (XVII) with isopropenyl methyl ether[6] (Saucy–Marbet reaction 3) will furnish (XIX). From (XIX), dehydrolinalool (XX) is obtained by addition of sodium acetylide.[3] This important intermediate is then transformed into pseudoionone (XXI) by three different routes. As before, treatment with diketene leads to the acetoacetate (XXII), which can be pyrolyzed to (XXI)[3,4]; acid-catalyzed reaction of (XX) with isopropenyl methyl ether furnishes XXI.[7] Finally, rearrangement of dehydrolinalyl acetate in the presence of silver catalyst (Saucy–Marbet reaction 1)* and subsequent hydrolysis gives citral (XV); base-catalyzed condensation of

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* Saucy–Marbet reactions 1,[6,6a] 2,[7] 3.[6]

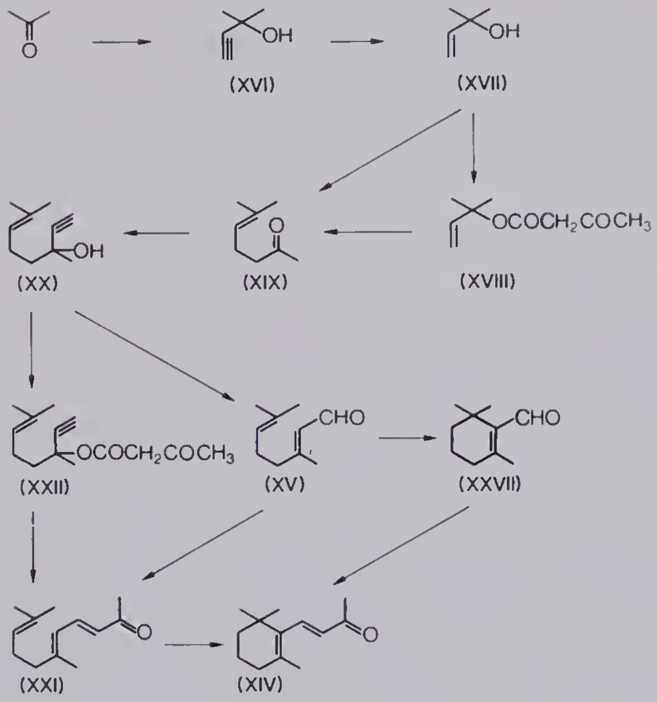
[3] W. Kimel, J. D. Surmatis, J. Weber, G. O. Chase, N. W. Sax, and A. Ofner, *J. Org. Chem.* **22**, 1611 (1957).

[4] W. Kimel, N. W. Sax, S. Kaiser, G. G. Eichmann, G. O. Chase, and A. Ofner, *J. Org. Chem.* **23**, 153 (1958).

[5] BASF, *BP* 848,931 (1960).

[6] G. Saucy and R. Marbet, *Helv. Chim. Acta* **50**, 2091 (1967).

[7] G. Saucy and R. Marbet, *Helv. Chim. Acta* **50**, 1158 (1967).



(XV) with acetone gives (XXI).[8,9] Under controlled acidic conditions, (XXI) is then cyclized to (XIV).[10–12]

In nature, the biosynthesis of carotenoids follows the usual pattern of a terpenoid synthesis. Three units of acetyl-CoA ($3 \times C_2$) will give mevalonic acid (C_6), which is decarboxylated to the isoprenoid building block isopentenyl pyrophosphate (C_5). Dimerization leads to geranyl pyrophosphate (C_{10}), trimerization to farnesyl pyrophosphate (C_{15}), tetramerization then to geranylgeranyl pyrophosphate (C_{20}). Dimerization of the C_{20} unit and dehydration finally yields a carotenoid (C_{40}).

$$\begin{tikzcd}
3\times C_2 \arrow[r] & C_6 \arrow[r, "-C_1"] & C_5 \arrow[r, "+C_5"] & C_{10} \arrow[d, "+C_5"] \\
& C_{40} & C_{20} \arrow[l, "+C_{20}"'] & C_{15} \arrow[l, "+C_5"']
\end{tikzcd}$$

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[8] G. Saucy, R. Marbet, H. Lindlar, and O. Isler, *Helv. Chim. Acta* **42**, 1945 (1959).

[8a] H. Schlossarczyk, W. Sieber, M. Hesse, H. J. Hansen, and H. Schmid, *Helv. Chim. Acta* **56**, 875 (1973).

[9] A. Russel and R. L. Kenyon, *Org. Synth. Collect. Vol.* **3**, 747 (1955).

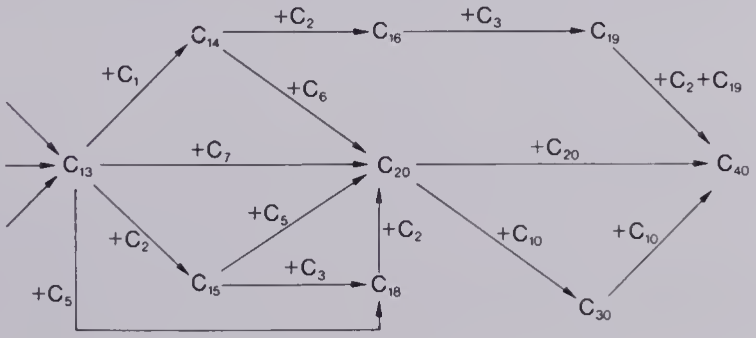
[10] H. J. V. Krishna and B. N. Joshi, *J. Org. Chem.* **22**, 224 (1957).

[11] F. Hoffmann-La Roche & Co. Ltd., *BP* 803,765 (1958).

[12] Glaxo Laboratories, Ltd., *BP* 833,088 (1960).

In other words, twenty-four acetyl groups (forty-eight carbon atoms) will be converted to one carotenoid molecule. Not regarding enzymes and various cofactors also involved in the biosynthesis, nature makes use essentially of only one starting material (C_2 unit) and one type of intermediate reagent (C_5 unit). For a review of the biosynthesis of carotenoids, see Goodwin.[13]

In contrast to nature, syntheses of carotenoids *in vitro* are not as restricted in their selection of intermediates and chemical routes. This was already demonstrated by the synthesis of (XIV). The construction of the carotenoid molecule from (XIV) is now being effected in a great variety of ways. In addition, the various two- and three-carbon reagents employed differ from process to process. One common intermediate is the C_{20} compound vitamin A alcohol (XXIII). The synthesis of β-carotene of Hoffmann-La Roche by-passes (XXIII).



In devising a synthesis of a carotenoid from (XIV), one should keep in mind that in building up the polyunsaturated molecule from (XIV), the addition of smaller molecular subunits should preferably occur in such a way that carbon–carbon bond formation is immediately followed by introduction of a double bond. Each intermediate will then already possess its required unsaturation. Specific introduction of double bonds later in the synthesis could give rise to complications and consequently to lower yields. The number of reactions suitable for this purpose is limited, and only a few selected ones have found extensive use in carotenoid synthesis.

Using common characteristic mechanistic features, these reactions may be classified into three major types.[14] In all three reaction types, one substrate is a carbonyl compound such as an aldehyde or a ketone. In type 1, the carbonyl compound is treated with a reagent, which, due

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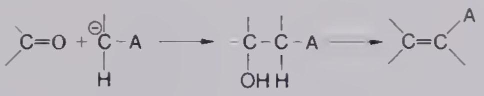
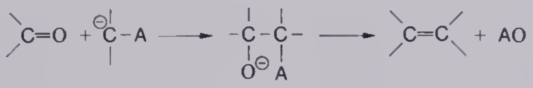
[13] T. W. Goodwin, *in* "Carotenoids" (O. Isler, ed.), p. 577. Birkhaeuser, Basel, 1971.

[14] F. Kienzle, *Pure Appl. Chem.* **47**, 183 (1976).



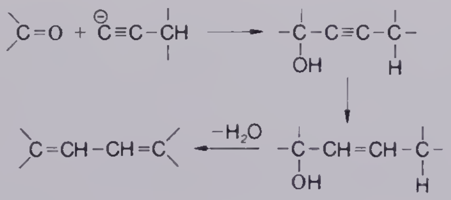
to the presence of an activating group, possesses an acidic proton. An intermediate hydroxy compound is not stable but loses water to give an olefin. The activating group of the reagent is retained. Included in this reaction type is the aldol condensation, the Knoevenagel condensation, the Reformatsky reaction, and the enol–ether condensation. The last reaction does proceed initially with a different mechanism, but the intermediate is of a similar type, and so its inclusion in type 1 may be justified.

In the second major reaction type, olefination occurs with loss of the activating group. Here we find the reactions of carbonyl compounds



with phosphoranes (Wittig olefination), with phosphates (Horner olefination), and with isonitriles (Schöllkopf olefination).

In the third reaction type, a carbonyl compound is condensed with an alkali metal or magnesium acetylide. The intermediate acetylenic carbinol is partially hydrogenated before water is split off to give the olefin.



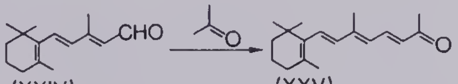
A general observation one can make of all these reactions is that olefin formation is not stereospecific. Usually, mixtures of cis and trans olefins are obtained, although one isomer may predominate. Furthermore, none of these reactions is applicable in all cases. The selection of one or another reaction depends on a careful weighing of the particular advantages. Economic criteria, such as availability of starting material, yields in reaction steps, amounts of side-products that cannot be recycled, simplicity of reaction conditions, number of steps (overall yield), as well as energy requirements, will influence the final choice for a synthesis.

In the following, we shall list the advantages and disadvantages of the various reactions enumerated above together with examples where these reactions are in actual use in industrial carotenoid and vitamin A syntheses.

A. Aldol Condensation[15]

The acid- or base-catalyzed self-condensation or mixed condensation of aldehydes and ketones leads initially to β-hydroxyaldehydes or ketones. An α,β-unsaturated carbonyl compound is the result of dehydration. The reaction is economically very attractive, because the auxillary chemicals, such as alkali hydroxides, that are needed are very cheap. Unfortunately, numerous side reactions have limited wider application. The higher reactivity of aldehydes over ketones very often gives rise to self-condensation rather than mixed condensation when both are brought together. There is, furthermore, the possibility of reaction of the substrates with the product such as a Michael-type addition to the α,β-unsaturated compound or even polymer formation. Products of a Cannizzaro reaction (disproportionation of aldehyde to the corresponding acid and alcohol through hydride transfer) are also often found. And finally, since the first reaction step is reversible, high yields are often not achieved. However, in mixed condensations when acetone is one of the substrates, yields may be very high. A modification of the aldol condensation that uses as one substrate a Schiff base may be advantageous for mixed condensations.[16]

In industrial processes, the aldol condensation is being used by Philips–Duphar[17] and by A. E. C. Société de Chimie Organique et Biologique[18] for the conversion of (XXIV) to (XXV). The synthesis of citranaxanthin (XII) from (XI) is being effected in a similar way (BASF)[31]. Interestingly, each time, it is a mixed condensation with acetone as one reaction partner.



(XXIV) (XXV)

B. Knoevenagel Condensation[19]

The base-catalyzed condensation of an aldehyde or ketone with a compound having an activated methylene group will give after dehydration, depending on the activating group, an α,β-unsaturated ester, nitrile, or nitro compound. The reaction is equally well applicable to aldehydes or ketones. The usually mild experimental conditions and the

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[15] A. T. Nielson and W. J. Houlihan, *Org. React.* **16**, 1 (1968).

[16] H. Reiff, *Neuere Methoden Pre. Org. Chem.* **6**, 42 (1970).

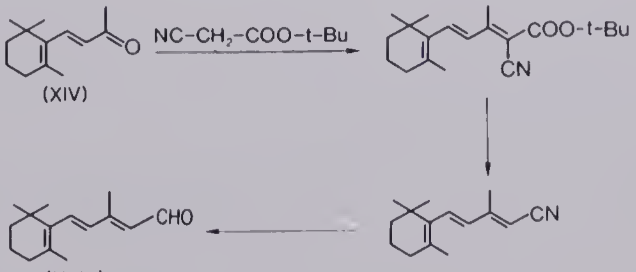
[17] J. G. J. Kok and R. van Morselaar, *Chem. Weekbl.* p. 48 (1973).

[18] A. E. C. Société de Chimie Organique et Biologique, *USP* 3,145,233 (1964); *FP* 1,243,824 (1960).

[19] G. Jones, *Org. React.* **15**, 204 (1967).

high yields would make this condensation quite attractive for polyene synthesis. However, it is primarily a route to α,β-unsaturated acids, esters, or nitriles. Furthermore, the chain extension is usually limited to two carbon atoms. We have already seen that in all the common chain extension reactions, one substrate should be an aldehyde or ketone. For the continuation of a synthesis, it would be desirable to have intermediates with such a functional group. The products of a Knoevenagel condensation must therefore be reduced. On a laboratory scale, this is achieved with a straightforward hydride reduction. For an industrial synthesis, however, the relatively expensive hydride reagents are not too attractive. The most preferred reagent for that purpose is diisobutylaluminum hydride (Dibal).

It is therefore not surprising that in the only industrial application of this reaction (Philips–Duphar),[17] the conversion of (XIV) into (XXIV) has apparently been discarded in favor of another route.[20]



(XIV)

(XXIV)

C. Reformatsky Reaction[21,22]

The reaction of aldehydes and ketones with an α-haloester in the presence of zinc is another valuable procedure for the synthesis of α,β-unsaturated acids and esters. As mentioned for the Knoevenagel condensation, the expensive hydride reduction of these products limits the application of this reaction. Furthermore, side reactions such as coupling of reagent ester or addition of the zinc compound to the ester carbonyl, enolizations, and aldolizations may result in a decreased yield. A replacement of Zn by other metals like Mg or Li might be possible in special cases.[22]

Although this reaction has been tested thoroughly for industrial application[23,24] in polyene synthesis, there seems to be only one process

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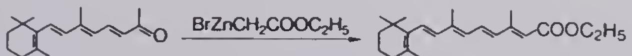
[20] *Chemisch Weekblad* p. 13 (1974).

[21] R. L. Shriner, *Org. React.* **1**, 1 (1942).

[22] M. W. Rathke, *Org. React.* **22**, 423 (1975).

[23] K. Eiter, E. Truscheit, and H. Oediger, *Angew. Chem.* **72**, 948 (1960).

[24] FBy, *DBP* 1,075,598 (1960).

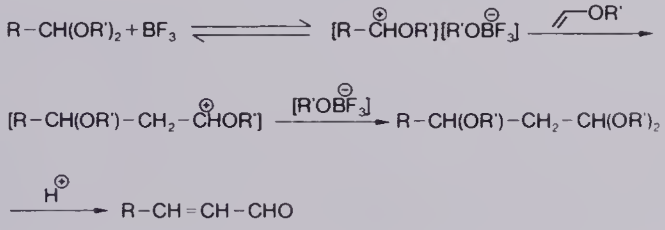


(XXV) (XXVI)

where it is actually employed, namely, for the conversion of (XXV) to the C_{20} ester (XXVI) (Philips–Duphar).[17]

D. Enol–Ether Condensation[25,26]

The condensation of an acetal with an enol in the presence of a Lewis acid will also lead to α,β-unsaturated aldehydes or ketones. The mechanistic path of this condensation is different, however, from the aforementioned reactions.[26]

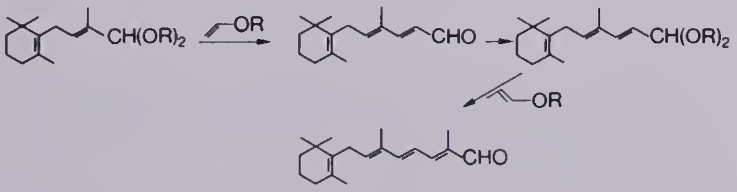


$$\mathrm{R{-}CH(OR')_2 + BF_3} \rightleftharpoons [\mathrm{R{-}\overset{\oplus}{C}HOR'}][\mathrm{R'O\overset{\ominus}{B}F_3}] \xrightarrow{/\!\!/\!-\mathrm{OR'}}$$

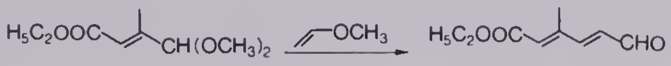
$$[\mathrm{R{-}CH(OR'){-}CH_2{-}\overset{\oplus}{C}HOR'}] \xrightarrow{[\mathrm{R'O\overset{\ominus}{B}F_3}]} \mathrm{R{-}CH(OR'){-}CH_2{-}CH(OR')_2}$$

$$\xrightarrow{\mathrm{H^{\oplus}}} \mathrm{R{-}CH{=}CH{-}CHO}$$

It is a very good and relatively cheap method for a two- or three-carbon extension. Reactions with more carbon atoms containing enol ethers, e.g., methyl isoprenyl ether, give lower yields. A serious side reaction is the further condensation of the intermediate acetal with a second molecule of enol ether, giving rise to polymerlike products. The strongly acidic reaction conditions for the hydrolysis step may also often cause decomposition of products. Nevertheless, a successful industrial example is found in the β-carotene synthesis of Hoffmann—La Roche, where the method is used twice, first for a two-carbon extension and then using propenyl ether for a three-carbon extension.



Another example is found in the preparation of a vitamin A acid intermediate (Roche).



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[25] S. M. Makin, *Russ. Chem. Rev.* (*Engl. Transl.*) **38**, 237 (1969).

[26] R. I. Hoaglin and D. H. Hirsh, *J. Am. Chem. Soc.* **71**, 3468 (1949).

E. Wittig Olefination[27]

The reaction between an aldehyde or ketone and a phosphorane has become in most situations calling for concomitant carbon–carbon bond and double bond formation the first reaction to be tried. High yields and high selectivity with rarely any side reactions are attractive features of this method. However, there are disadvantages that may often tip the balance in favor of some of the other reactions.

Reaction of the bulky phosphorane $[(C_6H_5)_3P{=}CR_1R_2]$ with a carbonyl compound is greatly influenced by steric hindrance. For instance, Wittig olefination with an aldehyde of the type of β-cyclocitral (XXVII), a situation often encountered in carotenoid synthesis, gives only low yields of olefin. Ketones, too, are not easily reacted with a phosphorane; i.e., for the synthesis of tri- and tetrasubstituted olefins, the Wittig olefination may be less suited. Furthermore, although there is no limit to the number of carbon atoms introduced in that way into the molecule (a limitation encountered with the aforementioned methods) there exists a limitation in the structure of the reagent. Phosphoranes with good leaving groups on the β-carbon suffer elimination. The most serious drawback, however, is found with the by-product triphenylphosphine oxide. On an industrial scale, where column chromatography is out of the question, its separation from the product may be quite difficult. In carotenoid synthesis the removal of this by-product is often achieved through trituration of the solid product with 80% aqueous methanol or through extraction of a hexane solution of the product with the same aqueous alcohol. To make the Wittig olefination on a large scale economic, it is furthermore, a necessity to recycle the triphenylphosphine. A number of efficient processes for that purpose are known.[28–31] Unfortunately, none of these is a true catalytic process. They either use stoichiometric amounts of relatively expensive reducing agents or produce large quantities of by-products. Despite these shortcomings, the Wittig olefination is one of the most efficient and economic methods for carbon–carbon double bond formation in carotenoid synthesis. Several examples of industrial exploitation of this method are known.

In the technical BASF synthesis of vitamin A acetate (XIII) the phosphonium salt (XXVIII) is condensed with γ-acetoxytiglinaldehyde.

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[27] A. Maerker, *Org. React.* **14**, 270 (1966).

[28] G. Wunsch, K. Wintersberger, and H. Geierhaas, *Z. Anorg. Allg. Chem.* **369**, 33 (1969).

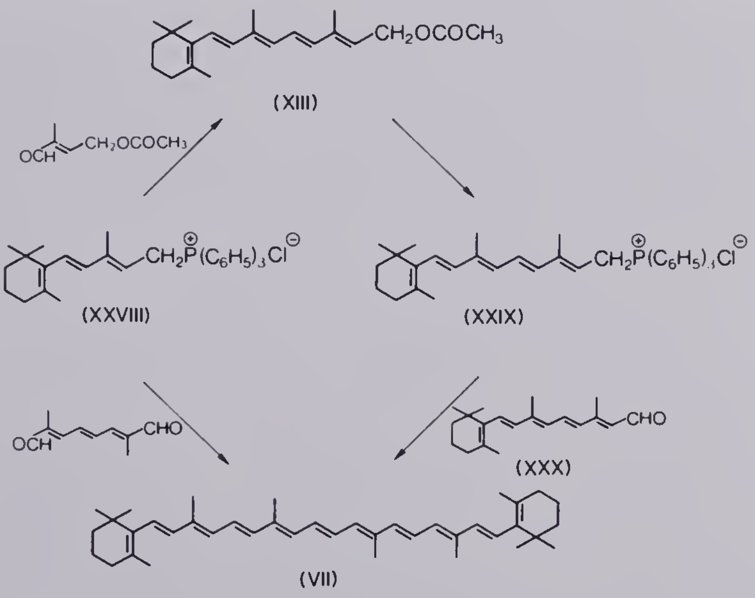
[29] Shell, *USP* 3,261,871 (1966).

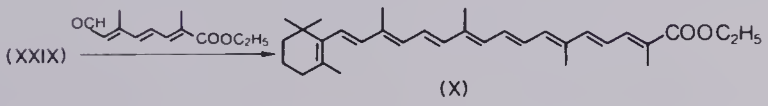
[30] BASF, *DBP* 1,247,310 (1966).

[31] H. Pommer, *Angew. Chem.* **72**, 911 (1966); H. Pommer and A. Nürrenbach, *Pure Appl. Chem.* **43**, 527 (1975).

The same company also produces β-carotene (VII) from (XXVIII) by condensation of 2 moles of (XXVIII) with one mole of a C_{10} dialdehyde.[31] From (XIII), the phosphonium salt (XXIX) is obtained, which may be reacted with vitamin A aldehyde (XXX) to (VII) (Roche) or with a C_{10} aldehyde ester to give the apocarotenoid (X) (Roche).

It should be mentioned that phosphonium salts, being phase transfer catalysts, should undergo the Wittig olefination in a two-phase system. This is indeed the case.[32] An industrial application of this method is so far not known, but the advantages might be considerable.





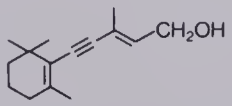
Some of the disadvantages of the Wittig olefination are not present when the phosphonium salts are replaced by phosphonates (Horner olefination). The phosphonates are less sensitive to steric hindrance, thus tri- and tetrasubstituted olefins can be obtained from reactions with ketones. The by-product, a phosphate, is water soluble and easy to separate from the usually water-insoluble products. On the other hand, the difficulties associated with regenerating a phosphonate from the phosphate have made this reaction uneconomic from an industrial point of view. No large scale industrial carotenoid synthesis makes use of this method.

[32] G. Merkl and A. Merz, *Synthesis* p. 295 (1973).

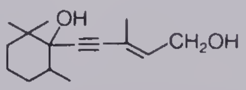
The recently discovered carbonyl olefination with the help of isonitriles[33,34] has successfully been used for a laboratory scale synthesis of β-carotene.[35] Thus, retinyl isonitrile gave (VII) in 60% yield upon condensation with retinal (XXX). However, the difficulties associated with the syntheses of isonitriles, as well as the many side reactions that may accompany the method, make an industrial exploitation of this new olefination process unlikely.

F. Acetylide Addition

The most widely used method for carbon–carbon bond formation in vitamin A and carotenoid synthesis is the addition of an alkali metal or magnesium acetylide to an aldehyde or ketone. The reaction might be very economical when sodium or even catalytic amounts of an alkali hydroxide can be used for that purpose. The next step in the reaction sequence is usually a partial reduction of the triple bond to a double bond. Ideally, this should be possible with hydrogen in the presence of a catalyst. In many examples, that is indeed the case. The catalyst most commonly used is palladium on calcium carbonate poisoned with lead (Lindlar catalyst) in the presence of traces of quinoline.[36,37] Unfortunately, catalytic partial reduction is not always possible economically. Steric hindrance may prevent the addition of hydrogen, particularly in situations where the triple bond is adjacent to the cyclohexenyl end group as it is in (XXXI) and (XXXII). The more expensive partial reduction of the triple bond with hydride reagents, such as lithium aluminum hydride or diisobutylaluminum hydride, is possible for propargylic alcohols, i.e., when a hydroxyl group is adjacent to the triple bond.[38–40]



(XXXI)



(XXXII)

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[33] U. Schöllkopf and F. Gerhart, *Angew. Chem.* **80**, 842 (1968).

[34] D. Hoppe, *Angew. Chem.* **86**, 878 (1974).

[35] F. Kienzle, *Helv. Chim. Acta* **56**, 1671 (1973).

[36] E. N. Marvell and T. Li, *Synthesis* p. 457 (1973).

[37] H. Lindlar, *Helv. Chim. Acta* **35**, 446 (1952).

[38] J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.* p. 1094 (1952).

[39] O. Isler, H. Lindlar, M. Montavon, R. Rüegg, G. Sauey, and P. Zeller, *Helv. Chim. Acta* **39**, 2041 (1956).

[40] D. E. Loeber, S. W. Russel, T. P. Toube, B. C. L. Weedon, and J. Diment, *J. Chem. Soc.* p. 404 (1971).

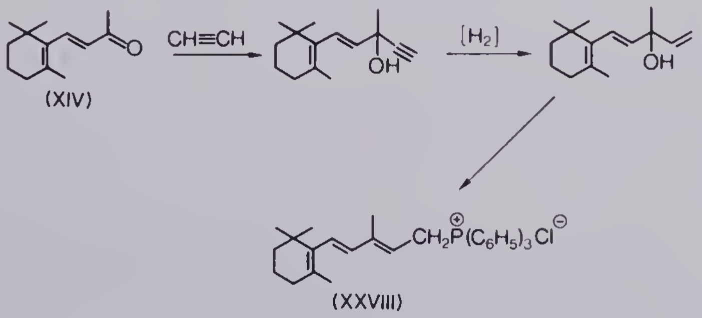
In contrast to the catalytic reduction which will give predominantly the cis olefin, hydride reduction will lead to the trans isomer. In this way a stereochemical control over the product is possible.

Introduction of the double bond, at the position where the new single bond has been created through acetylide addition, may now occur after partial hydrogenation in two ways:

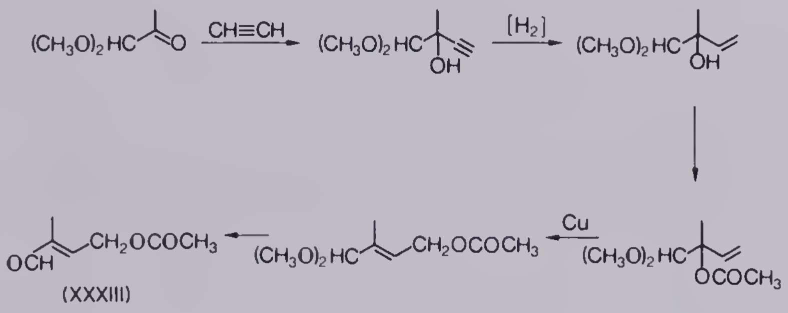
$$\text{—CHOH—CH=CH—CH}_2\text{—} \longrightarrow \text{—CH=CH—CH=CH—}$$

$$\text{—CHOH—CH=CH}_2 \longrightarrow \text{—CH=CH—CH}_2\text{OH}$$

The strongly acidic conditions necessary in the first case are often unfavorable to the product and may cause side reactions. Furthermore, the elimination may not proceed in the desired direction, but rather into other parts of the molecule (retro-formation). In the rearrangements, side reactions are less likely, especially when no acidic catalysts are involved.



Industrial examples are numerous. The important phosphonium salt (XXVIII) of the vitamin A synthesis of the BASF is prepared in the following way.[41] In the same process, the important intermediate γ-acetoxytiglinaldehyde (XXXIII) is obtained using a copper-catalyzed rearrangement.[41]



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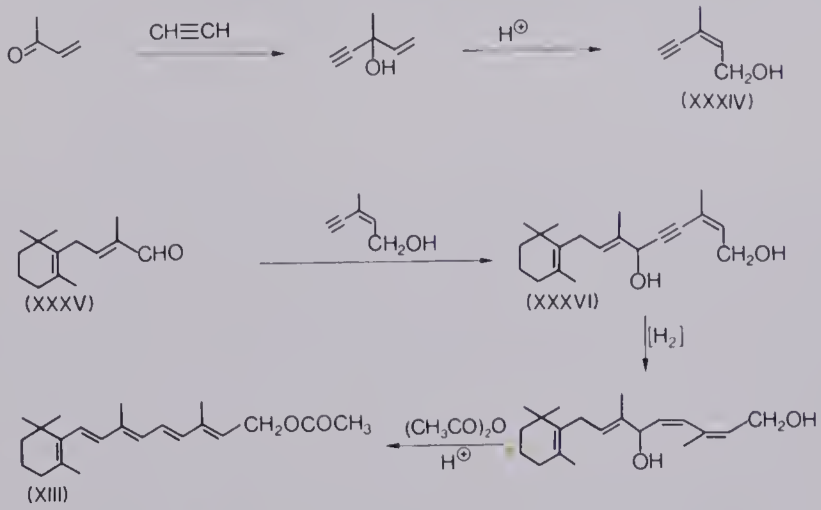
[41] W. Reif and H. Grassner, *Chem.-Ing.-Tech.* **45**, 646 (1973).

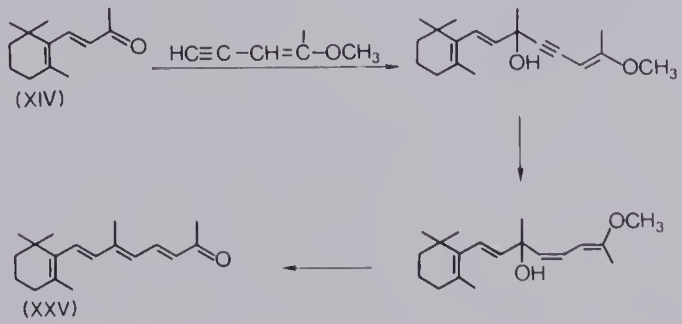
In the Roche vitamin A synthesis, the *cis*-pentol (XXXIV) is produced by an acid-catalyzed rearrangement. The alcohol (XXXIV) in turn is condensed with the aldehyde (XXXV) to give an acetylenic carbinol (XXXVI). Partial hydrogenation followed by acetylation and elimination of water finally furnishes vitamin A acetate (XIII).



In a recently published modification of the vitamin A synthesis of Philips–Duphar the indicated acetylenic compound is added to β-ionone (XIV).[20] Hydrogenation and elimination of water leads then to the ketone (XXV).

In the technical β-carotene synthesis of Hoffmann-La Roche, two moles of the aldehyde (XXXVII) condense with 1 mole of acetylene. Elimination of water, followed by partial hydrogenation, yields β-carotene (VII).[42]

Another recent technical application is found in the synthesis of citral (XV) from dehydrolinalool (XX). For this rearrangement, the presence of a vanadium catalyst is necessary.[43]



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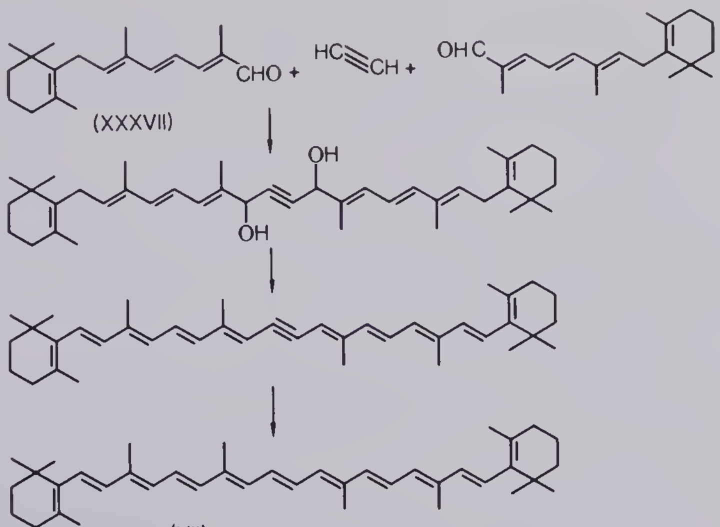
[42] O. Isler, H. Lindlar, M. Montavon, R. Rüegg, and P. Zeller, *Helv. Chim. Acta* **39**, 249 (1956).

[43] H. Pauling, D. A. Andrews, and N. C. Hindley, *Helv. Chim. Acta* **59**, 1233 (1976).

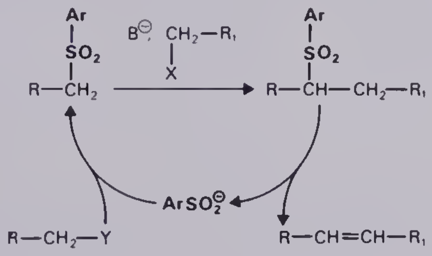


(XXXVII)

(VII)

G. Olefinations with Arylsulfinic Acids

So far, we dealt with the carbon–carbon bond and double bond forming reactions that are actually employed in technical vitamin A and carotenoid syntheses. These reactions could be divided into three major types. Unfortunately, none of these reactions was ideal. It is therefore not surprising that efforts are still being made to find new and better methods for this purpose. One particularly interesting example is the olefination with the help of sulfones.[44–48] Although this reaction has found no application yet in a technical synthesis, its advantages demonstrated in several laboratory scale carotenoid syntheses may well make it a suitable candidate for industrial use. In contrast to the



X = Cl, Br; Y = X, OH

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[44] G. W. Fenton and C. K. Ingold, *J. Chem. Soc.* p. 705 (1930).

[45] M. Julia and D. Arnould, *Bull. Soc. Chim. Fr.* p. 743 (1973).

[46] M. Julia and D. Arnould, *Bull. Soc. Chim. Fr.* p. 746 (1973).

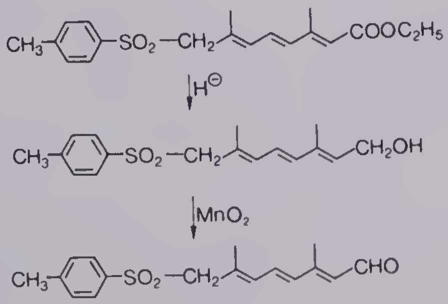
[47] Rhône-Poulenc, *BeP* 778,254 (1972); 783,672 (1972); 794,871–4 (1973); 794,934 (1973); 794,944 (1973); Deutsche Offenlegungschrift (*DOS*) 2,317,962 (1973); 2,318,001 (1973); 2,319,518 (1973); 2,319,783 (1973); 2,355,898 (1974).

[48] Rhône-Poulenc, *BeP* 770,958 (1972); 783,671 (1972).

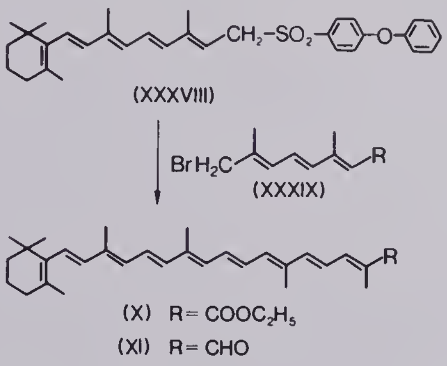
other reactions, where one substrate always was a carbonyl compound, carbon–carbon bond formation is here brought about through alkylation of a suitable arylsulfone with an alkyl halide. From the resulting intermediate, an arylsulfinic acid is eliminated to give the olefin.

The most remarkable feature of this reaction is the fact that the activating group, the arylsulfinic acid, can be recycled without any chemical modifications. This is to be compared with the Wittig olefination where triphenylphosphine oxide had to be reduced to triphenylphosphine before it could be used again for the preparation of a phosphonium salt. However, a serious drawback of the reaction is found in the need to have additional activation in the molecule. For instance, α-alkylation of the sulfone will only proceed in the presence of such strong bases as alkyl lithium or potassium *tert*-butoxide, if no other activating substituent (e.g., carbonyl, double bonds) is attached to the α-carbon. For large-scale commercial use, these bases might be too expensive. Furthermore, alkylation requires an activated halide such as an allyl halide. This puts some further restrictions on the generality of this method. And finally, to split off the arylsulfinic acid, the β-proton in the intermediate sulfone should be sufficiently acidic. This again calls for some additional activation, possibly through a carbonyl function. Side reactions, such as allylic substitutions, are also encountered.

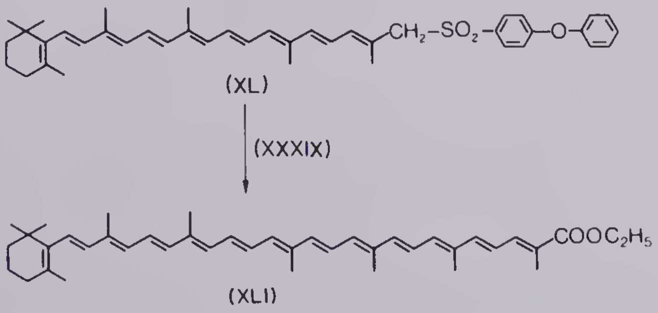
There is, however, one advantage that could make sulfones useful intermediates for the synthesis of special polyenes. The relative chemical inertness of sulfones to reductions, oxidations, and other reactions makes it possible to carry out chemical transformation on other parts of the sulfone-bearing molecule prior to olefination.[14] Thus, the following sequence of reactions could be carried out.[14]



Although this new method has only recently been applied for the first time to polyene synthesis, many examples for its successful use are already known. The synthesis of the apocarotenoids (X) and (XI) was carried out using the sulfone (XXXVIII), easily prepared from vitamin A alcohol.[49,49a]



Reduction of (X) or (XI) gave the corresponding alcohol, which could be converted to the sulfone (XL). Condensation of (XL) with (XXXIX) furnished then the torularhodin ester (XLI).[49]



In the two examples mentioned above, the sulfones (XXXVIII) and (XL) are activated enough to permit alkylation in the presence of sodium methoxide. Furthermore, the intermediate sulfone will eliminate sulfinic acid so readily that an isolation of it would be rather difficult.

In another example, the important intermediate (XLV) for the synthesis of 2,2′-dinorcarotenoids could only be obtained via sulfone (XLII). A Wittig olefination was unsuccessful here, probably for steric reasons.[14,50]

Elimination of phenyl sulfinic acid however, proved possible only after oxidation of (XLIII) to the aldehyde (XLIV). Compound (XLV) was then converted in the usual way (Wittig olefination) to 2,2′-dinorcanthaxanthin (XLVI), which in turn could be oxidized to 2,2′-dinorphoeniconone (XLVII) and violerythrin (XLVIII).[50] The latter can be

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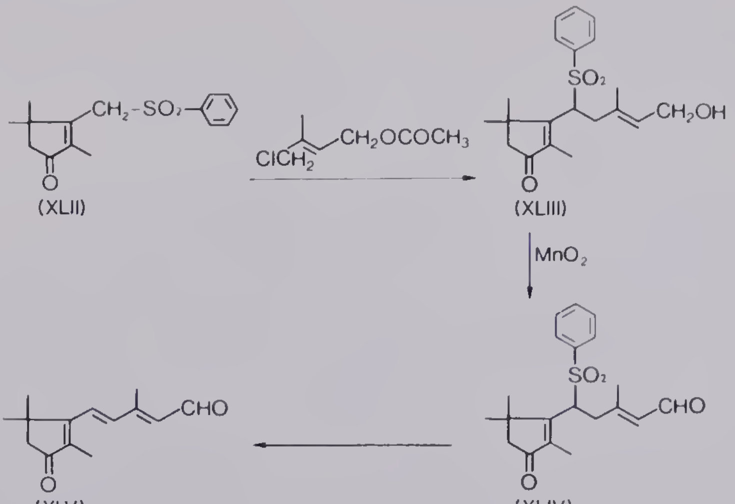
[49] A. Fischli and H. Mayer, *Helv. Chim. Acta* **58**, 1492 (1975).

[49a] P. S. Manchand, M. Rosenberger, G. Saucy, P. A. Wehrli, H. Wong, L. Chambers, M. P. Ferro and W. Jackson, *Helv. Chim. Acta* **59**, 387 (1976); A. Fischli, H. Mayer, W. Simon, and H. F. Stoller, *ibid.* p. 397.

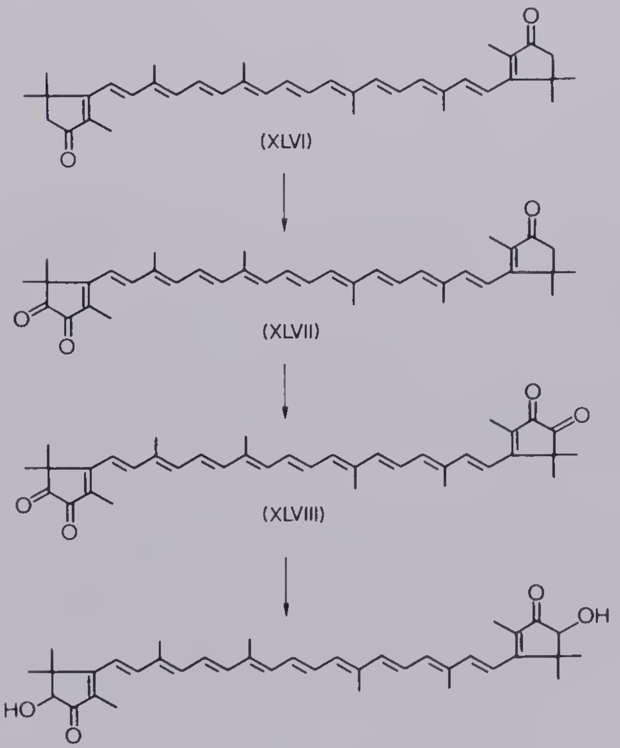
[50] F. Kienzle and R. Minder, *Helv. Chim. Acta* **59**, 439 (1976).



(XLII) (XLIII) (XLIV) (XLV)

reduced quantitatively[51] to actinioerythrol (XLIX), a carotenoid occurring in the sea anemone *Actinia equina*.

Still another application of the new method is found in the synthesis of 15,15′-didehydro-β-carotene (LII) from 2 moles of sulfone (L) and



(XLVI) (XLVII) (XLVIII) (XLIX)

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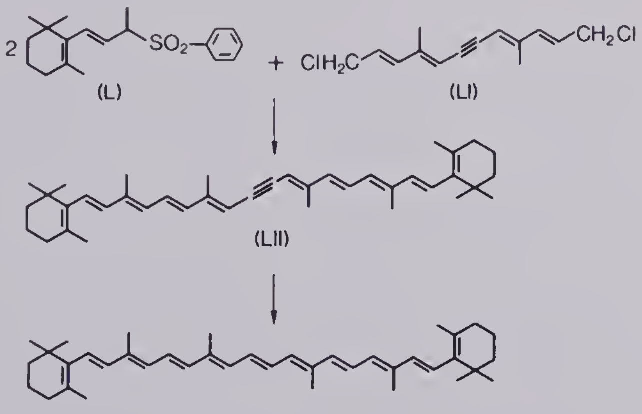
[51] S. Hertzberg, S. Liaaen-Jensen, C. R. Enzell, and G. W. Francis, *Acta Chem. Scand.* **23**, 3290 (1969).

1 mole of the dichloro compound (LI). Here, elimination of phenylsulfinic acid proceeds with great ease under the reaction conditions of the alkylation.[52]



(VII)

H. Miscellaneous Reactions

In all the above-mentioned reactions, two substrates with different functional groups are reacted together to form first a carbon–carbon single bond and eventually a carbon–carbon double bond. For an unsymmetrical product, such a method will most likely always be followed. However, if the end product is symmetrical, as many carotenoids are, dimerization of just one kind of a C_{20} compound could be a more economical synthetic route. A precedent is found in the biosynthesis where geranylpyrophosphate is dimerized to phytoene. And indeed, several recent synthetic attempts in this direction look promising. Thus, vitamin A aldehyde (XXX) is reported to dimerize in 85% yield to (VII) in the presence of a low-valent titanium reagent.[53] Using a reagent prepared from one mole of tungsten hexachloride and 2 moles of butyllithium,[54] the same reaction furnishes (VII) in 25% yield.[55] β-Carotene may also be obtained in 35% yield through oxidative coupling of (XXIX).[56] Finally, conversion of vitamin A alcohol (XXIII) to the allylic sulfone (LIII) with subsequent base treatment leads to (VII) in 24% yield.[57]

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[52] A. Fischli and H. Mayer, *Helv. Chim. Acta* **58**, 1584 (1975).

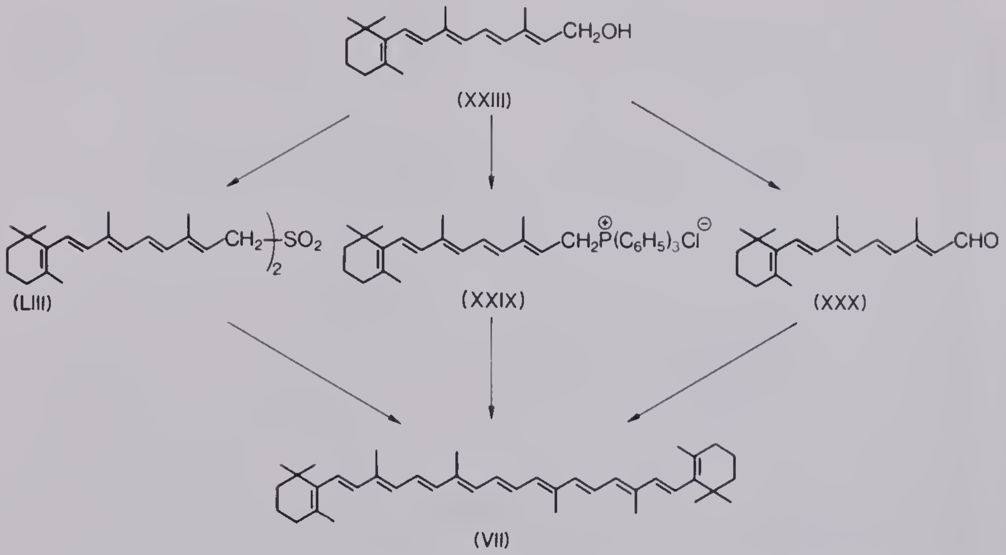
[53] J. E. McMurry and M. P. Fleming, *J. Am. Chem. Soc.* **96**, 4708 (1974).

[54] K. B. Sharpless, M. A. Umbreit, M. T. Nieh, and T. C. Flood, *J. Am. Chem. Soc.* **94**, 6538 (1972).

[55] F. Kienzle, unpublished results.

[56] H. J. Bestmann, O. Kratzer, R. Armsen, and E. Maekawa, *Justus Liebigs Ann. Chem.* **1973**, 760 (1973).

[57] G. Büchi and R. M. Freidinger, *J. Am. Chem. Soc.* **96**, 3332 (1974).



Although these reactions are not yet economical enough to compete with the more conventional condensations, they may become very attractive if such reactions could be carried out catalytically.

I. Stereochemistry of Olefination

The stereochemistry of carotenoids can be discussed under three main headings: (a) geometric isomerism about the carbon–carbon double bonds; (b) conformation about the carbon–carbon single bonds; and (c) the absolute configuration of any chiral groups. An excellent discussion of the whole topic is found in Weedon.[58] For the carotenoids we have discussed so far, which are produced on a large scale, only the problem of the occurrence of geometrical isomers during their synthesis is of importance.

Most naturally occurring carotenoids possess the all-trans configuration.[59] The best known carotenoid with a cis double bond is the diapocarotenoid bixin (LIV), the major pigment of annatto.[60] There are many reports of the isolation of other mono- or di-cis carotenoids, but it is often not clear whether these are present as true natural products or are merely artifacts formed during isolation. Of great importance too, are the 11-*cis*-retinal (LV) and (LVI), which have been found to be the prosthetic groups of the visual purple of vertebrates, insects, and mollusks.[61]

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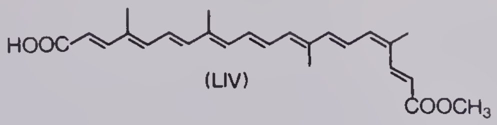
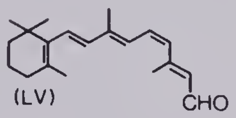
[58] B. C. L. Weedon, *in* "Carotenoids" (O. Isler, ed.), p. 267. Birkhaeuser, Basel, 1971.

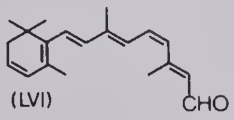
[59] O. Straub, *in* "Carotenoids" (O. Isler, ed.), p. 771. Birkhaeuser, Basel, 1971; O. Straub, "Key to Carotenoids." Birkhaeuser, Basel, 1976.

[60] P. Karrer and E. Jucker, "Carotinoide." Birkhaeuser, Basel, 1948.

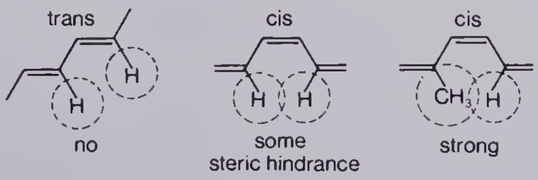
[61] G. A. J. Pitt, *in* "Carotenoids" (O. Isler, ed.), p. 717. Birkhaeuser, Basel, 1971.


(LIV)


(LV)


(LVI)

It is obvious that the formation of only one geometrical isomer in an olefination would be a highly desirable feature of a reaction. Unfortunately, none of the methods we have discussed will lead stereospecifically to either a cis or a trans olefin, although one of them may greatly predominate. So one is either faced with the problem of separating the products of or finding some means by which the unwanted isomer might be converted into the desired one. This is indeed often possible. As already pointed out by Pauling,[62] differences in steric interaction between trans and cis olefins may explain differences in stability.



Of course, the severity of steric interaction depends on the position of the double bond in a polyene chain. Consequently, some isomers are easier to isomerize than others. For instance for vitamin A- or β-carotene-type polyenes experience has shown that under normal conditions, cis isomers of the 7,8 double bond are practically nonexistent. Only under photochemical conditions could some of these isomers be detected.[63–65] The cis isomers at the 11,12-, 13,14-, and 15,15′-position may be isolated, but heating in hexane or heptane, or irradiation in the presence of catalytic amounts of iodine is usually sufficient for an isomerization to the trans form. However, the apparent stability of compounds with cis configuration at the 9,10 double bond presented the synthetic chemist with a problem. For example, a Wittig olefination using phosphonium salt (LVII) and the aldehyde (LVIII) will give a

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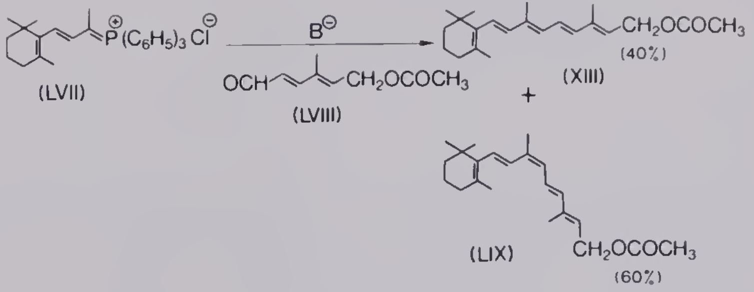
[62] L. Pauling, *Fortschr. Chem. Org. Naturst.* **3**, 203 (1939).

[63] V. Ramamurthy, G. Tustin, C. C. Yau, and R. S. H. Liu, *Tetrahedron* **31**, 193 (1975).

[64] V. Ramamurthy and R. S. H. Liu, *Tetrahedron* **31**, 201 (1975).

[65] A. E. Asato and R. S. H. Liu, *J. Am. Chem. Soc.* **97**, 4128.



mixture of vitamin A acetates with the 9-cis compound (LIX) predominating. But indications from recent patent literature suggest that irradiation in the presence of some sensitizer[66] or treatment with some noble metal catalyst[67] may even isomerize a 9-cis compound into its trans form.

Generally speaking, one should be aware of the ease with which carotenoids or intermediates in their synthesis can isomerize. Heat and light should be avoided as much as possible once a pure isomer has been obtained.

III. Future Development

Of the more than three hundred naturally occurring carotenoids, only five are at present manufactured on a technical scale, and they have been in production for several years. As a matter of fact, the last carotenoid to be made commercially available was citranaxanthin (XII) in 1968. Since that time, the major industrial research efforts were concentrated either on improving existing syntheses or on finding new routes to the old products. This is not too surprising. The relatively complex structure of a carotenoid molecule can only be constructed in a multistep synthesis. As a consequence, even the simplest carotenoids are expensive to produce in comparison to other synthetic colorants. Thus, their use was considered only when either the price of the colorant was negligible compared to that of the finished product or when no other substitute was available. This situation will most likely change. Many of the synthetic food and feed colorants, especially the azo compounds (e.g., Amaranth, also called Red 2), have become suspected of being carcinogenic. Even if such a suspicion could be disproved with certainty, the stigma attached to this class of compounds will cause many consumers to switch to guaranteed harmless alternatives. Clearly the most

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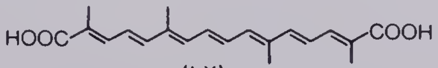
[66] BASF, *DBP* 2,210,800.

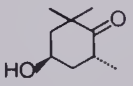
[67] F. Hoffmann-La Roche & Co., Ltd., *BeP* 819,012 (1975).

attractive alternatives are the carotenoids, the natural pigments of food and feed.

Of course, industry is aware of such a development and efforts are being made to devise technical syntheses of other carotenoids. Priority is thereby given to carotenoids that are natural constituents of food whose use is wide spread. Furthermore, "new" carotenoidal colorants may either enlarge the presently limited color range, which extends from yellow to orange-red, or have some special field of application. As possible candidates, one may mention here the yellow Zeaxanthin (VIII), the pigment of corn and major pigment of egg-yolk; the yellow crocetin (LX), the pigment of saffron; the red astaxanthin (VI), the major pigment of crustacea, salmon, and trout; the dark red torularhodin ester (XLI); and finally, the blue violerythrin (XLVIII).



(LX)



(LXI)

The most striking feature of the carotenoids zeaxanthin (VIII) and astaxanthin (VI) is the fact that they both possess two chiral carbon atoms. As to be expected in nature, these two carotenoids occur in their optically active form. Thus, (VIII) has the $3R,3'R$ and (VI) the $3S,3'S$ configuration. A technical synthesis of these two compounds even as racemates presents quite a challenge, since most likely one cannot use the readily available vitamin A alcohol as an intermediate, but would have to design a complete new total synthesis. To devise a technical synthesis of the optically active products is even more challenging. Nevertheless, a recent report[68] by chemists of Hoffmann-La Roche indicates the feasibility of a technical production of $(3R,3'R)$-zeaxanthin (VIII), starting from (LXI), readily available as a fermentation product. Starting with the same ketone (LXI), $(3S,3'S)$-astaxanthin (VI) can also be synthesized.[69] Thus, technical production of these two carotenoids will most likely be achieved in the near future.

Syntheses of crocetin (LX) and torularhodin ester (XLI) would rely on intermediates from already existing syntheses of other carotenoids and thus present no great technical problems. Their eventual commercial production will depend on economic considerations.

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[68] H. Mayer, W. Boguth, H. G. W. Leuenberger, E. Widmer, and R. Zell, *Abstr., Int. Symp. Carotenoids, 4th, 1975*, p. 43 (1975).

[69] F. Kienzle, unpublished results.

IV. Conclusion

The synthesis of a carotenoid with a relatively simple structure seems to be not a too difficult task. The various key olefination reactions are economic enough to make them attractive even for large-scale industrial use. However, it is also apparent that each process leaves something to be desired.

In judging the value of a particular procedure, we used criteria such as cost of reagents, simplicity of reaction conditions, energy requirements, and side-product formation (pollution). These criteria are, of course, not only valid for carotenoid syntheses, but also for any other synthesis. The relative importance of each of these factors may depend on circumstance. With regard to the present competitive situation, the costs play a dominant role. However, in the long run, pollution control may impose more expensive solutions.

Obviously, catalytic processes will be the ultimate goal and the search for these will continue. Catalytic processes are cheap, eliminate auxiliary chemicals such as acids and bases, and cut down the amount of pollutants. Enhanced use of readily available petrochemicals like ethylene, butadiene, and isoprene as starting materials may lead, upon dimerizations and oligomerizations with subsequent introduction of functional groups,[70] to carotenoid intermediates now only accessible through relatively expensive syntheses.

It should be remembered that the translation of a laboratory-scale total synthesis of such complicated and sensitive molecules as carotenoids into a process for tons of product represents one of the outstanding achievements of industrial chemistry and engineering and deserves great admiration.

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[70] F. Kienzle and R. Minder, *Helv. Chim. Acta* 58, 27 (1975).

AUTHOR INDEX

SUBJECT INDEX

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