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The Chemistry of SYNTHETIC DYES

VOLUME VI

Reactive Dyes

Edited by

K. VENKATARAMAN

*National Chemical Laboratory
Poona, India*



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PREFACE

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

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

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

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

I am deeply indebted to the authors for accepting my invitation. I must also thank the companies who made it possible for their leading scientists to spare the necessary time. The plan for this multiauthor effort took concrete shape during ten days I spent in the Research Department of Farbenfabriken Bayer; I am greatly indebted to Professor Petersen; Dr. Delfs, and their colleagues for valuable suggestions. I am grateful to Dr. R. R. Davies of the Research Department, Imperial Chemical Industries (Dyestuffs Division), Manchester, who has helped

me in many ways. My thanks are also due to Dr. R. B. Mitra, Mr. J. V. Rajan, Dr. N. R. Ayyangar, and Mr. V. Parameswaran for assistance in the editorial work. Academic Press has handled production of the volumes with its usual efficiency, and it is a pleasure to thank the staff for their cooperation. Finally, I wish to make grateful acknowledgment of the hospitality of the National Chemical Laboratory provided by the Director, Dr. B. D. Tilak, and the Director-General of Scientific and Industrial Research, Dr. Atma Ram, without which I could not have undertaken this project.

K. VENKATARAMAN

PREFACE TO VOLUME VI

Unlike the earlier volumes, Volume VI is devoted solely to the reactive dyes because of the outstanding technical importance of the reactive dyes and their entire development some years after the publication of Volumes I and II.

During the preparation of this volume, "Fibre-Reactive Dyes," by W. F. Beech (Logos Press, London, 1970) appeared, and a book published earlier in Poland, "Barwniki Reaktywne," by A. Lukos and W. Ornaf (Wydawnictwo Przemyslu Lekkiego i Spozywezcgo, Warsaw, 1966) became available to us.

The present treatment covers three distinct aspects of reactive dyes in three chapters: reactive groups, chromophore systems, and application. Special attention is drawn to the reactive groups which have attained commercial success, but because the chemistry of other reactive groups is no less fascinating, the relevant patent literature is discussed systematically and thoroughly in the first chapter. Chapter II includes detailed descriptions of methods of preparation of typical and technically important reactive dyes. The technology and basic chemistry of the application of reactive dyes to textile fibers are discussed in the final chapter.

K. VENKATARAMAN

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VOLUME I

- I. Introduction
- II. Raw Materials
- III. Intermediates
- IV. Diazotization and Diazonium Salts
- V. Classification of Dyes
- VI. Application of Dyes
- VII. Color and Its Measurement
- VIII. Color and Chemical Constitution
- IX. Nitroso Dyes
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- XII. Monoazo and Disazo Dyes
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- XV. Trisazo and Polykisazo Dyes
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- I. Sulfur Dyes
- II. Dye-Fiber Affinity. Physical Chemistry of Dyeing
- III. Applications of Synthetic Dyes to Biological Problems
- Author Index—Subject Index

LIST OF ABBREVIATIONS

Manufacturing companies (CI abbreviations have generally been followed):

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

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

Journals, Reports, and Books:

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

BIOS	British Intelligence Objectives Sub-Committee Final Report
CA	Chemical Abstracts
CI	Colour Index, 2nd edition, 1956
CIOS	Combined Intelligence Objectives Sub-Committee Report

CIS	Colour Index, 2nd edition, Supplement 1963
CSD	The Chemistry of Synthetic Dyes, Academic Press, 1952
FIAT	Field Intelligence Agency Technical Report
PB	Technical Report of the Office of the Publication Board, Office of the Technical Services of the U.S. Department of Commerce
Ullmann	Ullmanns Encyclopädie der Technischen Chemie

Patents:

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

CHAPTER I

REACTIVE DYES: REACTIVE GROUPS

E. Siegel

DYESTUFF RESEARCH LABORATORY, FARBENFABRIKEN
BAYER A. G., LEVERKUSEN, GERMANY

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I. Introduction

Reactive dyes are of unique importance in the supplementary volumes of *The Chemistry of Synthetic Dyes*, because they were unknown in 1952 when Volumes I and II were published. There was no mention of reactive dyes in *Colour Index* (1956), and it was only in the *Supplement* (1963) that it was possible to include a section on reactive dyes. The first reactive dye for cotton was marketed by ICI in 1956, although the basic concept of chemical combination between cellulose and a dye probably dates back to 1895 when Cross and Bevan esterified cellulose with benzoyl chloride and used the benzene ring for nitration, reduction, diazotization, and coupling with components such as dimethylaniline. Since a brief account of the historical development of reactive dyes has been given in Vol. III, the three chapters on reactive dyes in this volume are devoted to a systematic treatment classified under the heads: Chapter I, Reactive Groups; Chapter II, Chromophore Systems; and Chapter III, Application and Properties. Because the chemistry of reactive dyes is at present restricted almost entirely to patent literature, there is an exhaustive

TABLE I
MAJOR COMMERCIAL TYPES OF REACTIVE DYES FOR CELLULOSE

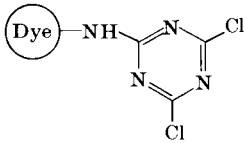
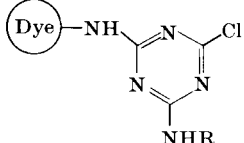
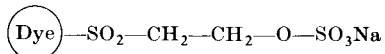
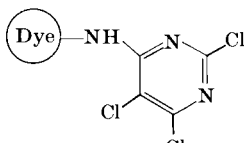
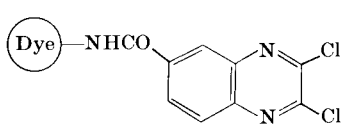
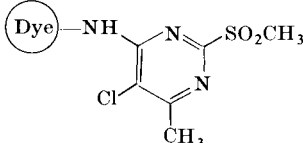
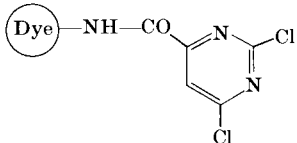
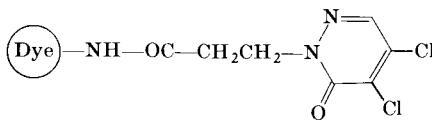
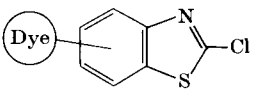

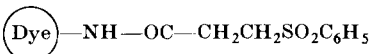
<i>Structure</i>	<i>Commercial brand name</i>	<i>Firm</i>	<i>Year of introduction</i>
	Procion	ICI	1956
	Procion H Cibacron	ICI CIBA	1957 1957
	Remazol	Hoechst	1958
	Reacton Drimaren	Geigy Sandoz	1959 1959
	Levafix E	Bayer	1961
	Levafix P	Bayer	1966
	Reactofil	Geigy	1968
	Primazin P	BASF	1964

TABLE I (Continued)

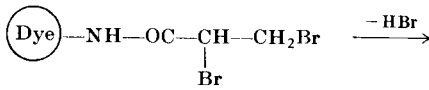
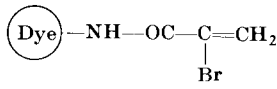
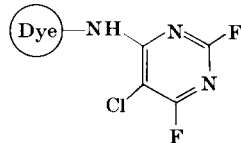
<i>Structure</i>	<i>Commercial brand name</i>	<i>Firm</i>	<i>Year of introduction</i>
	Elisiane	Francolor	1963
	Levafix	Bayer	1958
	Solidazol	Cassella	1964

coverage of patents in the first two chapters, and the priority date of each patent is specified in view of the worldwide interest in the production of reactive dyes.

The term "reactive dye" normally refers to a dye applicable to cotton, because the technical importance of reactive dyes is essentially for cotton and rayon. In principle, a reactive dye should contain a leaving group (X) which can undergo nucleophilic displacement by a hydroxyl group of cellulose in the presence of aqueous alkali ($\text{Dye-X} + \text{Cell-O}^- \rightarrow \text{Dye-O-Cell} + \text{X}^-$), or an activated C=C bond which is able to add to a hydroxyl group of cellulose ($-\text{CH}=\text{CH}_2 + \text{Cell-OH} \rightarrow -\text{CH}_2-\text{CH}_2-\text{O-Cell}$). The dye-fiber compound may have the proper-

TABLE II

MAJOR COMMERCIAL TYPES OF REACTIVE DYES FOR WOOL AND POLYAMIDE

<i>Structure</i>	<i>Commercial brand name</i>	<i>Firm</i>	<i>Year of introduction</i>
1:2 Metal complex dye—NH—OC—CH=CH ₂	Procilan	ICI	1964
	Lanasol	CIBA	1966
	Verofix	Bayer	1970
	Drimalan F	Sandoz	1970

ties of an ester or ether; the precise nature and stability of the dye-fiber bond will depend on the reactive group. The structures of the major types of reactive dyes for cotton and the commercial brand names are listed in Table I.

Reactive dyes in which chemical combination with cellulose takes place under acid conditions are also known; and methods have been developed in which dyes containing amino or other nucleophilic groups are applied to cellulose in the presence of compounds containing bridging groups. These are of relatively minor practical value, but are included in this review.

Selected reactive dyes in the commercial ranges for cotton have found limited application to wool and related fibers. Reactive dyes specifically designed for wool, silk, and polyamide fibers are classified separately with distinctive group names for the commercial products (Table II). They offer few advantages of normal wet-fastness or brilliance of shade in comparison with appropriately chosen acid and chrome dyes. The main reasons for the use of dyes of this class are their excellent fastness against repeated washing, especially on shrinkproof wool, and the simpler dyeing methods compared with chrome dyes.

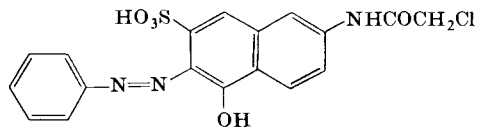
Methods for the preparation of reactive dyes are described by Schündehütte in Chapter II, and the factors governing the applicability of a dye as a reactive dye under practical conditions of dyeing or printing are discussed by Hildebrand in Chapter III.

II. Reactive Groups Bound to the Colorant

A. ALIPHATIC CARRIER SYSTEMS OF MOBILE GROUPS

1. *Substituted Alkane Monocarboxylic Acid Amide*

a. Substituted Acetamides. Supramin Orange R



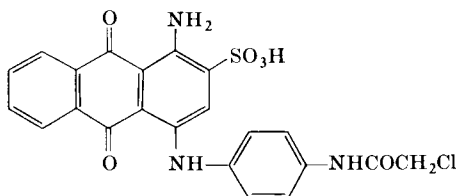
introduced in 1930 by Clingestein¹ (Bayer)^{1a} was probably the first wool dyestuff in which an improvement of the wet-fastness properties was

¹ The citations need not necessarily be the first publications; furthermore they do not indicate the legal patent position. Parenthetical notations represent day, month, and year.

^{1a} BP 341,461.

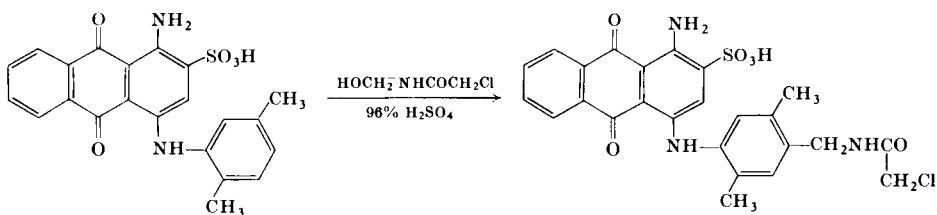
achieved by incorporation of the chloroacetyl group capable of reaction with wool keratin. Special wool dyestuffs containing chloroacetylamino groups are still described today,^{2, 2a, 3} although none of them reacts chemically in sufficiently high percentages with wool, so that—except in the case of 1:2 metal complexes of the Procilan⁴ type, which in themselves already possess a high affinity—good fastness to potting is not attained.

The dyeing of cellulosic textiles with dyestuffs containing chloroacetylamino groups, e.g.,



was first described by BASF⁵ in 1957, and later also by other firms.⁶ The fixation yields of these chloroacetylamino reactive dyestuffs are also not particularly high on cellulosic fibers.

In the production of chloroacetylamino reactive dyestuffs, besides the acylation of dyestuffs containing amino groups² or sulfonamide groups,⁴ e.g., with chloroacetyl chloride, use is also frequently made of the Tscherniac-Einhorn reaction, in which under the influence, for example, of *N*-methylolchloroacetamide in 96% sulfuric acid on a dye with aromatic nuclei which easily undergo electrophilic substitution, a chloroacetylaminomethylene group is introduced.³



² CIBA, DBP 1,016,230 (15.12.1953).

^{2a} BASF, FP 1,212,162 (31.8.1957); S, BeP 605,297 (24.6.1960); Gy. BeP 608,990 (11.10.1960); S, BeP 617,509 (12.9.1961).

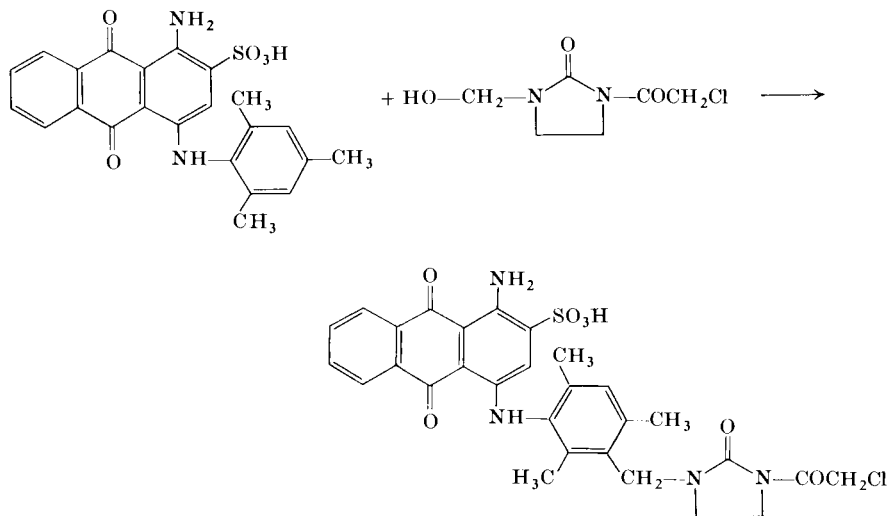
³ Gy, DBP 1,111,317 (23.4.1958); BeP 577,990 (23.4.1958); S, SP 401,302 (9.3.1961); BeP 618,604 (12.6.1961); 625,916 (22.12.1961); Gy, BeP 627,436 (24.1.1962).

⁴ ICI BeP 579,968 (23.6.1958); S, BeP 618,069 (7.6.1961); FBy, BeP 669,432 (11.9.1964).

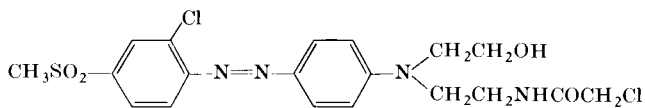
⁵ BASF, BP 830,371 (23.3.1957).

⁶ FH, BeP 582,072 (27.8.1958); S, BeP 605,297 (24.6.1960).

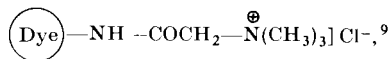
In an interesting variant, not the methylol compound of chloroacetamide, but that of *N*-chloroacetyleneurea, is used.^{6a}



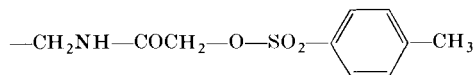
Reactive disperse dyes for polyamide fibers are also obtained by both of the above-mentioned syntheses,⁷ in which amino groups in aliphatic side chains can also be chloroacetylated.⁸



Halogen is by far the most frequent mobile group attached to the acetamide residue. In addition, there are also quaternary ammonium groups in dyestuffs free from sulfo groups of the type



sulfonyloxy groups



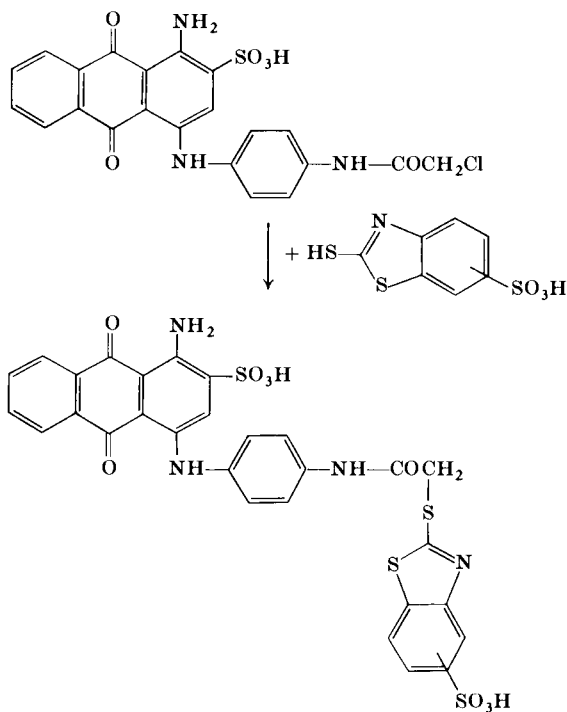
^{6a} S, *BeP* 619,084 (22.6.1961).

⁷ CIBA, *BeP* 598,707 (31.12.1959); S, *BeP* 604,093 (24.5.1960).

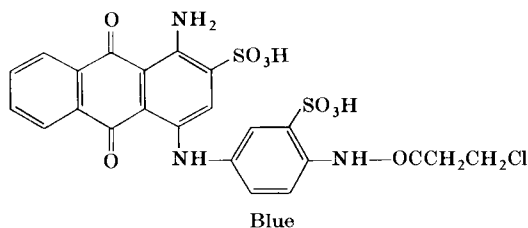
⁸ ICI, *BP* 877,667 (8.5.1959).

⁹ FH, *BeP* 638,180 (3.10.1962); S, *BeP* 608,932 (6.10.1960).

in wool-reactive dyes,¹⁰ and residues of mercaptans, dithiocarbamates, and the thiocyanate radical, which are introduced into the fundamental chloroacetyl amino dyes by halogen exchange with the corresponding sulfur compounds.¹¹



b. Substituted Propionamides. i. β -Halopropionamides. In 1953 Ciba described wool-reactive dyes containing β -chloropropionylamino groups² and in 1956 recognized the suitability of β -chloropropionylamino dyestuffs, which are in most cases freely water-soluble and possess little affinity, for the continuous dyeing and printing of cellulosic fibers.¹²



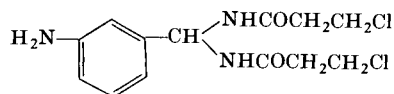
¹⁰ FBy, *BeP* 669,432 (11.9.1964).

¹¹ ICI, *FP* 1,282,781 (21.1.1960); *BP* 903,432 (21.1.1960).

¹² CIBA, *BeP* 560,032 (14.8.1956).

Other companies have likewise worked intensively in this field in subsequent years.^{5, 13-15}

Subsequently, cellulose-reactive dyes with *two* aliphatic haloacylamino groups in the molecule were described by Bayer¹⁶ and Ciba,¹⁷ the introduction of both reactive groups into diazo components such as



being effected by condensation of 3-nitrobenzaldehyde with 2 moles of β -chloropropionamide in strong acids according to USP 2,475,846 and subsequent reduction of the nitro group.¹⁷ Most of the patent claims mentioned in Section A.1,a for the introduction of chloroacetamidomethylene groups into dyestuffs easily capable of electrophilic substitution (e.g., ref. 3) also include β -halopropionylamidomethylene residues.

In certain of the above-mentioned patent specifications,¹²⁻¹⁵ it is assumed that, under the influence of added alkali, hydrogen halide splits out of the β -halopropionylamino group, resulting in the acrylamide group, which is capable of addition to the hydroxyl groups of cellulose. Militating against this mechanism is, however, the fact that the conditions for total hydrogen halide separation are very drastic: in BeP 570,437¹⁸ heating with soda solution is the method used. Zollinger, among others, therefore presumes a direct nucleophilic substitution of halogen by the cellulose anion, following an $\text{S}_{\text{N}}2$ mechanism. Of late, β -halopropionylamino groups in reactive 1:2 metal complex dyestuffs for wool are again being mentioned more frequently.¹⁹

ii. α,β -Dihalopropionamides. α,β -Dihalopropionamides were developed principally by Ciba in 1957 in cellulose-reactive dyes, such as the bluish red²⁰

¹³ CFM, BeP 565,279 (1.3.1957); DBP 1,256,818 (1.3.1957); 1,092,144 (22.2.1958); BeP 576,104; 576,105 (26.2.1958); 578,465 (7.5.1958); 581,442 (7.8.1958).

¹⁴ CIBA, BeP 565,376 (5.3.1957); 565,448 (7.3.1957); 565,484 (8.3.1957), 565,650 (12.3.1957).

¹⁵ FH, BeP 566,648 (10.4.1957).

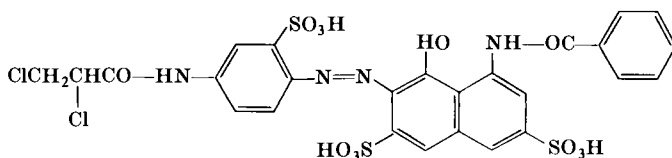
¹⁶ FBy, DBP 1,245,307 (8.8.1957).

¹⁷ CIBA, BeP 572,571 (1.11.1957); 585,763 (18.12.1958).

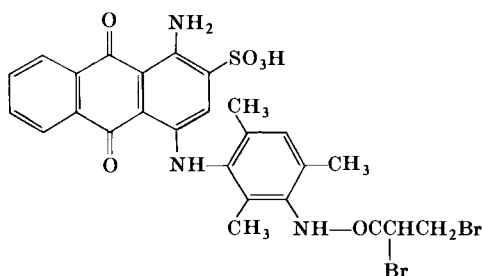
¹⁸ FH, BeP 570,437 (17.8.1957).

¹⁹ ICI, BP 1,001,836 (4.9.1962); 1,033,166 (9.5.1963); 1,037,892 (29.11.1963); FBy, BeP 669,432 (11.9.1964).

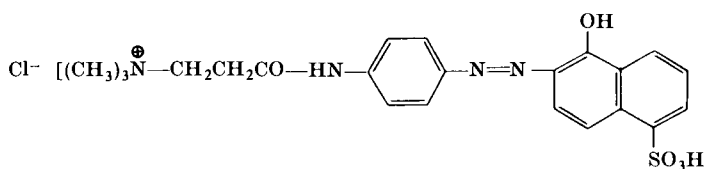
²⁰ CIBA, BeP 567,435 (7.5.1957); BASF, DBP 1,124,172 (17.10.1959).



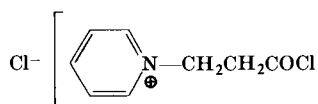
and recently in wool-reactive dyes (Lanasol dyes), e.g., the bright reddish blue²¹



iii. *β-Quaternary ammonium propionamides*. It was recognized by BASF in 1959/1960 that substitution of the halogen in the *β*-position by a quaternary ammonium group gives dyestuffs which react equally well with cellulose. These dyes can be produced by reaction of the corresponding *β*-chloropropionylamide dyestuffs with molar quantities of a tertiary amine,²² by uniting suitably substituted diazo and coupling components,²³



or by acylation, e.g., of tetrazaporphine dyestuffs containing amino groups with *N*-(2-chlorocarbonyl)ethylpyridinium chloride²⁴:



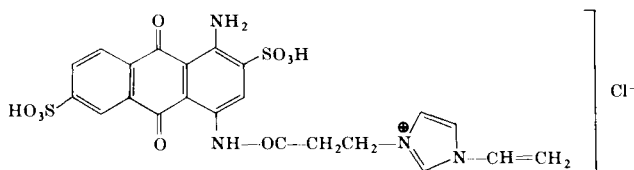
²¹ BASF, *BeP* 683,734 (7.7.1965); *DP* 6,609,467 (7.7.1965).

²² BASF, *DBP* 1,124,172 (17.10.1959).

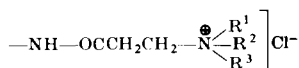
²³ BASF, *DBP* 1,135,589 (12.9.1959).

²⁴ BASF, *DBP* 1,137,155 (21.4.1960).

N-Vinylimidazole was also used as a tertiary base.²⁵



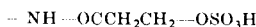
Later, ICI²⁶ and Hoechst²⁷ also claimed dyestuffs containing the reactive group



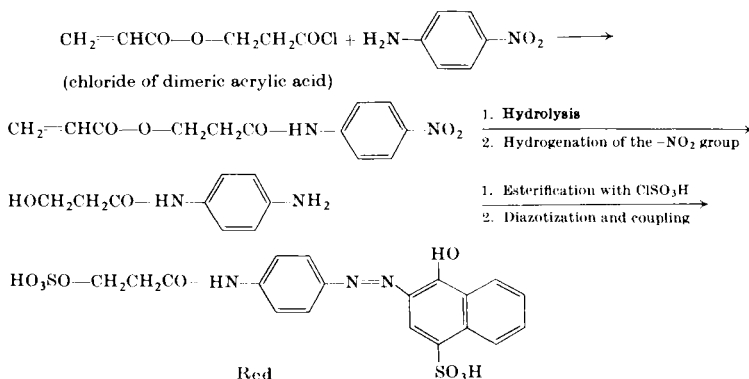
R^1-R^3 = hydrocarbon residues

and the corresponding dyeing processes, the application of Farbwerke Hoechst²⁷ relating only to basic dyestuffs which except for the pendent quaternary ammonium groups contained no water-solubilizing groups.

iv. β -Sulfatopropionamides. In 1958, in a survey "Zur Kenntnis der Reaktivfarbstoffe"²⁸ concerning reactive dyes, Wegmann mentioned the group



in water-soluble reactive dyestuffs. In the following year, BASF discovered a technically viable process for the production of β -sulfatopropionylamides²⁹ and in 1961 introduced reactive dyes of this type³⁰ (Primazin dyestuffs).³¹



²⁵ BASF, *BeP* 616,439 (15.4.1961).

²⁶ ICI, *BeP* 619,731 (3.7.1961); *BP* 958,899 (3.7.1961).

²⁷ ICI, *BeP* 638,180 (3.10.1962).

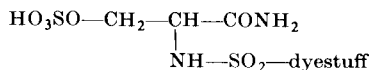
²⁸ J. Wegmann, *Textil-Praxis* **13**, 1056-1061 (1958).

²⁹ BASF, *BeP* 593,868 (8.8.1959).

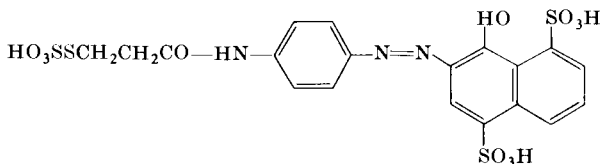
³⁰ BASF, *BeP* 593,869 (8.8.1959); *FP* 1,268,154 (22.9.1959).

³¹ *J. Soc. Dyers Color.* **78**, 584 (1962); *Melliand Textil.* **43**, 850 (1962).

In an interesting variant due to Sandoz, the dyestuff is bound not by the carbamide group, but by a sulfonylamino group in the α -position.³²

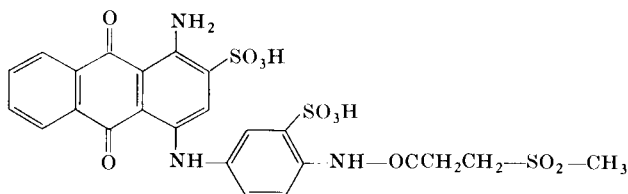


Finally, mention must be made of the analogous β -thiosulfatopropionamide dyestuffs of Farbwerke Hoechst, which are easily obtained from the corresponding β -chloropropionylamide dyes by halogen exchange with thiosulfate.



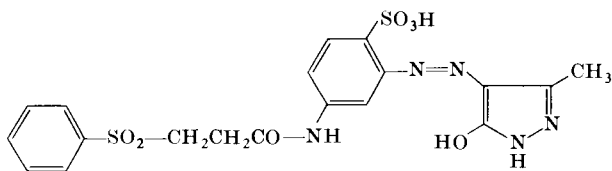
They are suitable as reactive dyestuffs for cellulose and wool.³³

v. β -Sulfonylpropionamides. The mobile sulfonyl group which has recently achieved technical importance was first described by BASF in anthraquinone dyestuffs of the type



and later also in corresponding azo and phthalocyanine dyes.³⁴

Simultaneously, Cassella recognized the value of this reactive group.³⁵ This firm later worked the field thoroughly³⁶ and in 1964 introduced Solidazol dyestuffs,³⁷ a range particularly suitable for textile printing.



Greenish yellow

³² S, *BeP* 643,924 (22.2.1963).

³³ FH, *BeP* 672,011 (6.11.1964); *FP* 1,461,879 (24.12.1964).

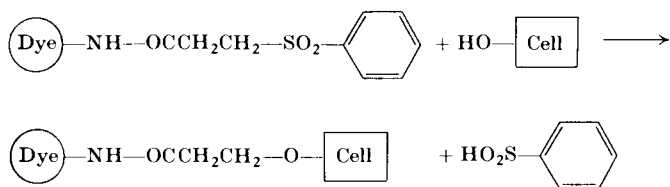
³⁴ BASF, *BeP* 606,947 (13.8.1960); 617,435 (10.5.1961).

³⁵ CFM, *SZ* 371,780 (2.2.1961).

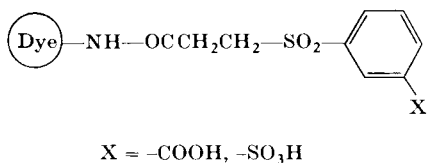
³⁶ CFM, *FP* 1,335,328 (27.9.1961); 1,345,490; 1,345,491 (27.1.1962); 1,346,180 (2.2.1962).

³⁷ *Melliand Text. Rep.* 4, 203 (1964).

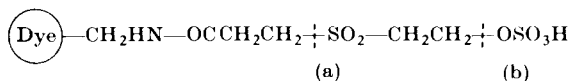
In the reaction with cellulose, benzenesulfinic acid splits out.



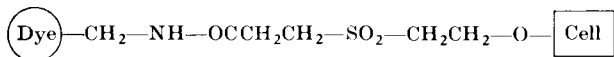
Subsequently, Cassella also claimed dyes containing water-solubilizing groups in the mobile sulfonyl group.³⁸



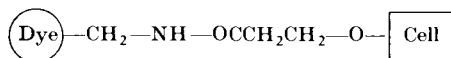
Sumitomo protected dyes containing the bireactive group [as β -sulfonylpropionamide (a) and β -sulfatoethyl sulfone residues (b)].³⁹



The advantage of this combination of two different reactive groups may be due to the fact that under more energetic dyeing conditions the less alkali-resistant β -sulfonylethyl-cellulose bond at first formed



is dissolved, the extremely wash-fast β -propionylamide bridge

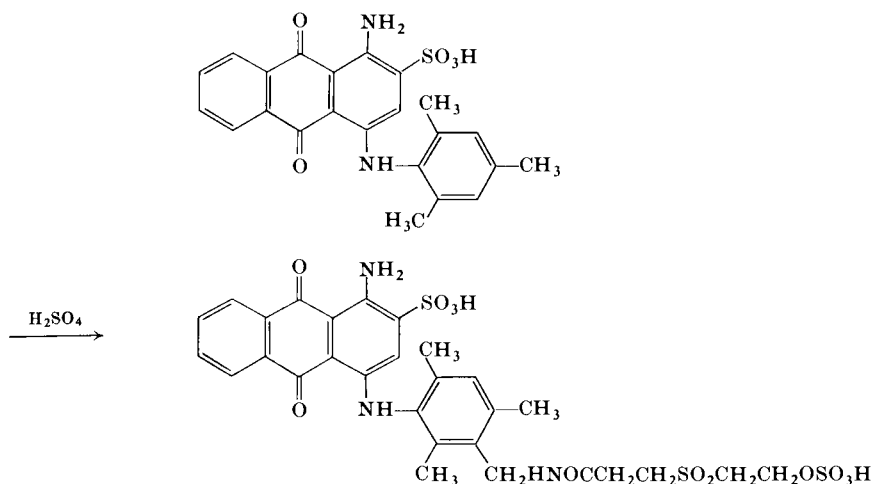
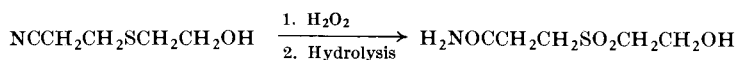


to the cellulose being formed with separation of β -hydroxyethylsulfinic acid.

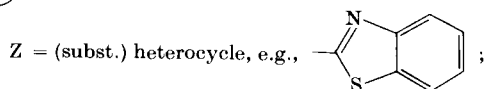
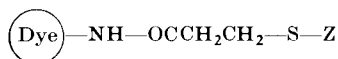
³⁸ CFM, *FP* 1,432,259 (5.5.1964).

³⁹ NSK, *BeP* 661,532 (24.3.1964); *JP* 11,350/66 (27.3.1964); *DP* 6,609,213 (1.7.1965); *JP* 9,792/67 (1.4.1964); 7,271/67 (24.3.1964); 8,945/68 (24.3.1964); 7,272/67 (27.3.1964); 3,176/67 (2.4.1964); 7,051/68 (10.6.1964); 12,936/68 (30.1.1965) see also *JP* 7, 052/68 (18.7.1964).

The method of production is as follows:



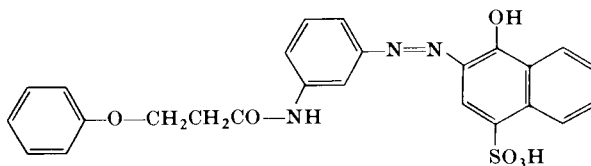
vi. Other β -substituted propionamides. The previously mentioned ICI patents¹¹ also comprise propionylamides with mobile groups in the β -position of the general formula



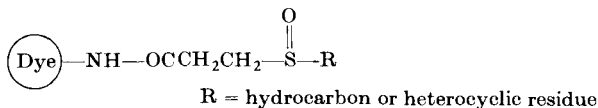
(subst.) hydrocarbon residue ;

or $-\text{CN}$, $-\text{C}(=\text{S})-\text{N}(\text{C}_2\text{H}_5)_2$ and similar groups

vii. β -Thioether and ether groups. β -Thioethers and ethers, particularly β -phenoxypropionylamides

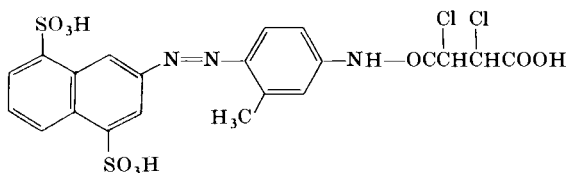


have been claimed by BASF⁴⁰ and Cassella,³⁵ the last-named firm also mentioning *sulfoxide groups in the β -position*.

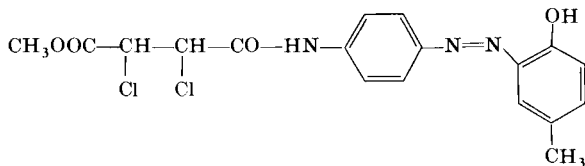


2. Substituted Alkane Dicarboxamides

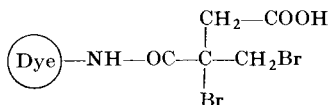
Similar in mechanism and therefore in application to the β -halopropionamides are the dyestuffs developed by Japanese firms, e.g., from dichlorosuccinic anhydride, dichlorosuccinomethyl ester chloride,⁴¹ or dibromoisitaconic anhydride⁴² and dyes containing amino groups capable of acylation.



Yellow



Yellow disperse dyestuff for polyamide fibers⁴¹



3. Substituted Alkane Monocarboxylates

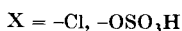
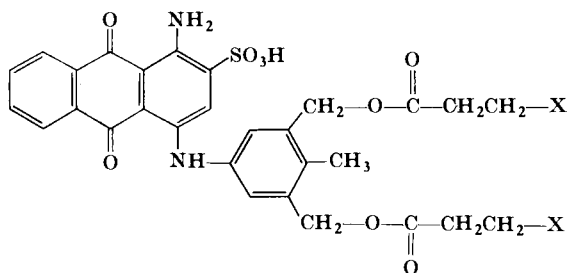
In water-soluble cellulose-reactive dyestuffs, such as the blue,⁴³

⁴⁰ BASF, *BeP* 607,331 (23.8.1960); 619,785 (5.7.1961).

⁴¹ MCI, *SP* 6,833/62 (9.6.1961); *JP* 26,740/63 (9.6.1961); 20,236/63 (15.7.1962).

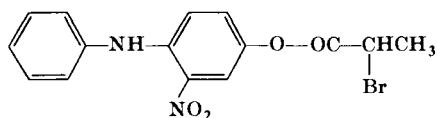
⁴² Kogyo Gitsutsuin, *JP* 28,115/64 (9.4.1963).

⁴³ G, *USP* 3,278,515 (31.12.1962).



the propionic ester bond may become partly saponified under the alkaline conditions of the fiber reaction or during washing at the boil, and this is reflected in the fixation yield and fastness to washing.

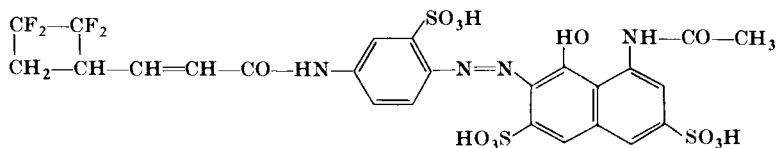
On the other hand, for the milder conditions of application of reactive disperse dyestuffs, e.g., of the type⁴⁴



on wool, the stability to hydrolysis of the ester group is sufficient. Dyes with ester-like bonded reactive groups have no technical importance.

4. Substituted Cycloalkane Carboxamides

a. *Fluorocyclobutanecarboxamides*. This new reactive dyestuff group, which is very interesting for its chemistry and application, was discovered in 1963 by Farbwerke Hoechst and worked intensively.⁴⁵

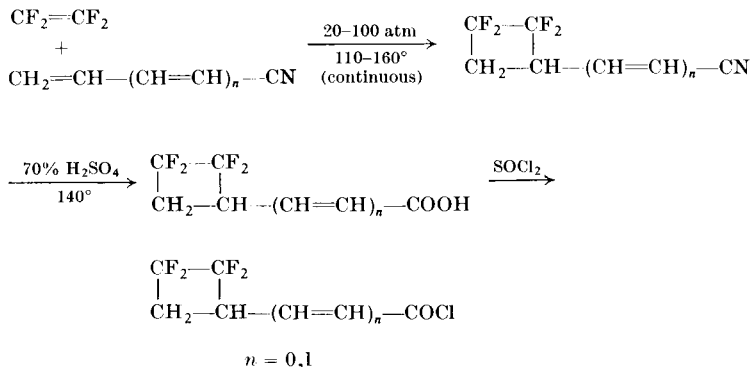


Bluish red

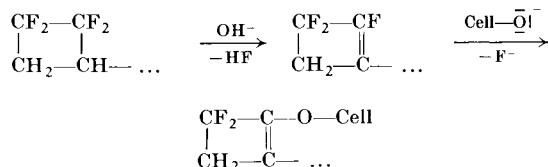
⁴⁴ ICI, BP 877,666 (8.5.1959).

⁴⁵ FH, FP 1,412,793 (28.10.1963); 1,416,172 (27.11.1963); 87,615 (28.2.1964); 1,429,761 (4.4.1964); 1,448,600 (30.9.1964); BeP 686,922 (15.9.1965); 719,375 (12.8.1967).

The essential reactive components are synthesized from ethylene tetrafluoride and acrylonitrile or 1-cyanobutadiene.⁴⁶



The dyeing process consists in splitting out HF followed by nucleophilic substitution of the fluorine atom remaining on the double-bonded carbon by cellulose anions.

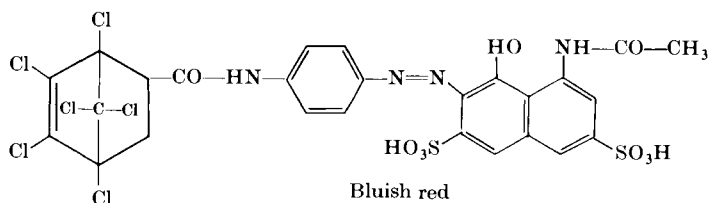


Dyestuffs of this type give good fixation yields when applied from a long liquor at 60–80°, and when synthesized from β -(2,2,3,3-tetrafluorocyclobutyl)acrylic chloride, also dyeings with very good fastness to washing and acid cross-dyeing; the carbamide bridge formed with 2,2,3,3-tetrafluorocyclobutylcarboxylic chloride is susceptible to hydrolysis and the dyeings do not therefore possess such good wet-fastness properties.⁴⁶

b. Other Substituted Cycloalkane Carboxamides. From hexachlorocyclopentadiene and acrylic acid or maleic acid or their derivatives, diene addition products are obtained in a smooth reaction, which in the form of their acid chlorides or anhydrides are useful reactive components.⁴⁷

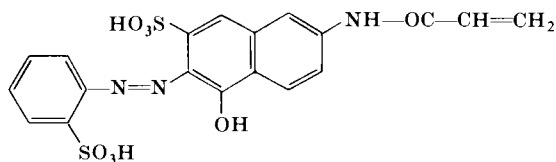
⁴⁶ F. Meininger, *Chimia (Aarau)* Suppl., p. 156 (1968). O. Scherer, K. Uhl, and H. Millauer, "Symposium on Fluoro-Organic Compounds," Birmingham, 1968; O. Scherer, *Fortschr. Chem. Forsch.* **14**, 225 (1970). FH, *FP* 87,666 (1,416,172) (28.2.1964); *BeP* 719,373; 719,378 (12.8.1967).

⁴⁷ BASF, *BeP* 612,603 (13.1.1961).



5. Alkene Monocarboxamides

a. Acrylamides and Crotonamides. Similar to reactive dyes with β -chloropropionylamide groups, those containing acrylamide groups, e.g., the brilliant orange



are also fairly slow in their reaction. They are less suitable for the dyeing of cellulosic materials from a long liquor than for pad-dyeing processes and, particularly, for textile printing, where they are distinguished by good stability of the alkaline printing pastes. The crotonamide group is even less reactive.

Reactive dyes of these two groups were described in 1957 by Cassella,¹³ Ciba,⁴⁸ Hoechst,⁴⁹ and BASF.⁵⁰

Up to the present, acrylamide reactive dyestuffs have found no technical application for the dyeing of cellulosic fibers. On the other hand, they have achieved practical importance for wool in the Procilan dyestuffs of ICI.

In addition to a series of patents for specific metal-free dyes containing acrylamide residues (BASF,⁵¹ ICI⁵² and Ciba,^{17, 53}) which are mostly conceived as wool dyestuffs, special mention must be made of the

⁴⁸ CIBA, *BeP* 565,447 (6.3.1957).

⁴⁹ FH, *BeP* 569,964 (31.7.1957).

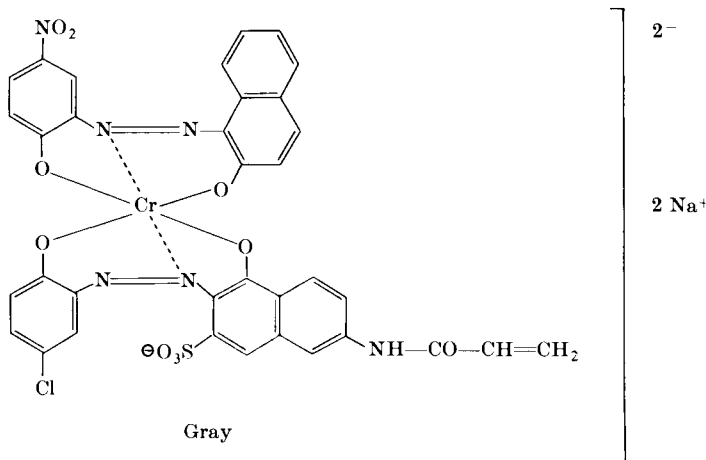
⁵⁰ BASF, *BeP* 573,862 (13.12.1957); 573,863 (14.12.1957); *DBP* 1,069,565 (23.5.1958); *BeP* 582,944 (25.9.1958); 583,050 (30.9.1958).

⁵¹ BASF, *DBP* 1,052,016 (7.5.1957).

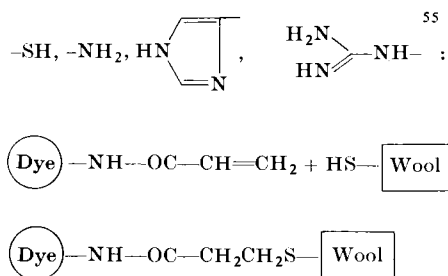
⁵² ICI, *FP* 1,352,295 (29.1.1962); 1,346,756 (7.2.1962); *BeP* 617,961 (24.5.1961); 626,967 (10.1.1962); 629,325 (8.3.1962); *BP* 1,037,648 (4.9.1963).

⁵³ CIBA, *FP* 1,343,211 (29.12.1961).

systematic work of ICI on 1:2 metal complex dyes for wool with this reactive group,^{19, 54} resulting in the introduction of Procilan dyestuffs, e.g.,⁴³



Applied by a simple and protective dyeing method, this dyestuff group attains almost the fastness level of afterchrome dyes, due solely to the fact that a high percentage (over 80%) of absorbed dyestuff reacts chemically with the strongly nucleophilic groups of the wool protein

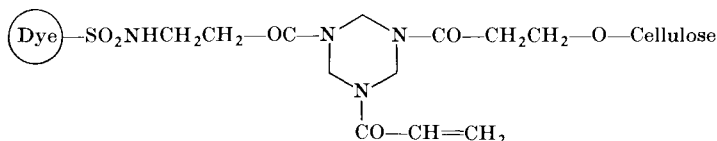
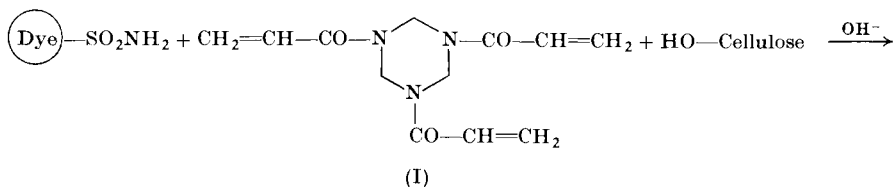


In another field, the fiber-reactive acrylamide group has achieved technical importance: Basazol dyestuffs introduced by BASF in 1963, which are free from reactive groups, contain mobile hydrogen atoms,

⁵⁴ ICI, *BeP* 591,397 (12.6.1959); *BP* 966,803 (25.1.1962); 995,261; 995,365 (29.5.1962); 1,020,820 (24.4.1963); 1,020,801; 1,020,802 (3.5.1963); 1,084,251 (17.1.1964); *DP* 6,604,615 (9.4.1965).

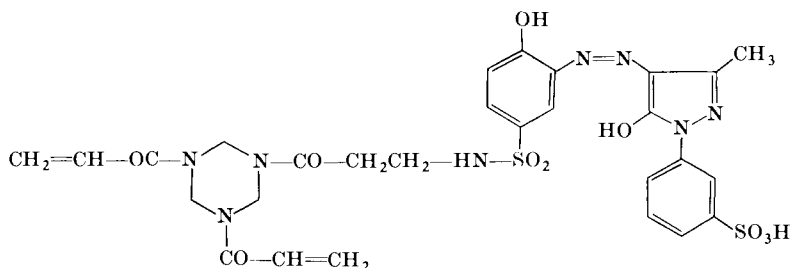
⁵⁵ *J. Soc. Dyers color.* **80**, 158, 283 438, and 649 (1964).

e.g., attached to a sulfonamide nitrogen, and are linked with cellulose by polyfunctional fixation components, e.g., (I).⁵⁶



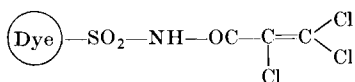
Triacryloformal (I), which acts as a fixation component, is easily obtained from acrylonitrile and paraformaldehyde.⁵⁷

A variant, in which dyestuffs containing triacryloformal residues, such as the yellow-brown 1:2 cobalt complex of



are applied, is technically less valuable.⁵⁸

b. Substituted Acrylamides. i. Haloacrylamides. Mono-, di-, and trihaloacrylamides are claimed in numerous patent applications, mostly concerning reactive dyes for wool, often in conjunction with unsubstituted acrylamides. In these cases, the haloacroyl group may also be bound to the dyestuff by a sulfonamide bridge.^{4, 59}



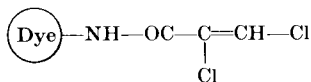
⁵⁶ BASF, *BeP* 609,825 (2.11.1960).

⁵⁷ A. Ballauf and R. Wegler, *Chem. Ber.* **81**, 527 (1948).

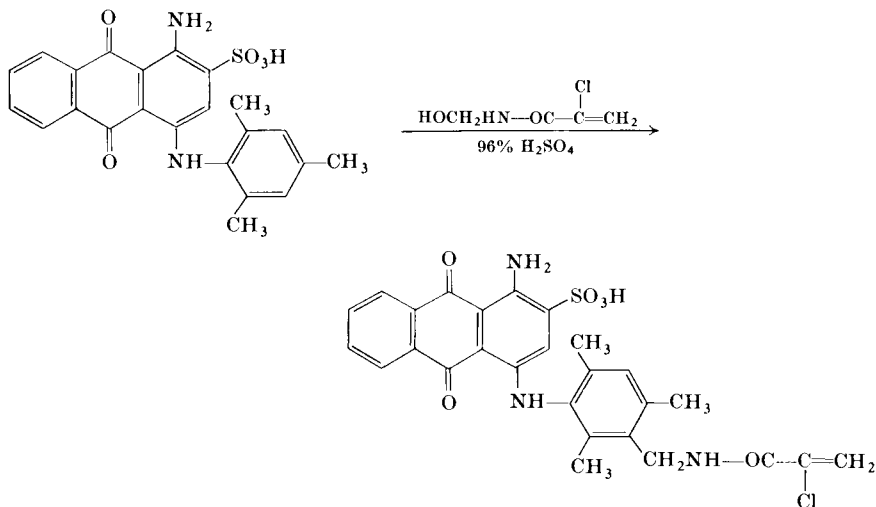
⁵⁸ BASF, *BeP* 619,906 (8.7.1961); V. F. Borodkin, *Khim. Tekhnol. (Alma-Ata)* **8**, No. 6, 993-995 (1965).

⁵⁹ ICI, *BP* 995,261; 995,365 (29.5.1962); FBy, *BeP* 661,237 (21.3.1964).

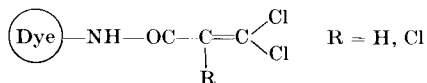
There are both 1:2 metal complex dyes^{4, 54, 59} and also metal-free azo⁶⁰ and anthraquinone dyes²¹ with haloacrylamide groups. In the latter case, the α -bromoacrylamide group gives particularly high fixation yields on wool.²¹ α,β -Dichloroacryloylamino dyes of the azo, anthraquinone, and phthalocyanine series^{60a} have been patented by GAF.



The introduction of haloacrylamidomethylene groups by condensation of haloacrylamides and formaldehyde or its functional derivatives with dyes easily capable of electrophilic substitution,⁶¹ including 1:2 metal complex dyes,⁶² is likewise described.



As reactive residues in cellulose dyes, haloacrylamide groups are mentioned by Cassella,¹³ Ciba,⁴⁸ BASF,²² and Sandoz.^{63, 64} Noteworthy on the one hand are the β,β -di- and α,β,β -trihaloacrylamide dyestuffs⁶³ of the type



⁶⁰ ICI, *BeP* 617,961 (24.5.1961); 626,967 (10.1.1962); 629,325 (8.3.1962); *BP* 1,037,648 (4.9.1963).

^{60a} G, *BP* 1,154,596; 1,155,754; 1,159,122 (21.10.1965).

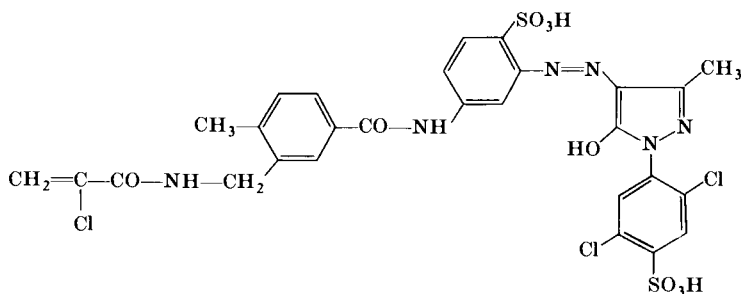
⁶¹ S, *BeP* 603,420 (4.5.1960); 607,750 (31.8.1961); 634,044 (22.8.1962).

⁶² FBV, *BeP* 669,432 (11.9.1964).

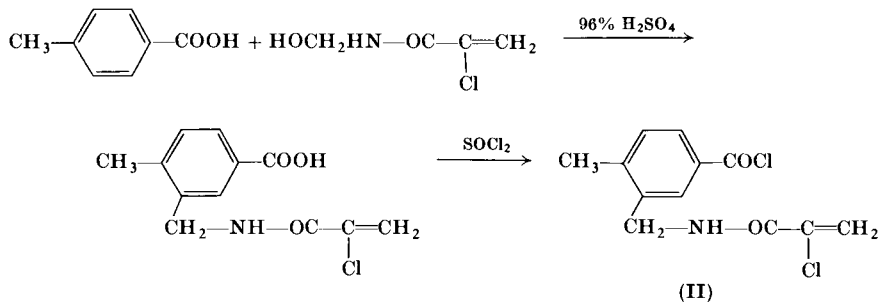
⁶³ S, *BeP* 588,362 (20.3.1959).

⁶⁴ S, *BeP* 608,052 (12.9.1960).

which also react as vinylogous carboxylic halides, and, on the other hand, dyestuffs⁶⁴ such as

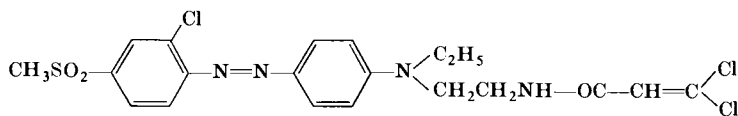


whose affinity is increased by introducing a benzoylamide group between the dye and the fiber-reactive α -haloacrylamide residue, thereby improving their suitability for the dyeing of cellulosic fibers. The synthesis is carried out by the following reaction:



followed by acylation of dyes containing amino groups with the carbonyl chloride (II).

Cellulose dyestuffs based on haloacrylamides have achieved no technical importance. The same applies to polyamide disperse dyestuffs with these reactive groups.⁶⁵

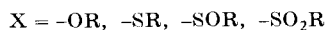
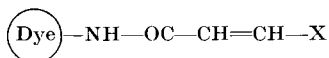


Perlon; orange

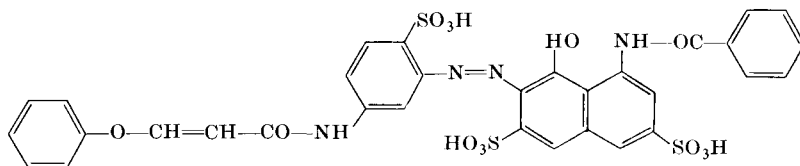
ii. *Other substituted acrylamides.* In patent applications filed by Cassella,^{35, 36} relating mainly to β -sulfonylpropionamide dyestuffs (Section A,1,b), acrylamide dyestuffs substituted by ether, thioether,

⁶⁵ S, *BeP* 594,910 (15.9.1959).

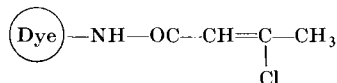
sulfone, or sulfoxide groups in the β -position are also described and claimed. Cellulose hydroxyl groups can add to the double bond of such reactive groups, and also react with them by substitution of the β -substituent X, which represents a vinylogous carboxylic acid function.



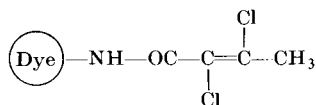
e.g.,³⁶



c. Substituted Crotonamides. At an early date, cellulose-reactive dyestuffs with β -chloro- or β -bromocrotonamide groups were mentioned by Cassella,⁶⁶ Geigy,⁶⁷ and Sandoz,⁶⁸

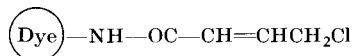


their reactivity being comparable to that of β -haloacrylamide dyes. The same applies to the α,β -dichlorocrotonamides



mentioned by Mitsubishi.⁶⁹

On the other hand, γ -halocrotonamides^{65, 70}



are reactive groups which, besides adding to the double bond, can also react as allyl chlorides or vinylogous chloroacetamides.

The γ,γ,γ -trichlorocrotonamide group, reactive in the same sense but more hydrophobic, was introduced by ICI into 1:2 metal complex

⁶⁶ CFM, DBP 1,180,079 (2.11.1957).

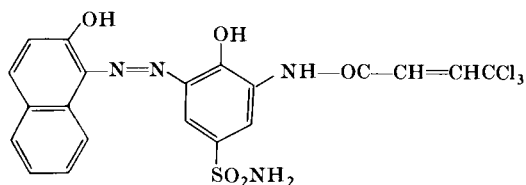
⁶⁷ Gy, BeP 583,801 (21.10.1958).

⁶⁸ S, BeP 584,832 (28.11.1958).

⁶⁹ MCI, JA 20,366 (7.7.1961).

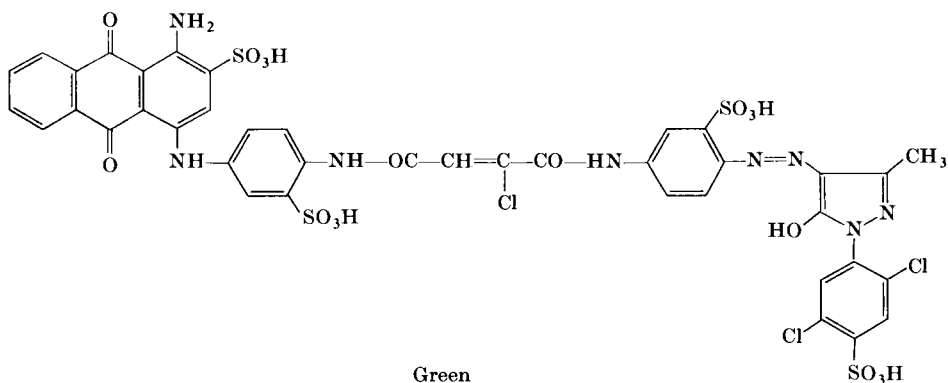
⁷⁰ S, BeP 589,247 (10.4.1959).

dyestuffs for wool,^{71, 72} e.g., the bordeaux-shade cobalt 1:2 complex of the dyestuff⁷²

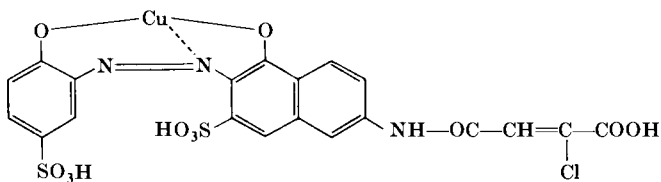


6. Alkene Dicarboxamides

a. Diamides. The advantage of chlorofumaric dichloride as a reactive component is that two small, differently constituted amino dyestuff molecules, e.g., a yellow and a blue, can be linked with it to form more highly substantive, green reactive dyes, for example, with a minimum of ballast,⁷³ since chlorofumaric dichloride is simultaneously a bridge link and a reactive group, similar to the likewise trifunctional cyanuric chloride.



b. Monoamidocarboxylic Acids. Where chlorofumaric dichloride is replaced by chloromaleic anhydride, acylation of 1 mole of amino dyestuff gives monoamidocarboxylic acids, such as⁷⁴



which are suitable for the pad-dyeing of cellulosic fibers.

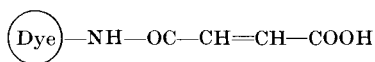
⁷¹ ICI, BeP 628,031 (7.2.1962).

⁷² ICI, BeP 627,971 (7.2.1962).

⁷³ CIBA, BeP 571,522 (27.9.1957).

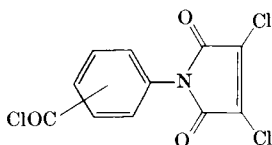
⁷⁴ CIBA, BeP 571,570 (27.9.1957).

The halogen-free group



was first mentioned by Cassella in cellulose-reactive dyes¹³ and by Sandoz in 1:2 metal complex dyestuffs for wool.⁷⁵ Later, Mitsubishi Chem. Ind. patented halotriazine dyestuffs, which also contained monoamides of alkenedicarboxylic acids as further reactive groups.⁷⁶

c. Cyclic Halomaleinimides. Sumitomo describes the production of reactive dyestuffs by acylation of dyes containing amino groups with carboxylic or sulfonic halides of *N*-aryl halomaleinimides (or halo-succinimides), such as^{76a}

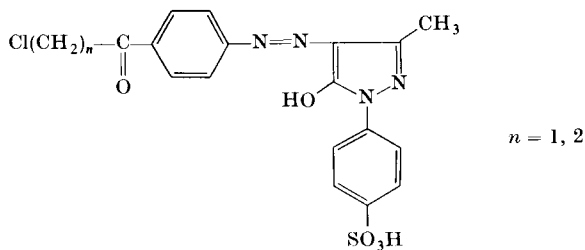


7. Alkine Carboxamides

In a Ciba patent describing mainly acrylamide dyestuffs, propiolic chloride, $\text{CH}\equiv\text{C}-\text{COCl}$, is also mentioned as a reactive component.⁴⁸

8. Substituted Aliphatic Ketones

The suitability of dyestuffs containing chloromethyl or β -chloroethyl aryl ketone groups, such as



for the dyeing of cellulose in the presence of alkalies was recognized by BASF⁵ and General Aniline.⁷⁷ Equally good reactivity with cellulose is

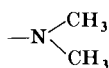
⁷⁵ S, *SP* 370,501 (18.4.1958).

⁷⁶ MCI, *JP* 23,972/64 (1.5.1962); 23,973/64; 23,974/64 (8.5.1962).

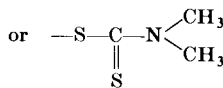
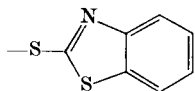
^{76a} NSK, *JP* 24,545/67; 24,546/67 (7.10.1964).

⁷⁷ G, *USP* 3,232,927 (31.12.1962).

shown by phenyl ethyl ketone groups with other mobile groups in the β -position, such as

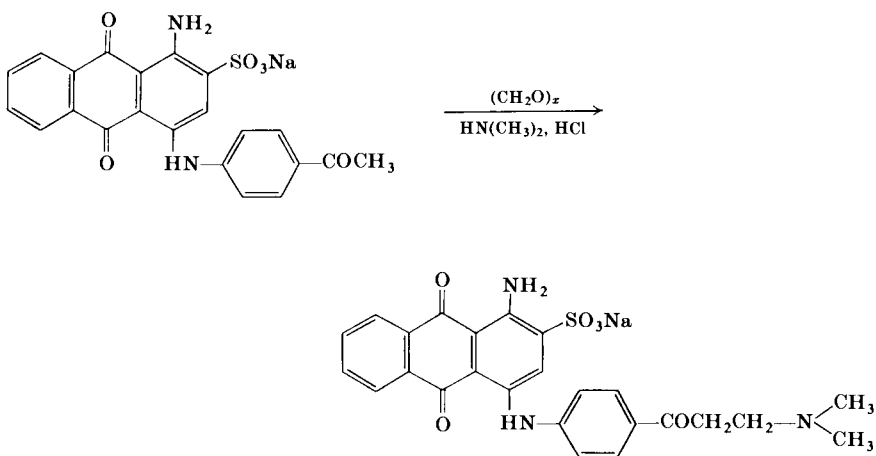


Ref. 78

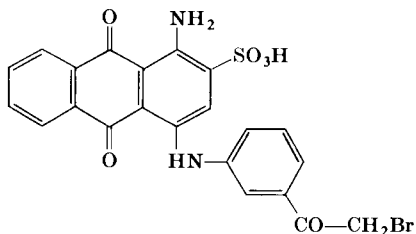


Ref. 79

In the case of β -dialkylaminoethyl aryl ketones, synthesis from the essential acetophenone derivatives⁷⁸ is particularly simple by the Mannich reaction.



Reactive dyes containing chloro- and bromoacetophenone groups, such as the blue



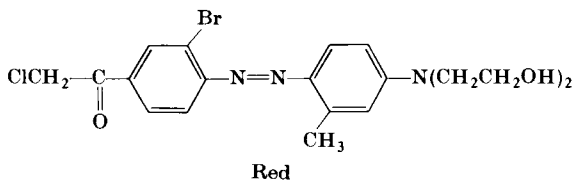
are recommended by Sandoz for the dyeing of wool and polyamide fibers.⁸⁰

⁷⁸ BASF, BP 857,391 (23.5.1958).

⁷⁹ ICI, BP 903,432 (21.1.1960).

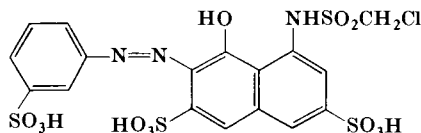
⁸⁰ S, BeP 608,149 (13.9.1960); 609,090 (12.10.1960).

Reactive disperse dyes for polyamide fibers also contain halomethyl ketone residues.⁸¹



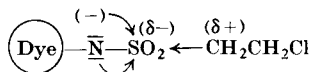
9. Amides of Substituted Aliphatic Sulfonic Acids

a. Substituted Methanesulfonamides. In chloromethyl sulfone groups the halogen atom is known to be extremely slow to react,⁸² for which reason the reactive dyestuffs produced from chloromethanesulfonyl chloride and claimed by Shikoku Chem. Ind.⁸³ react with cellulose difficultly and in moderate yield.



b. Substituted Ethanesulfonamides. i. β-Haloethylsulfonamides. In the first patents of Ciba¹² and Cassella¹³ for cellulose-reactive dyes containing β-halopropionylamide groups, β-haloethylsulfonamide residues were also claimed as reactive groups.

The acidity of the α-methylene hydrogen atoms is reduced by the sulfonamide bridge ionized in the alkaline medium, and the halogen atom is therefore inactivated for base-catalyzed elimination.



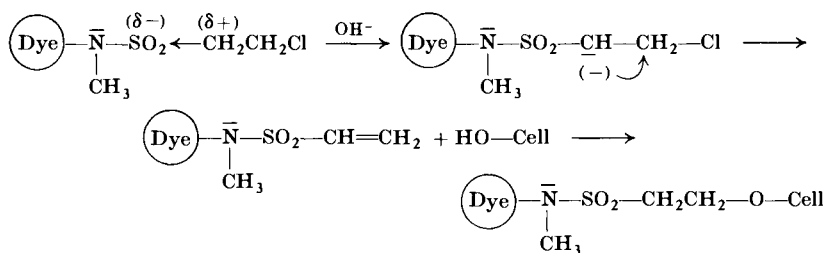
Definite progress was therefore made when in 1962 Farbwerke Hoechst alkylated the sulfonamide nitrogen of dyestuffs of this and similar types (β-sulfatoethylsulfonamides, vinylsulfonamides),⁸⁴ thus leading to much more reactive products.

⁸¹ ICI, *BP* 879,263 (1.10.1958); S, *BeP* 597,309 (11.12.1959).

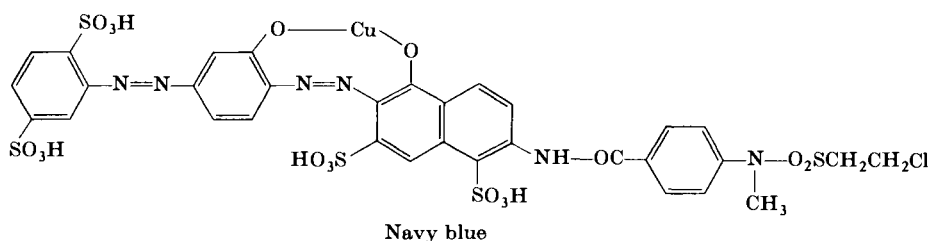
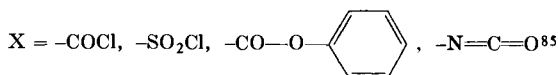
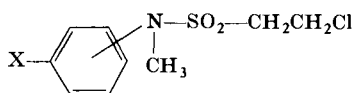
⁸² Schöberl, A., and Wagner, A., in Houben-Weyl, "Methoden der organischen Chemie," 4th ed., Vol. IX, p. 249. Thieme, Stuttgart, 1955.

⁸³ Shikoku Chem. Ind. Co., Ltd., *JP* 28,934/65 (1.10.1962); 4,867/66 (1.10.1962).

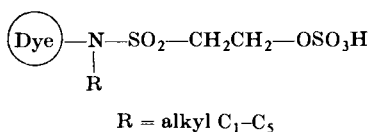
⁸⁴ FH, *BeP* 628,209 (8.2.1962).



Synthesis can also be achieved by reaction of dyestuffs containing amino groups with acylating benzene derivatives of the type



ii. β -Sulfatoethylsulfonamides. This reactive group developed exclusively by Farbwerke Hoechst, and on which Remazol D dyestuffs⁸⁶ introduced by this firm in 1964 are based, was claimed from the start only for *N*-alkyl-substituted sulfonamide nitrogen.⁸⁷

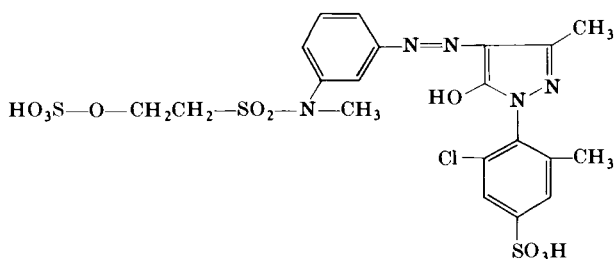


⁸⁵ FH, BeP 647,960 (14.5.1963); 649,112 (10.6.1963).

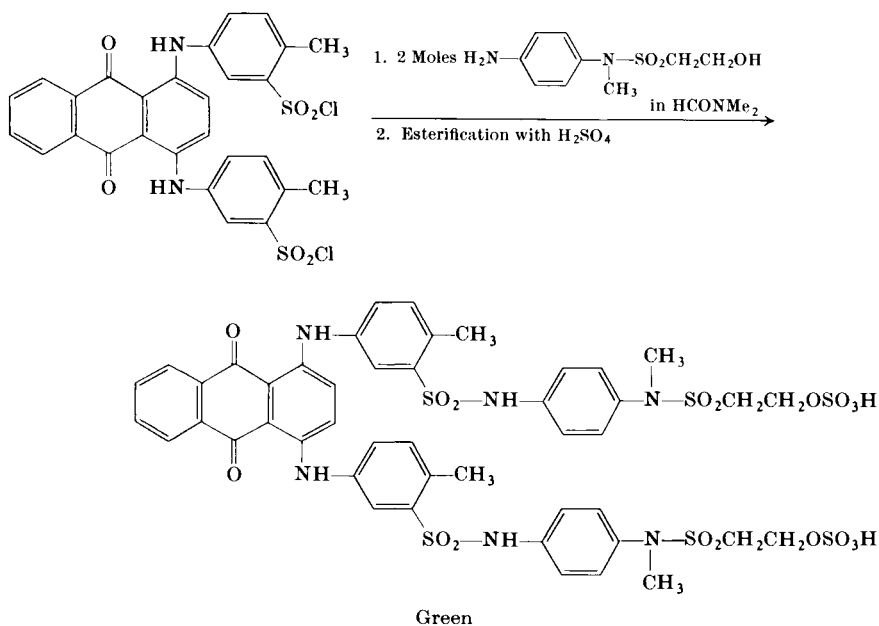
⁸⁶ F. Meininger, *Industrie Chimique Belge, Science* (1967), 36th Congr. Intern. Chim. Ind., Brüssel, Vol. III, p. 76; FH, BeP 614,415 (24.2.1961).

⁸⁷ FH, BeP 606,461 (22.7.1960); 621,776 (26.8.1961).

The production of azo dyes can be achieved, for example, by coupling of appropriately substituted components.⁸⁶

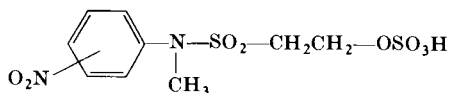


Other syntheses consist in the condensation of organic dyes containing reactive halogen atoms with suitable amino derivatives.⁸⁸



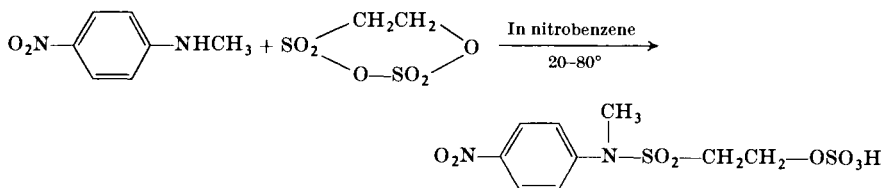
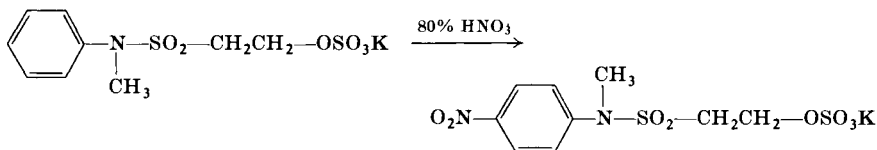
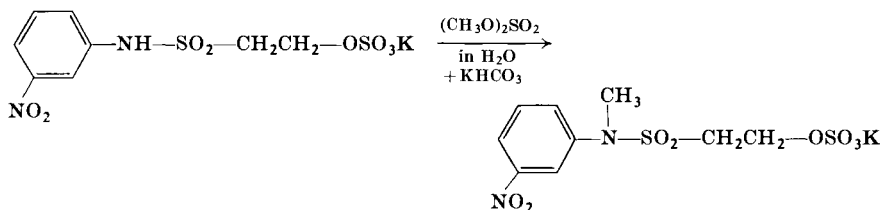
See also ref. 85.

The various production processes for the required intermediate products

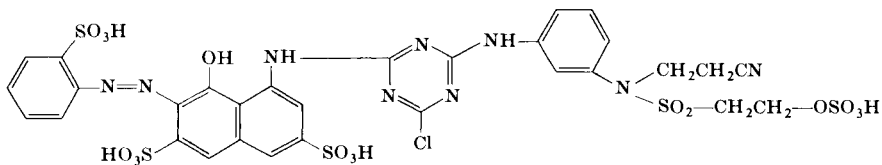


were developed thoroughly:

⁸⁸ FH, *B&P* 611,053 (1.12.1960).

(1) Acylation of secondary aromatic amines with carbylsulfate⁸⁹(2) Nitration of benzene derivatives containing reactive groups⁹⁰(3) Alkylation of corresponding secondary arylsulfonamides⁹¹

The analogous alkylation of dyes containing a secondary sulfonamide group is described in reference 84. A more recent application⁹² relates to dyes containing substituted alkyl residues (C₁-C₄) attached to the sulfonamide nitrogen.



Where, as in the present case, the alkyl residues are substituted negatively (CN group), this should lead to an increased reactivity.

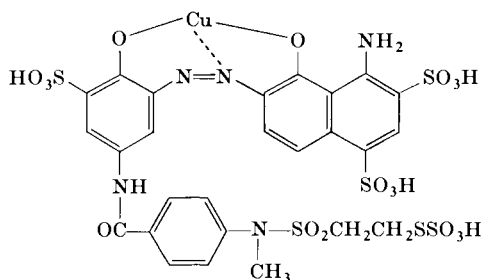
⁸⁹ FH, *DAS* 1,176,647 (12.1.1961); *DBP* 1,181,204 (6.5.1961).

⁹⁰ FH, *FP* 1,324,634 (6.6.1961).

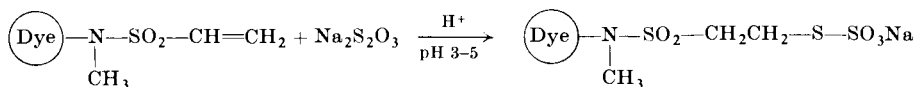
⁹¹ FH, *BeP* 621,260 (9.8.1961).

⁹² FH, *BeP* 639,251 (26.10.1962).

The β -thiosulfatoethylsulfonamides corresponding to the previously described β -sulfatoethylsulfonamides are also good reactive groups.⁹³

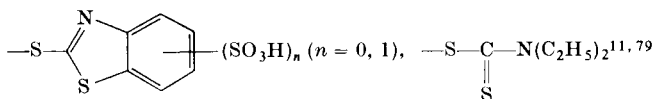


They are obtained by addition of sodium thiosulfate to the *N*-alkylvinylsulfonamide dyes.⁹³



In a number of applications, ethanesulfonamides substituted in the β -position by the following other mobile groups containing oxygen or sulfur

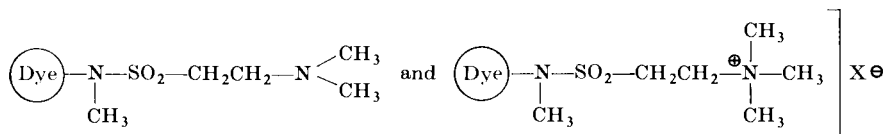
$\text{X} = -\text{OCOCH}_3^{85}; -\text{SO}_2\text{R}', -\text{SOR}', -\text{SR}'$
 $(\text{R}' = \text{hydrocarbon or heterocyclic residue})^{35, 36}$



were also included in the claims, in most cases without being supported by examples.

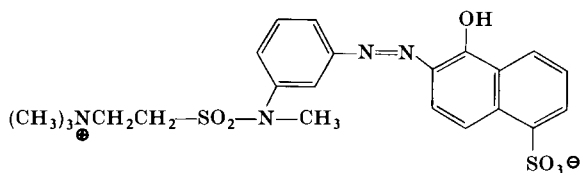
iii. β -Dialkylamino or quaternary ammonium ethanesulfonamides. In previously mentioned literature wide claims also include these reactive groups.²⁶ In ref. 9 the dyestuffs are free from sulfo groups; sulfonium groups in the β -position, $-\text{S}^+(\text{CH}_3)_2$, are also mentioned here.

On the other hand, three patents of Farbwerke Hoechst relate especially to reactive dyes of the types



⁹³ FH, BeP 668,012 (6.8.1964).

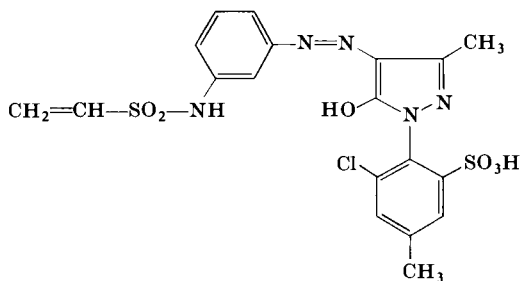
for example



Red

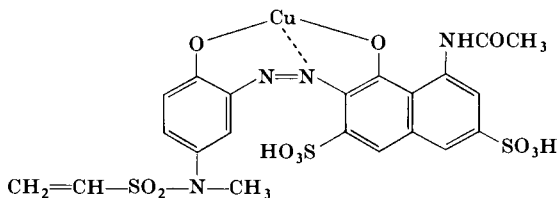
These dyes and their intermediates are produced, for example, by reaction of the corresponding β -halo or β -sulfatoethylsulfonamides, or of vinylsulfonamides, with secondary or tertiary amines and, possibly, subsequent quaternization. The reactivity of these basic mobile groups is at least as high as that of the fundamental β -halo or β -sulfato derivatives.⁹⁴

c. Vinylsulfonamides. BASF discovered in 1958 that the vinylsulfonamide group is able to react with cellulose in an alkaline medium.⁹⁵



Yellow

Good yields can, however, be achieved only by fixation in heat at temperatures exceeding 100°. Only the alkylation of the sulfonamide nitrogen, because the inactivating alkaline ionization to the sulfonamide anion is no longer possible, leads to more reactive dyestuffs, such as⁹⁶



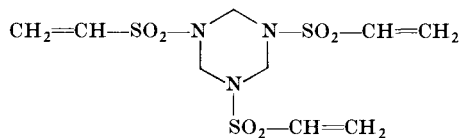
Violet

⁹⁴ FH, *BeP* 632,987 (29.5.1962); 638,176; 638,177 (3.10.1962).

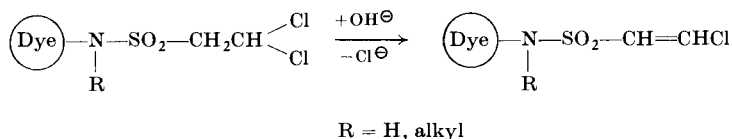
⁹⁵ BASF, *BeP* 583,430 (10.10.1958).

⁹⁶ FH, *BeP* 621,777 (26.8.1961).

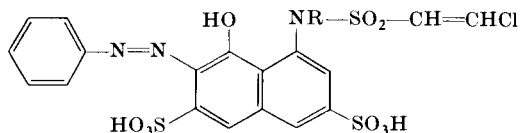
Vinylsulfonamides are also suitable for the synthesis of polyfunctional cross-linking components to link dyestuffs containing reactive hydrogen atoms (Basazol) and cellulose.⁹⁷



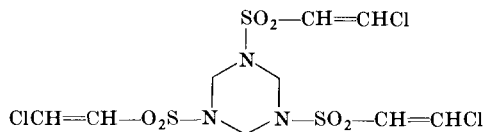
i. β -Chlorovinylsulfonamides. Dyestuffs or dyestuff intermediates containing amino groups capable of acylation yield at pH 5–7 and -30° to $+30^\circ$ in the presence of inert organic solvents with β -chlorovinylsulfonyl chloride, $\text{ClCH}=\text{CHSO}_2\text{Cl}$, or with β,β -dichloroethylsulfonyl chloride, $\text{Cl}_2\text{CH}-\text{CH}_2\text{SO}_2\text{Cl}$, the corresponding sulfonamides, the last-mentioned products being converted, before dyeing, into β -chlorovinylsulfonamides by addition of alkali^{97a}:



In this case also, *N*-alkylsulfonamides ($\text{R} = \text{alkyl}$) should be more reactive in the alkaline medium than dissociable amides attached to nitrogen ($\text{R} = \text{H}$). As examples, the red dyestuff



or the cross-linking agent



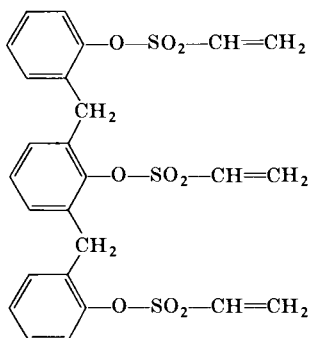
may be mentioned.^{97a}

⁹⁷ BASF, *DBP* 1,147,191 (23.2.1961).

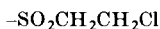
^{97a} FW, *EGP* 59,136 (28.10.1966); *BP* 1,112,789 (19.4.1967).

10. *Esters of Reactive Aliphatic Sulfonic Acids*

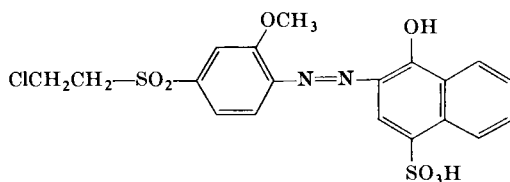
Because of the susceptibility of the sulfonic ester bond to hydrolysis, these esters are without importance. They were mentioned only once by BASF as polyfunctional cross-linking agents for dyes of the Basazol type.⁹⁸

11. *β-Substituted Ethyl Sulfones*

a. β-Haloethyl Sulfones. In 1950 Farbwerke Hoechst recognized that acid azo dyes containing the group



are able to react with textiles, particularly wool, in the presence of alkalis.⁹⁹ In 1956 Ciba claimed the dyeing of cellulose with these really reactive dyes, e.g.,



in an alkaline medium.¹⁰⁰

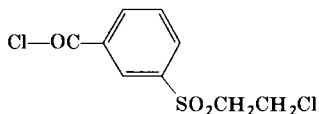
In addition to synthesis from diazo compounds containing *β*-chloroethyl sulfone groups and conventional coupling components, synthesis can also be accomplished by introduction of the *β*-chloroethyl sulfone

⁹⁸ BASF, *BeP* 631,511 (26.4.1962); *DAS* 1,119,253 (18.6.1960).

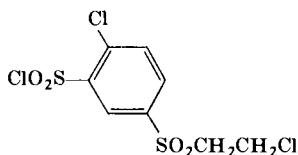
⁹⁹ FH, *DBP* 966,651 (4.7.1950).

¹⁰⁰ CIBA, *BeP* 560,034 (14.8.1956).

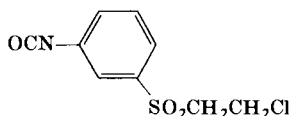
group into the completed dyestuff molecule. In this case, dyes containing amino groups are acylated with carbonyl chlorides, such as^{101, 102}



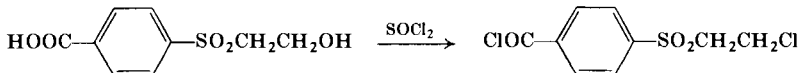
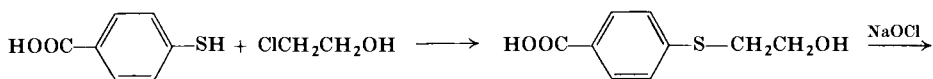
or with sulfonyl chlorides, such as^{102a}



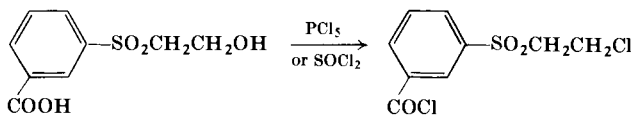
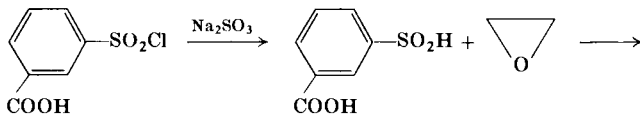
or with isocyanates, such as¹⁰³



Production of these reactive components is carried out as follows¹⁰¹:



or



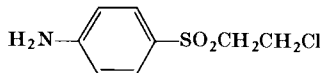
¹⁰¹ Crompton and Knowles Co., *USP* 3,098,096 (27.6.1960).

¹⁰² Crompton and Knowles Co., *USP* 3,261,658 (27.6.1960).

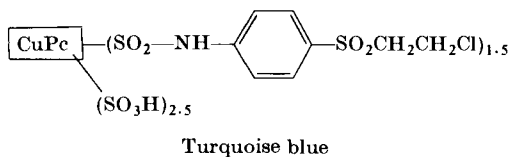
^{102a} K. Matsui, *JP* 8,943/68 (30.9.1964).

¹⁰³ FH, *BeP* 691,797 (24.12.1965).

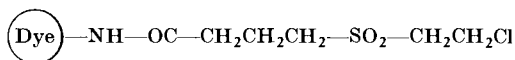
Also by condensation of copper phthalocyanine sulfonyl chlorides with amines, e.g.,



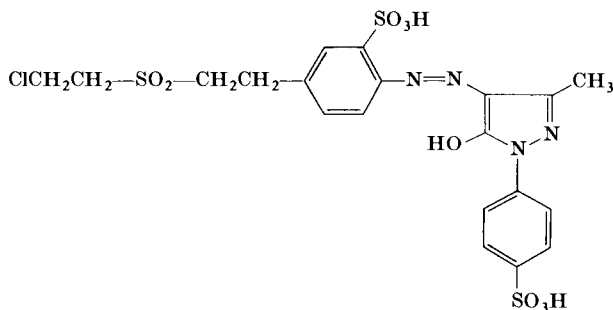
the reactive group can be introduced¹⁰⁴



Cassella has recently developed reactive groups in which the β -chloroethylsulfonyl group is not bound to an aromatic ring but to a non-aromatic cyclic system^{104a} or to an alkylene chain containing 3–11 carbon atoms^{104b} and is introduced, for example, through a carbonyl chloride group:



The direct linking of the dyestuff with the β -chloroethylsulfonyl group through an alkylene chain containing 2–8 carbon atoms is also described.^{104c}



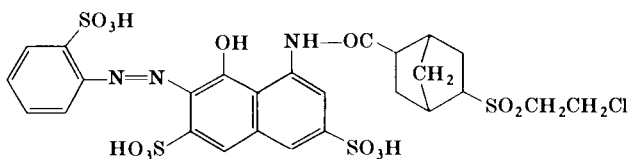
¹⁰⁴ Mitsui Kagaku Kogyo K.K., *BeP* 679,914 (24.4.1965).

^{104a} CFM, *BeP* 698,823 (21.5.1966).

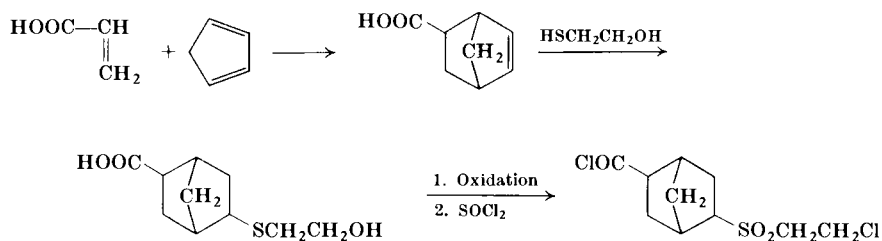
^{104b} CFM, *BeP* 705,839 (3.11.1966).

^{104c} CFM, *BeP* 699,119 (27.5.1966).

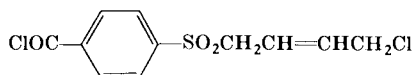
Dyestuffs such as



are notable for high brilliance and ease of rinsing clear in overprint styles. They have attained technical importance. The original synthesis of the reactive component proceeds through the following stages^{104a}:

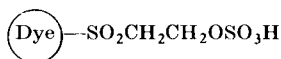


Noteworthy are reactive components extended by introduction of a vinyl group, such as



described by Sandoz.^{104d}

b. β-Sulfatoethyl Sulfones. Remazol dyestuffs of Farbwerke Hoechst, technically one of the most important reactive dyestuff ranges, contain the reactive group

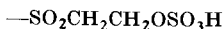


They are based on original patents of this firm concerning the fixation of water-soluble organic compounds containing β -sulfatoethyl sulfone groups on fiber materials in the presence of alkalis and at higher temperatures,¹⁰⁵ as well as a number of applications relating to dyestuffs

^{104d} S, *BeP* 712,595 (23.3.1967).

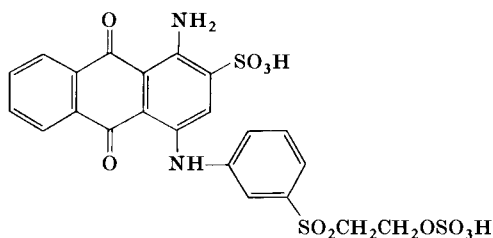
¹⁰⁵ FH, *DBP* 965,902 (19.7.1949).

containing sulfonic and carboxyl groups together with the reactive group¹⁰⁶:

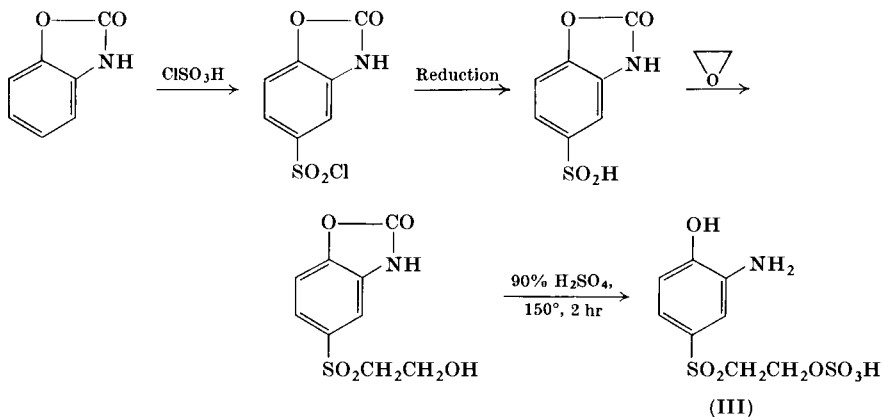


The importance of these dyestuffs, originally conceived for wool, for the dyeing of cellulosic fibers was presumably not fully recognized by Farbwerke Hoechst (see ref. 107) until the discovery of the first technically useful cellulose-reactive dyestuffs (Procion) by Rattee and Stephen (1954) and also by Ciba.¹⁰⁰

In 1957 Hoechst introduced Remazol dyestuffs, e.g., Remazol Brilliant Blue R,



and subsequently developed the field both on the dyestuff side (e.g., refs. 108 and 109) and also with regard to synthesis of the diazo and other dyestuff components already containing the reactive group $-\text{SO}_2-\text{CH}_2\text{CH}_2-\text{OSO}_3\text{H}$ (e.g., ref. 110).



¹⁰⁶ FH, DBP 960,534 (10.1.1950); 966,651 (4.7.1950); 925,121 (20.2.1952).

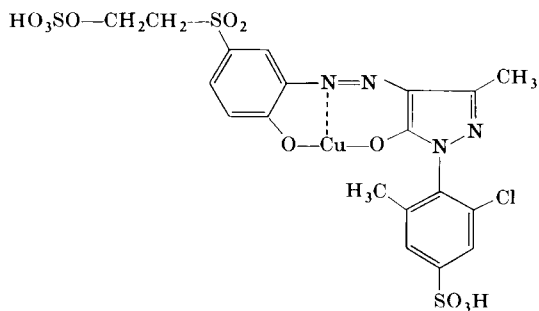
¹⁰⁷ J. Heyna, *Angew. Chem.* **74**, 966-969 (1962); Bhagwanth, M. R. R., Daruwalla, Sharma, V. N., and Venkataraman, K., *Textile Res. J.* **40**, 392 (1970).

¹⁰⁸ FH, BeP 577,140 (26.3.1958).

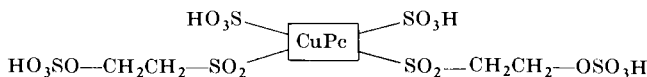
¹⁰⁹ FH, BeP 644,252 (23.2.1963).

¹¹⁰ FH, DAS 1,153,029 (6.10.1960).

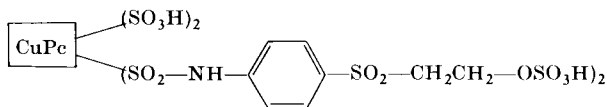
The aminophenol (III) is used in the synthesis of fast-to-light copper complex dyes, such as the yellow-brown¹⁰⁸



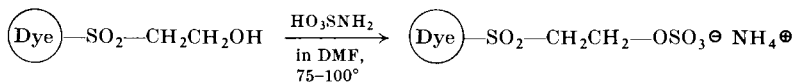
Turquoise shades are obtained by reduction of copper phthalocyanine sulfonyl chlorides containing sulfo groups to sulfinic acid, addition of ethylene oxide, and esterification with sulfuric acid¹⁰⁹:



Copper phthalocyanine sulfonyl chloride sulfonic acids can also be condensed with amines containing reactive groups.



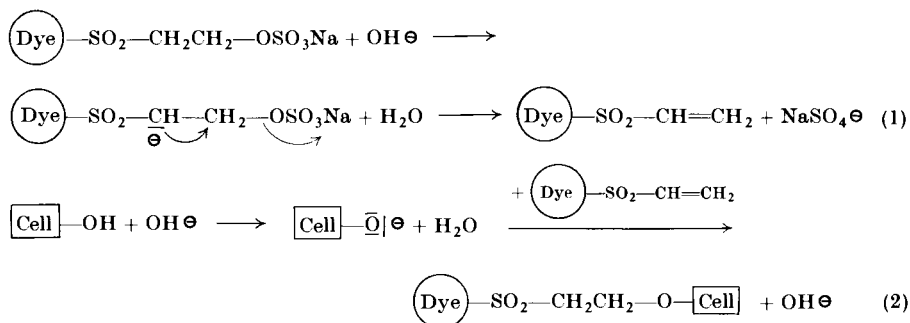
The esterification of the β -hydroxyethyl sulfone group with sulfamic acid instead of sulfuric acid offers the advantage that no excess acid remains to be neutralized, so that the dyestuffs are obtained in a purer salt-free form.¹¹¹



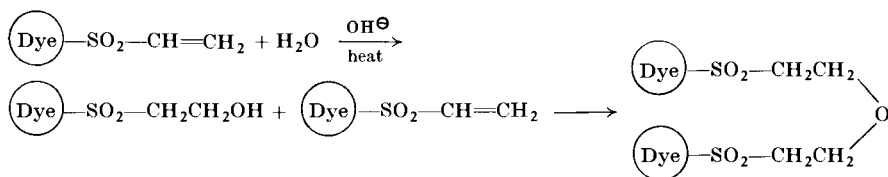
Remazol dyestuffs dye cellulosic fibers from a long liquor at 50–60° in the presence of soda ash and are therefore considered to be warm-dyers.

¹¹¹ FH, *BeP* 655,035 (29.10.1963); *GP* 1,235,470 (20.1.1964); *FP* 1,424,904 (18.2.1964); 1,425,060 (20.2.1964); *BeP* 664,700 (30.5.1964); 673,210 (2.12.1964).

The following reactions take place.¹⁰⁷ The addition of alkali leads very quickly even at room temperature to the separation of sulfate ions and conversion to the vinyl sulfone form [Eq. (1)], which adds to the cellulose anions present in the alkaline medium [Eq. (2)].

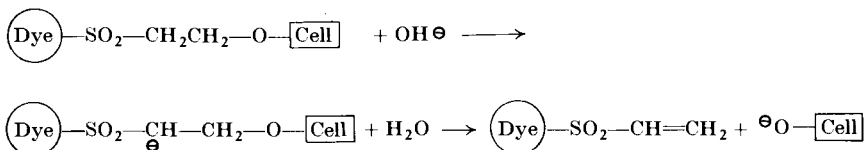


In side reactions the vinyl sulfone group adds water to give β -hydroxyethyl sulfone, which can react with a second molecule of vinyl sulfone dye to form the ether.¹⁰⁷



It is obvious that the fiber-dyestuff bond formed in these reactions breaks down with relative ease in an alkaline medium, i.e., the dyeings do not possess particularly high fastness to washing at the boil.

Also in this case the hydroxyl ions act on the acid α -methylene group.¹⁰⁷

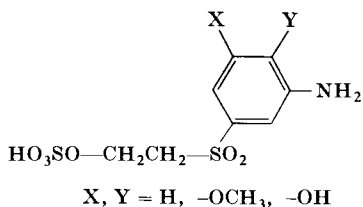


The cellulose-ether bond is nevertheless very resistant to acid hydrolysis, and this may be important in the event of storage in an acid atmosphere. Because the sulfate anion is easily split out, technical products always

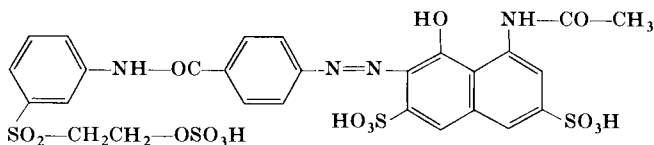
contain in addition to the intact reactive group small proportions of the vinyl sulfone and β -hydroxyethyl sulfone.¹¹²

In the reduction of Remazol dyes with stannous chloride and hydrochloric acid, β -hydroxyethyl sulfones are predominantly formed, and this has been utilized in the analysis of commercial products.^{112a}

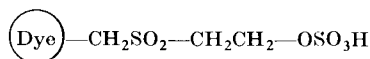
Most β -sulfatoethyl sulfone dyes on the market are produced, as shown above, from amines of the type



by diazotization and coupling or by condensation reactions. In addition, numerous other possibilities are described for introduction of the $-\text{SO}_2\text{CH}_2\text{CH}_2\text{OSO}_3\text{H}$ group into the dyestuff molecule. Farbwerke Hoechst has obtained more substantive reds by incorporation of an aminobenzoyl residue.¹¹³



In 1956 Ciba mentioned cellulose-reactive dyes which contain the sulfone group bound to the aromatic ring not directly, but through a methylene group.¹⁰⁰

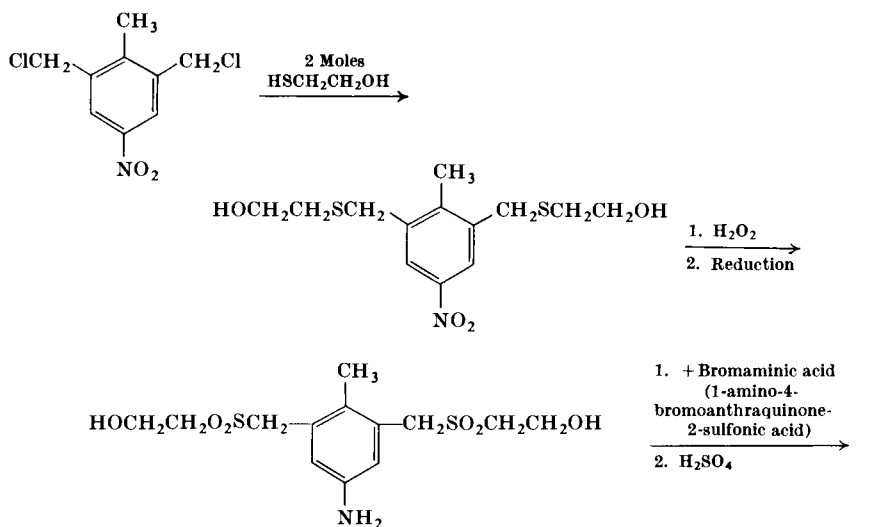


General Aniline and Film Company later developed this field systematically, synthesis being achieved, for example, by the following procedure:

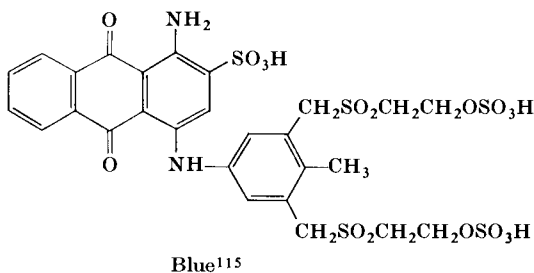
¹¹² L. A. Kovzhin and A. A. Kharkharov, *Tekhnol. Tekstil. Prom.* **3**, 95-97 (1963).

^{112a} J. Panchartek, Z. J. Allan, and I. Poskocil, *Collect. Czech. Chem. Commun.* **27**, No. 1, 268-275 (1962).

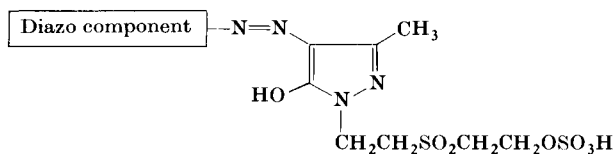
¹¹³ FH, *BeP* 592,853 (11.7.1959); 609,469 (22.10.1960).



Ref. 114



Corresponding types with only one reactive group are recommended by GAF as acid polyamide dyes.¹¹⁶ The β -sulfoethylsulfonyl group can also be bound to the dyestuff molecule through an ethylene bridge.^{116a}



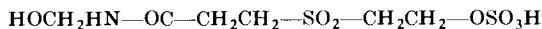
¹¹⁴ G, *USP* 3,019,266; 3,019,268 (8.12.1959).

¹¹⁵ G, USP 3,062,830 (27.11.1959); FP 1,282,761; 1,288,071 (30.12.1959).

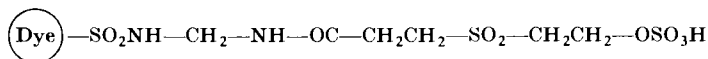
¹¹⁶ G, *SP* 13,653/62; 13,735/62; 13,946/62 (28.12.1961).

^{116a} NSK, *JP* 26,821/67 (12.10.1964).

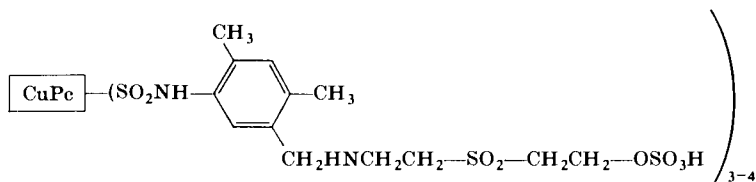
As already explained in Section II,A,1,*b,v*, Sumitomo Chemical Company introduced the methyrolamide



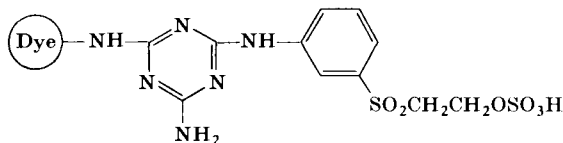
into electrophilically substitutable aromatic rings or sulfonamide groups of dyestuffs³⁹:



or



s-Triazine is claimed as a bridge link by Nippon Kayaku.¹¹⁷



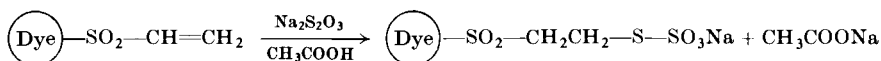
i. β-Thiosulfatoethyl sulfones. The thiosulfato ester group



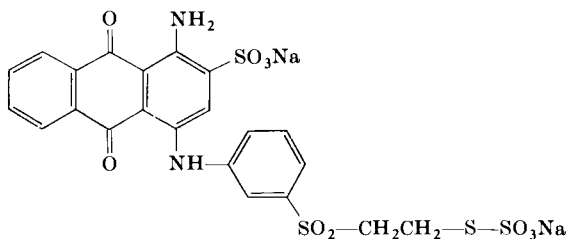
is a mobile group which reacts with cellulose as readily as the sulfate anion; on the other hand, in an aqueous alkaline medium it splits off less easily, i.e., the dyestuffs possess a higher stability in pad solutions and print pastes. They are produced by adding at pH 3–8.5 sodium thiosulfate to the vinyl sulfone form of the starting dye or of an intermediate product; the liberated alkali is neutralized by reaction with acetic acid.¹¹⁸

¹¹⁷ Nippon Kayaku Co., Ltd., *JP* 17,113/65 (25.7.1962).

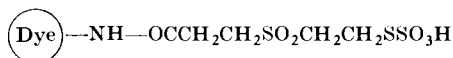
¹¹⁸ FH, *BeP* 650,713 (17.7.1963); 655,503 (7.11.1963); 666,192 (30.6.1964).



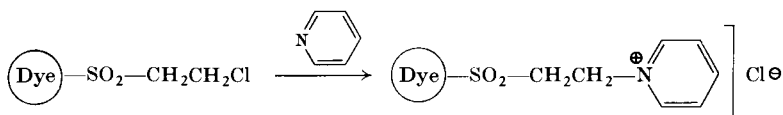
e.g., the blue



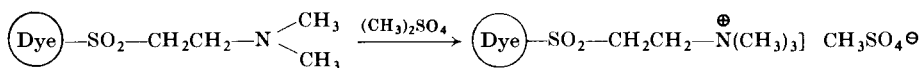
CO_2 may also be used to neutralize the caustic soda formed, as, for example, in the production of the group claimed by Sumitomo.^{116a}



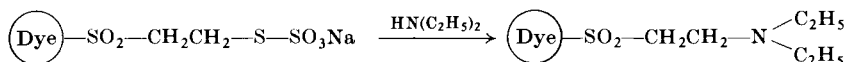
c. *β -Amino or β -Quaternary Ammonium Ethyl Sulfones.* In 1952 Hoechst described the production of these dyes from β -chloroethyl sulfones and tertiary amines:



or by quaternization of β -dialkylaminoethyl sulfones¹¹⁹:



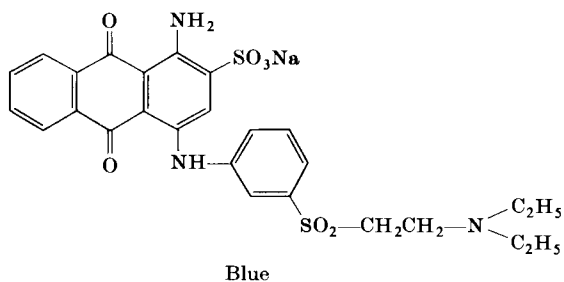
Other syntheses, e.g., from β -thiosulfatoethyl sulfones, were also subsequently mentioned.¹²⁰



¹¹⁹ FH, DAS 1,064,055 (10.9.1952).

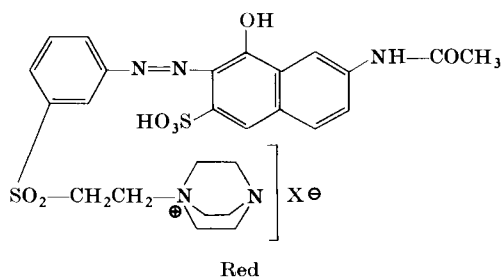
¹²⁰ FH, BeP 651,922 (16.8.1963).

Not until 1958 was the value of β -dialkylaminoethyl sulfone dyestuffs, e.g.,

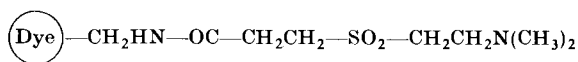


for the printing and dyeing of cellulose in presence of alkalis¹²¹ fully recognized.

In 1961 ICI made the same claim for dyes containing quaternary ammonium groups in the β -position.^{26, 122}



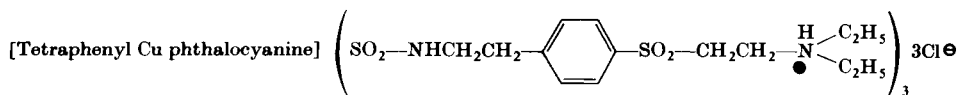
According to the principle of the condensation of substitutable dyes with *N*-methyrolamides of sulfonylcarboxylic acids mentioned in Section II.A.1,*b,v*,³⁹ this reactive group can also be introduced.



Dyestuffs of this type which are free from anionic, water-solubilizing groups, e.g.,

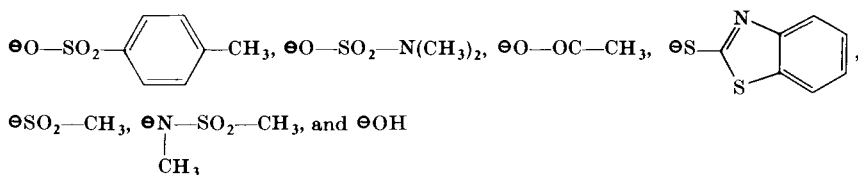
¹²¹ FH, *DAS* 1,103,886 (27.9.1958).

¹²² ICI, *BP* 969,033 (3.7.1961).



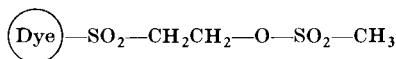
can be fixed on cellulosic materials in a weak acid medium from a long liquor or after padding with their neutral solution by a simple treatment in dry heat or by steaming.^{9, 123}

d. *Other β -Substituted Ethyl Sulfones.* In addition to the previously discussed, technically important mobile groups in the β -position of the ethyl sulfone carrier system, a large number of others, e.g.,

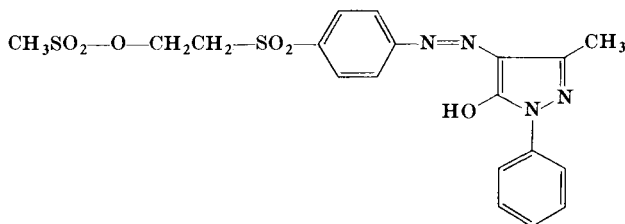


are described in the patent literature.

i. *β -Sulfonic ester groups.* β -Sulfonic ester groups



are probably most important for wool dyes, for which they were proposed in 1953 by Ciba¹²⁴; ICI also used this reactive group in 1:2 metal complex dyes.¹²⁵ This mobile group is also of value in reactive disperse dyes for polyamide fibers, e.g.,¹²⁶



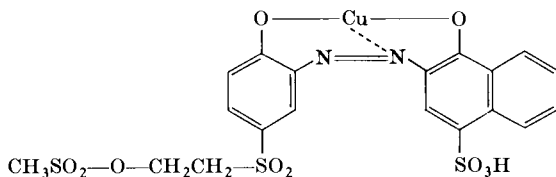
¹²³ FH, *BeP* 638,181 (3.10.1962).

¹²⁴ CIBA, *DAS* 1,001,437 (28.1.1953).

¹²⁵ ICI, *BeP* 585,284 (5.12.1958).

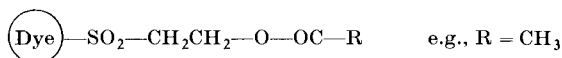
¹²⁶ ICI, *BP* 869,100; 877,250 (29.10.1958).

It was mentioned as the reactive group of cellulose dyes in the original dyeing patent of Ciba¹⁰⁰; ICI claimed azoic copper complex dyes, such as¹²⁷

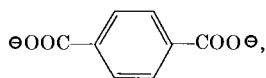


Sandoz described sulfonic ester anions as leaving groups not only in β -position to sulfonyl groups, but also on a variety of other carrier systems.^{127a}

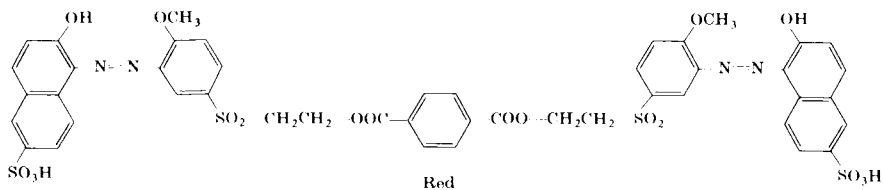
ii. β -Acyloxy groups. β -Acyloxy groups



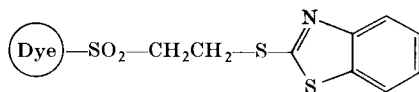
are suitable for water-soluble reactive dyes for cellulose^{128, 129} and also for water-insoluble reactive dyes for polyamides.¹³⁰ The use of terephthalic acid as a bifunctional mobile group,



is interesting.¹²⁹



iii. β -Heterylmercapto groups. Groups such as



¹²⁷ ICI, *FP* 1,285,552 (11.3.1960).

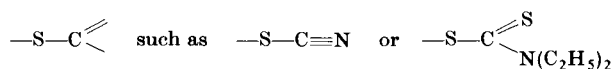
^{127a} S, *FP* 1,233,530 (25.10.1957).

¹²⁸ ICI, *FP* 1,274,732 (12.10.1959).

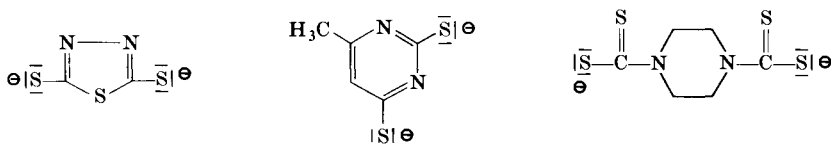
¹²⁹ ICI, *BP* 949,316 (14.7.1960).

¹³⁰ ICI, *FP* 1,274,731 (12.10.1959).

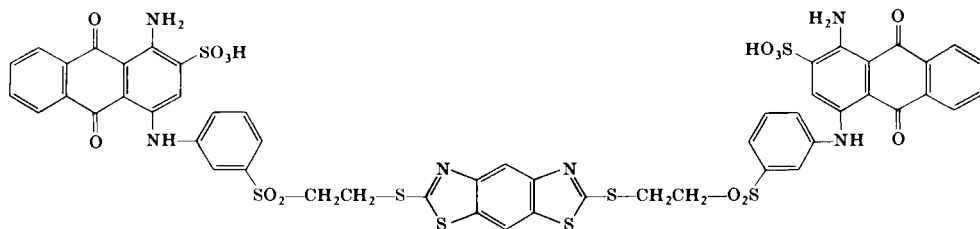
and other mercapto residues of the general structure



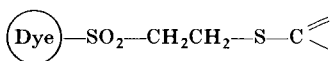
thanks to their high nucleophilic reactivity, can easily be introduced by substitution of the β -sulfatoethyl sulfone form or by addition to the vinyl sulfone group.¹¹ In this case also, bifunctional mobile groups such as



lead to doubly reactive dyes, e.g.,¹³¹

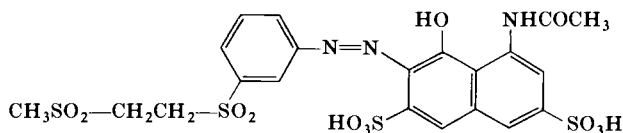


Reactive groups of the type described here



are suitable mainly for cellulose dyestuffs.⁷⁹

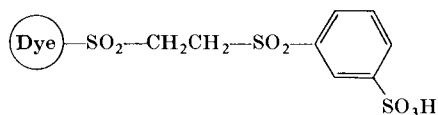
Less technical importance is possessed by *sulfonyl groups in the β -position*, e.g., in the red dye¹³²



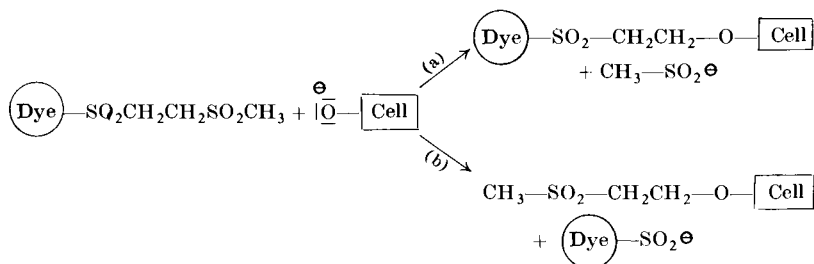
¹³¹ ICI, BP 949,624 (14.7.1960).

¹³² Traitements Chimique des Textiles, FP 1,323,016 (23.2.1962).

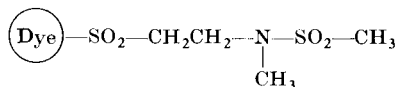
This also applies where they contain water-solubilizing groups¹³³



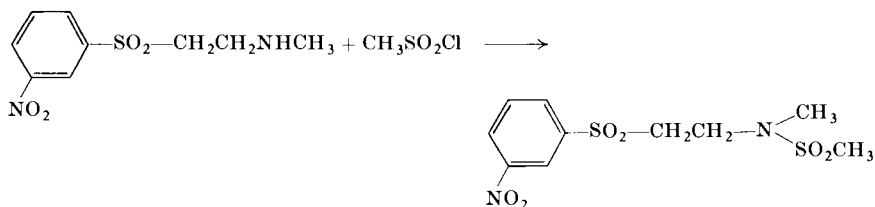
This is explained by the fact that γ -disulfones can split off a sulfinate anion on both sides, which, however, results in a cellulose dyeing only in case (a) (see ref. 134).



An unusual mobile group was discovered by Farbwerke Hoechst in the *N*-methylethanesulfonamide residue.¹³⁵



This can be produced by acylation of β -monomethylaminoethyl sulfones with methanesulfonyl chloride.



The reaction of these dyes with cellulose requires very energetic conditions.

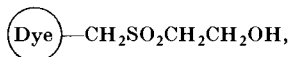
That the β -hydroxyethyl sulfone group on which Remazol dyestuffs and

¹³³ CFM, *FP* 1,432,259 (5.5.1964).

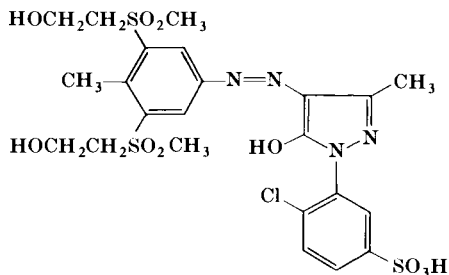
¹³⁴ Houben-Weyl, "Methoden der organischen Chemie," 4th ed., Vol. IX, p. 258, Thieme, Stuttgart, 1955.

¹³⁵ FH, *FP* 1,411,270 (20.8.1963).

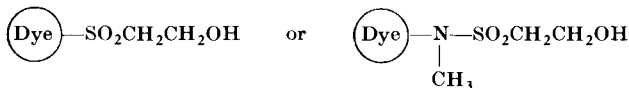
all other reactive β -esters are based is itself a useful reactive residue was first recognized by GAF in dyestuffs of the type



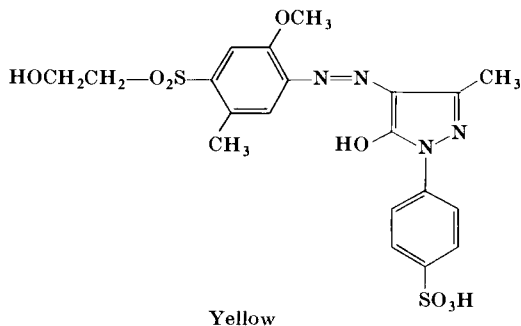
e.g., the yellow¹³⁶



Reaction with the fiber in the presence of alkali takes place, however, only on heating to higher temperatures.¹³⁷ According to a subsequent patent, similar behavior is shown by β -hydroxyethylsulfone or β -hydroxyethylsulfonyl-*N*-alkylamide groups bound to aromatic rings¹³⁸:



e.g.,



Fixation is obtained, for example, by treatment for 1 minute in dry heat at 200° in the presence of soda ash.

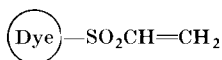
¹³⁶ G, *FP* 1,282,762 (30.12.1959); *USP* 3,277,075 (31.12.1959).

¹³⁷ G, *USP* 3,100,131 (4.1.1960).

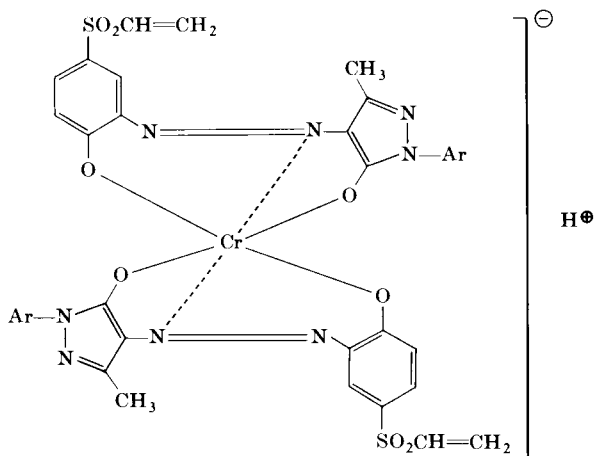
¹³⁸ FH, *FP* 1,416,127 (25.11.1963).

12. Vinyl Sulfones

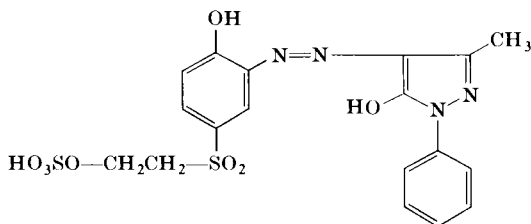
a. *Unsubstituted Vinyl Sulfones.* As stated above, the vinyl sulfone form is the really reactive intermediate stage in the alkaline application of β -substituted ethyl sulfone dyes. Farbwerke Hoechst therefore also claimed in 1950 within the scope of their basic applications in this field the "fixation of dyestuffs of the type



on bases of fibrous structure in presence of alkalis."¹³⁹ Technical importance has been gained by the free vinyl sulfone group in wool-reactive dyestuffs applied from a neutral bath, such as Remalan dyes of Farbwerke Hoechst.^{107, 140}



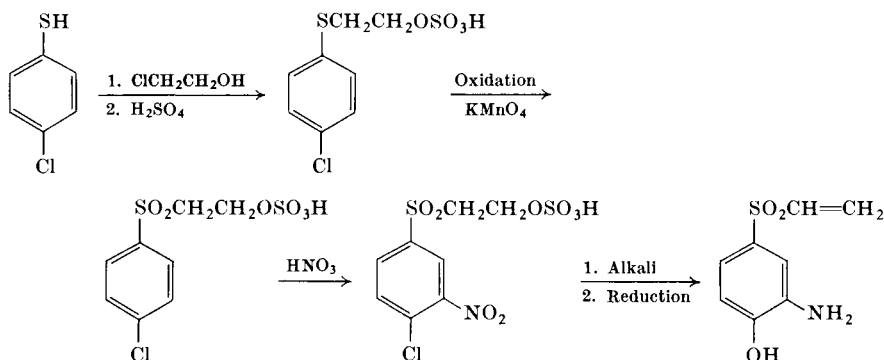
These dyestuffs are obtained by a short alkaline aftertreatment of the initially synthesized 1:2 metal complexes of the corresponding β -sulfatoethyl sulfone dyes, e.g., to the 1:2 chrome complex of ¹⁴⁰



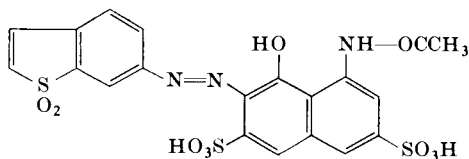
¹³⁹ FH, DBP 960,534 (10.1.1950).

¹⁴⁰ FH, DBP 953,103 (16.7.1954).

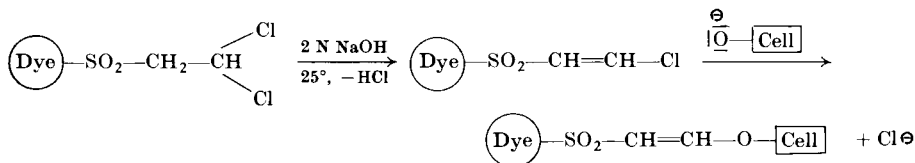
Also for Geigy, who obtained their water-soluble Irgalan dyestuffs, which are applied from a neutral bath, by introduction of the hydrophilic methyl sulfone group into 1:2 metal complexes free from sulfo groups, it was an obvious step to replace this group by the likewise hydrophilic vinyl sulfone residue which at the same time reacts with wool.¹⁴¹ Synthesis was carried out as follows:



As an original variant of the vinyl sulfone group, ACNA has recently described thiophene dioxide as a reactive component, especially for wool and polyamide dyestuffs.^{141a}



b. β -Halovinyl Sulfones. Wolf and Stefaniak discovered in 1964 that dyestuffs containing the β -chlorovinyl sulfone group or its preceding stage, the β,β -dichloroethyl sulfone residue, react with cellulose in an alkaline medium with nucleophilic substitution of the chlorine atom in the β -position, i.e., as vinylogous sulfonyl chloride.¹⁴²

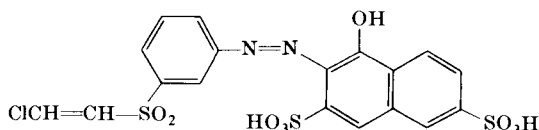


¹⁴¹ Gy, *FP* 1,118,705 (5.2.1954).

^{141a} Acna, *FP* 1,511,695 (14.1.1966).

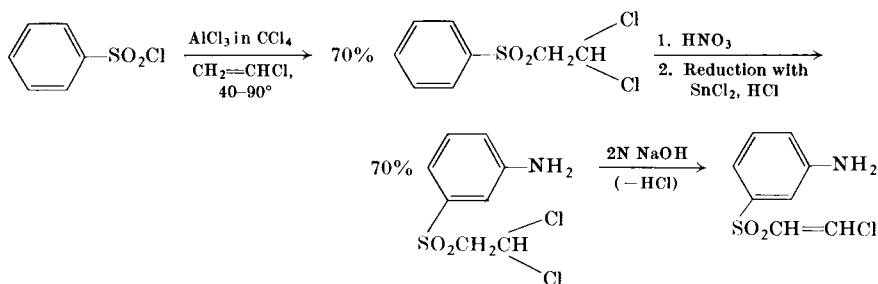
¹⁴² F. Wolf and St. Stefaniak, *Melliand Textilber.* **47**, 767-772 (1966).

For example, the dye

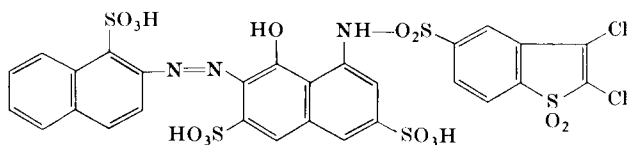


gives a bright reddish orange with an 85% fixation yield when applied to cellulose from a long liquor at 60° with an addition of trisodium phosphate (see Farbenfabrik Wolfen¹⁴³).

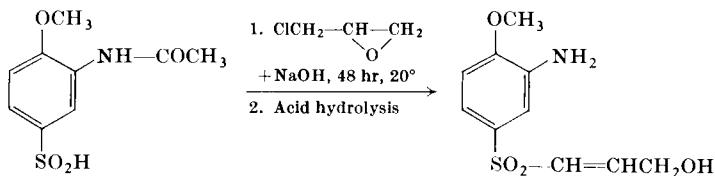
The intermediate products are synthesized as follows¹⁴²:



Moreover, Acna developed as cyclized variants of the (α), β -(di)halovinyl sulfone group dyestuffs containing 2,3-halobenzothiophene dioxide.^{143a}



c. Other Substituted Vinyl Sulfones. The intermediate products easily obtained from sulfinic acids and epichlorohydrin,¹⁴⁴

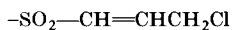


¹⁴³ FW, *BeP* 663,900 (13.7.1964); *RP* 181,213 (26.10.1964); *DP* 6,413,685 (25.11.1964).

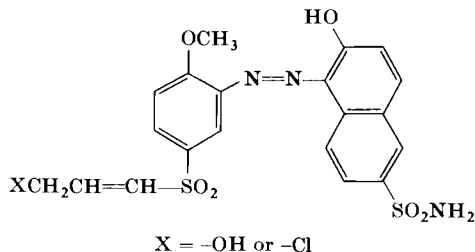
^{143a} Acna, *FP* 1,502,391 (3.12.1965).

¹⁴⁴ ICI, *BeP* 592,883 (13.7.1959); *FP* 1,302,434 (13.5.1960).

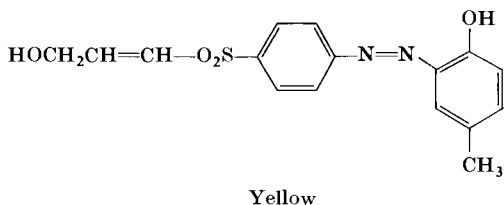
and also the 3'-chloropropene-1',2'-yl-sulfonyl compounds



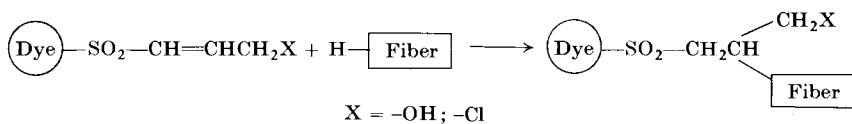
which can be obtained from them with chlorinating agents, are particularly suitable for the synthesis of wool-reactive dyes, such as the violet 1:2 chrome complex of¹⁴⁴



Polyamide disperse dyestuffs are also claimed.¹⁴⁵

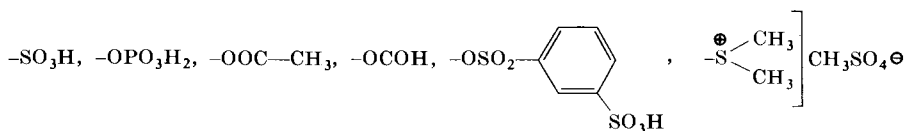


The nucleophilic groups of the fiber ($-\text{SH}$, $-\text{NH}_2$, $-\text{OH}$, etc.) are added to the double bond.



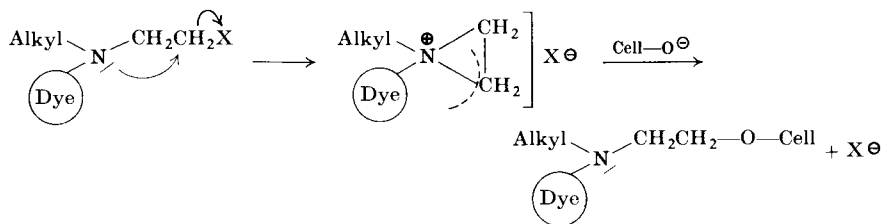
13. β -Substituted Ethylamine Derivatives

All ethylamine derivatives containing a group in the β -position which is capable of splitting off together with the bonding electron pair, e.g.,

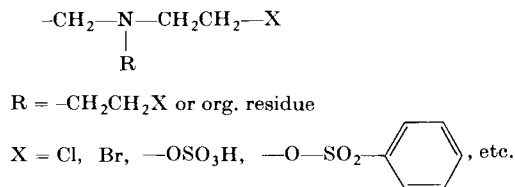


¹⁴⁵ ICI, BP 880,886 (13.7.1959).

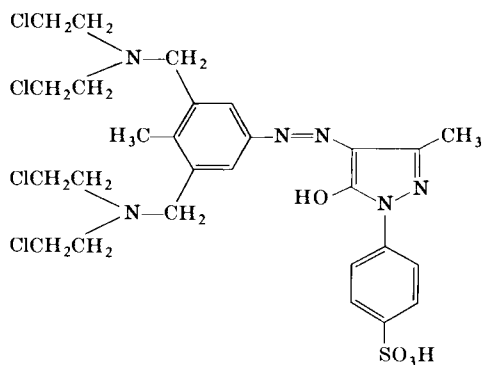
should react with cellulose in an alkaline medium according to the following scheme¹⁴⁶:



a. β-Haloethylamines. This reactive group was recommended by BASF at a very early date for the dyeing of cellulosic materials.¹⁴⁷ Bayer and Sandoz used fixation components containing several residues of $>\text{NCH}_2\text{CH}_2\text{Cl}$ together with dyes containing groups capable of alkylation.^{148, 149} GAF claimed dyestuffs with at least two groups



attached to a benzene nucleus of the dyestuff, e.g.,¹⁵⁰



¹⁴⁶ K. G. Kleb, E. Siegel and K. Sasse *Angew. Chem.* **76**, 423 (1964).

¹⁴⁷ BASF *DAS* 1,066,682/1,066,684 (19.12.1956); 1,067,773 (2.5.1957).

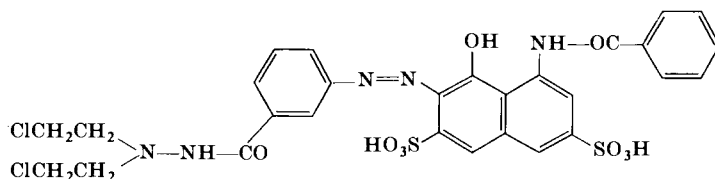
¹⁴⁸ FBy, *BeP* 574,366 (1.2.1958).

¹⁴⁹ S, *FP* 1,381,885 (8.2.1963); *BeP* 650,041 (5.7.1963).

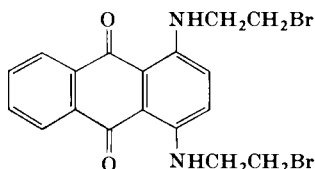
¹⁵⁰ G, *USP* 3,294,778 (20.11.1961).

(See also the ICI patent.¹⁵¹)

The *N,N*-bis(β -chloroethyl)hydrazide dyestuffs¹⁵² of the type

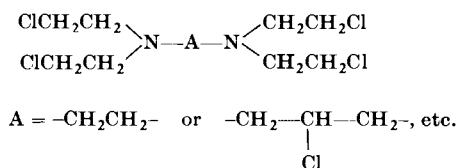


developed by Sandoz are an interesting variant. None of these products has gained any importance for cellulosic fibers. On the other hand, blue disperse dyestuffs, e.g.,

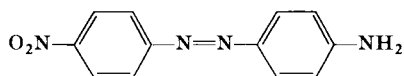


are of technical value for polyamide fibers. They confer higher fastness to washing than the corresponding β -chloroethylamino derivatives.¹⁵³

A number of fixation group patents relate to compounds such as



for the reactive dyeing of polyamide materials with dyestuffs containing substitutable amino or hydroxy groups, e.g.,¹⁵⁴



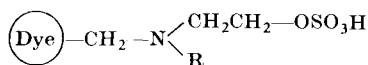
¹⁵¹ ICI, *BeP* 593,939 (10.8.1959).

¹⁵² S, *BeP* 639,274 (30.10.1962).

¹⁵³ ICI, *BP* 836,671 (24.1.1958).

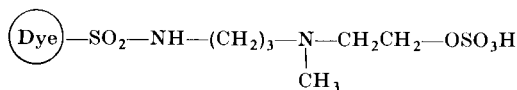
¹⁵⁴ S, *SP* 362,051 (5.5.1960); FW, *BP* 922,683 (11.5.1961); *FP* 1,292,454 (17.5.1961).

b. β-Sulfatoethylamines. Dyestuffs of the types



R = H, alkyl, $-\text{CH}_2\text{CH}_2\text{OSO}_3\text{H}$ ¹⁵⁵⁻¹⁶⁰

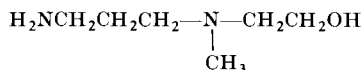
and



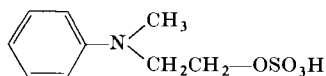
^{156, 161-164}

are the object of a whole series of patent applications. They possess a certain technical importance, particularly in the phthalocyanine range.^{155, 158, 159, 164} The β-sulfatoethylamine group is also suitable for increasing the solubility and, therefore, the vatting speed of vat dyestuffs.^{162, 163}

β-Sulfatoethylamines are produced either from chloromethylated phthalocyanines by condensation with β-hydroxyethylamines or from phthalocyaninesulfonyl chlorides and, for example,



The hydroxyl groups are subsequently esterified with sulfuric acid. Coupling with aniline derivatives, e.g.,



¹⁵⁵ BASF, *DAS* 1,061,009 (15.3.1957); *FP* 1,194,855 (7.5.1957).

¹⁵⁶ FBV, *BeP* 573,466 (28.1.1958).

¹⁵⁷ ICI, *BP* 868,285 (9.7.1958).

¹⁵⁸ G, *USP* 3,183,053 (19.12.1961); 3,170,931 (18.12.1962).

¹⁵⁹ G, *USP* 3,148,933 (19.12.1961).

¹⁶⁰ BASF, *BeP* 631,928 (6.5.1962).

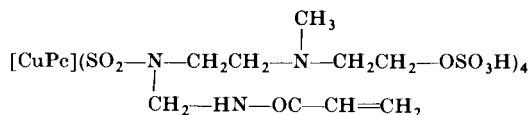
¹⁶¹ BASF, *FP* 1,277,867 (23.1.1960).

¹⁶² CIBA, *BeP* 612,622 (16.1.1961).

¹⁶³ CIBA, *BeP* 612,624 (16.1.1961).

¹⁶⁴ CIBA, *BeP* 700,966 (6.7.1966).

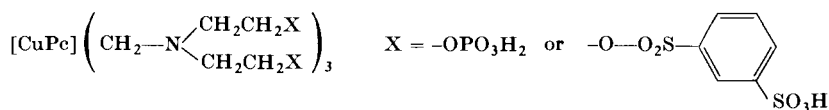
is also possible.¹⁶⁵ Ciba alkylated the secondary sulfonamide group in (V) with *N*-methylolamides of fiber-reactive acids and obtained in this way freely water-soluble polyfunctional phthalocyanine reactive dyes.¹⁶⁴



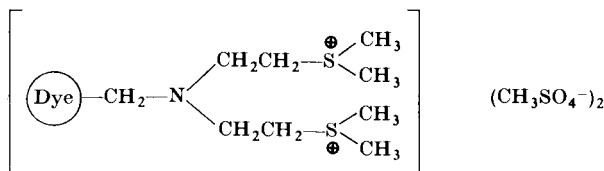
A serious disadvantage of all β -sulfatoethylamines is their tendency to self-condensation, i.e., an insufficient stability in alkaline printing pastes.

c. Other β -Substituted Ethylamines. Many of the previously mentioned patents relate generally to anions of strong acids, such as $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{OSO}_3\text{H}$, $-\text{IO}_3$, $-\text{OPO}_3\text{H}_2$, $-\text{OOC}\text{CCl}_3$, $-\text{OOCCHCl}_2$, $-\text{OOCCH}_2\text{Cl}$, $-\text{OOCH}$, $-\text{O}-\text{PO}(\text{OH})(\text{R})$, $-\text{O}-\text{O}_2\text{SR}$ ^{156, 158} in the β -position to the N atom.

GAF mentions the phosphoric acid and the *m*-sulfobenzene-sulfonic acid residues as being particularly suitable¹⁶⁶:



The sulfonium group in the β -position described by Francolor is split off, for example, as dimethyl sulfide, which may result in an odor nuisance.¹⁶⁶

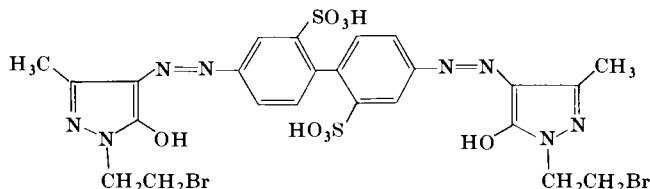


d. β -Haloethylpyrazolones. In these compounds, coupling component and reactive group are combined. In this case also, there may be a β -activation through the N-1 atom of the pyrazolone ring. If two such

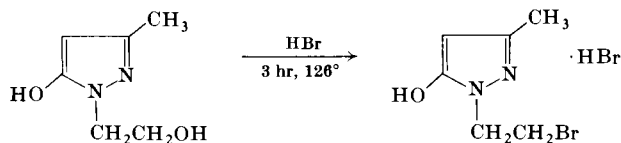
¹⁶⁵ BASF, BP 848,776 (2.1.1958).

¹⁶⁶ Fran, FP 1,461,687 (29.10.1965).

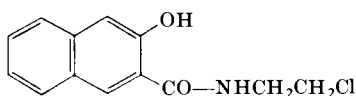
residues are present in the molecule, the fixation yield attains technically interesting values, e.g., in the reddish yellow¹⁶⁷



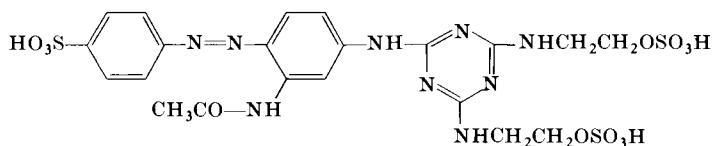
The fixation component is obtained as hydrobromide by esterification of 1-(β -hydroxyethyl)pyrazolone with boiling hydrobromic acid.



e. N-(β -Haloethyl) Amides and N-(β -Sulfatoethyl) Amides. This reactive group, which is mentioned in only a few cases, is very slow to react since the amide nitrogen atom in the β -position to the anionic mobile group is only slightly basic and can therefore cause activation in the manner of a neighboring group effect. BASF fixes under strong alkaline conditions coupling components such as



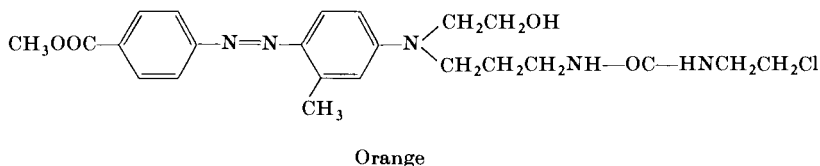
on cellulosic fibers and develops subsequently, for example, with diazotized 2,5-dichloroaniline to a red dyeing.¹⁴⁷ Francolor describes derivatives of aminotriazine and aminopyrimidine as reactive dyes,¹⁶⁸ e.g.,



¹⁶⁷ FB_y, BeP 587,098 (31.1.1959).

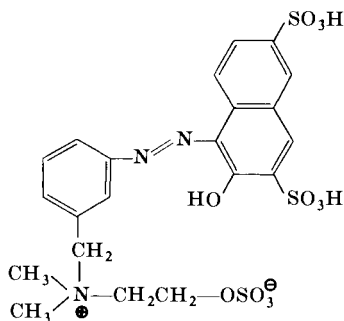
¹⁶⁸ Fran, FP 1,319,405 (18.1.1962).

The *N*- β -chloroethylurea group is claimed in reactive disperse dyes for polyamide fibers.¹⁶⁹



14. β -Substituted Ethylammonium Compounds

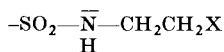
A quaternary ammonium group no longer possesses a lone electron pair and therefore cannot exert an activating effect on the anionic mobile group through a three-membered ring mechanism. An acidification of the α -methylene group, as in the case of the β -sulfatoethyl sulfone group, may be the starting point of the fiber reaction in this case. For example, the dyestuff



gives a wash-fast orange dyeing with caustic soda at 110°. ¹⁷⁰

15. β -Substituted Ethylamides of Sulfonic Acids

The reactivity of the group

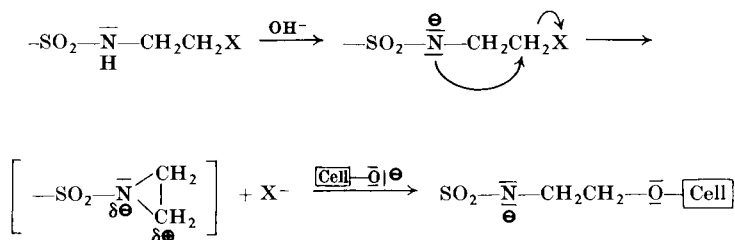


X = anionic mobile group

¹⁶⁹ FBy, *FP* 1,360,450 (7.5.1962).

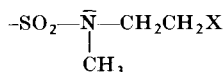
¹⁷⁰ FBy, *BeP* 589,127 (28.3.1959).

with cellulose in an alkaline medium is based on the neighboring group effect of the anion formed by dissociation on the sulfonamide nitrogen and proceeds through a reactive cyclic intermediate.¹⁴⁶



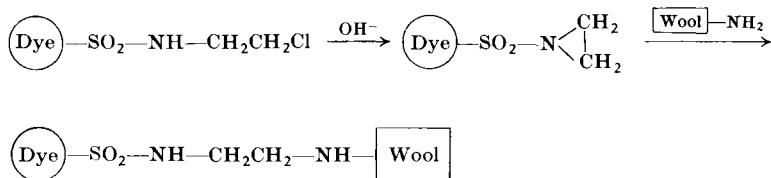
It is therefore obvious that only dissociable monoalkylamides of sulfonic acids possess sufficient reactivity for practical purposes.

N,N-Dialkylsulfonamides of the type



are of no technical importance.

a. β-Haloethylamides and β,γ-Dihaloethylamides of Sulfonic Acids.
In 1940 dyestuffs containing sulfo-β-chloroethylamide groups which achieved higher fastness to washing on wool than comparable dyes were described by I. G. Farbenindustrie.¹⁷¹ It was recognized by the same firm that ethylene sulfonimides are easily produced by the action of alkalies on these dyestuffs¹⁷² and are also capable of reaction with the amino groups of wool.¹⁷³

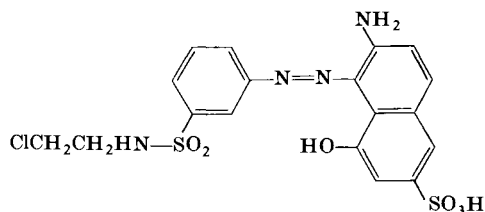
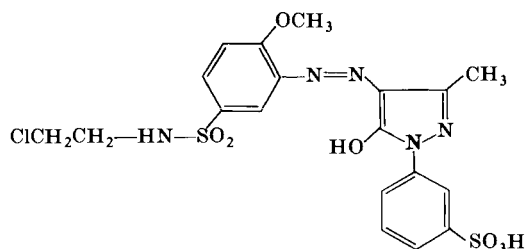


¹⁷¹ IG, *DRP* 743,766 (19.4.1940).

¹⁷² IG, *DRP* 698,597 (8.2.1939); Zen Go-Du, and L. S. Efros, *Zh. Obshch. Khim.* **33**, No. 3, 966-969 (1963).

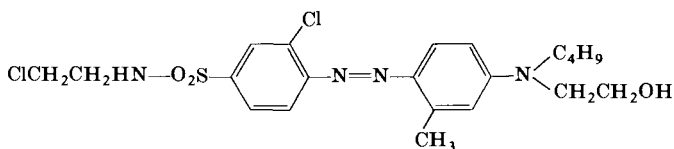
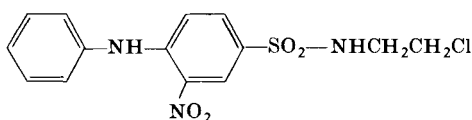
¹⁷³ IG, *DRP* 695,331 (29.4.1939).

Anionic water-soluble dyes containing *N*- β -haloethylsulfonamide groups, e.g.,



are fixed on cellulosic fibers from an aqueous-alkaline medium in shades which possess excellent wet-fastness properties.^{174, 174a} They are less suitable for dyeing from a long liquor than for continuous processes.

ICI also recognized that disperse dyestuffs of the nitro¹⁷⁵ and azo¹⁷⁶ ranges



¹⁷⁴ ICI, *BeP* 563,200 (14.12.1956); K. A. Bocenkova and V. F. Borodkin, *Khim. Khim. Tekhnol. (Alma-Ata)* 8, No. 3, 459-464 (1965).

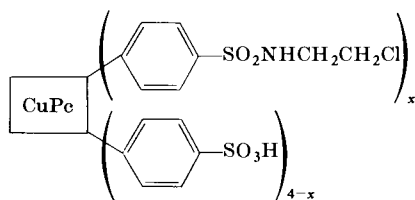
^{174a} CIBA, *DAS* 1,066,987 (14.8.1956); *BeP* 565,997 (25.3.1957).

¹⁷⁵ ICI, *BP* 821,963 (14.12.1956).

¹⁷⁶ Ufimcev, V. N., and Dašerskaja, L. D., ICI, *BeP* 571,743 (4.10.1957); Ufimtsev and Dashevskaya, *RP* 166,422 (8.6.1963).

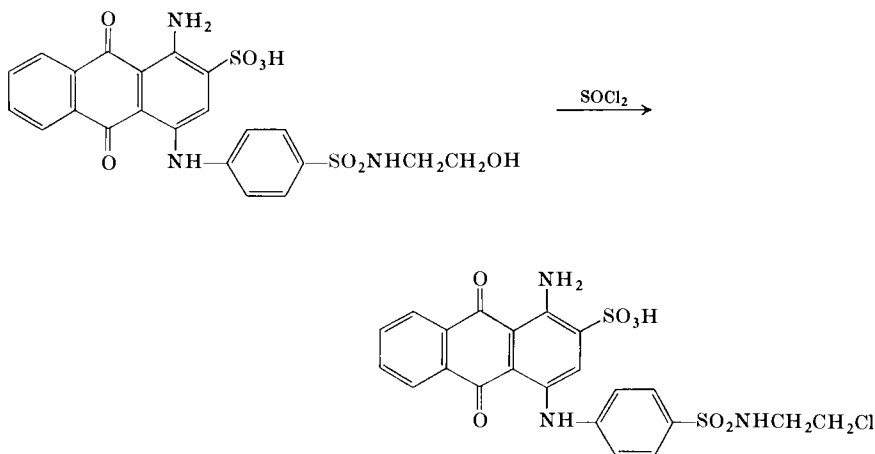
with such reactive groups produce dyeings with very good fastness to washing on polyamide fibers—particularly after an alkaline after-treatment—and in 1960 developed, *inter alia*, their Procinyl dyes on this basis.

BASF occupied themselves at a very early date with cellulose-reactive dyestuffs of this type and developed various syntheses to introduce the *N*- β -chloroethylsulfonamide group into the dyestuff molecule. In this way, water-soluble reactive dyes such as the green



are obtained from dyestuffs of the arylphthalocyanine range¹⁷⁷ or anthraquinone range,¹⁷⁸ which contain several chlorosulfonyl groups, by condensation with a deficiency of β -chloroethylamine and saponification of the excess chlorosulfonyl groups.

The conversion of an *N*- β -hydroxyethylsulfonamide group with thionyl chloride in the completed anthraquinone dyestuff molecule containing sulfonic groups is also possible.¹⁷⁹

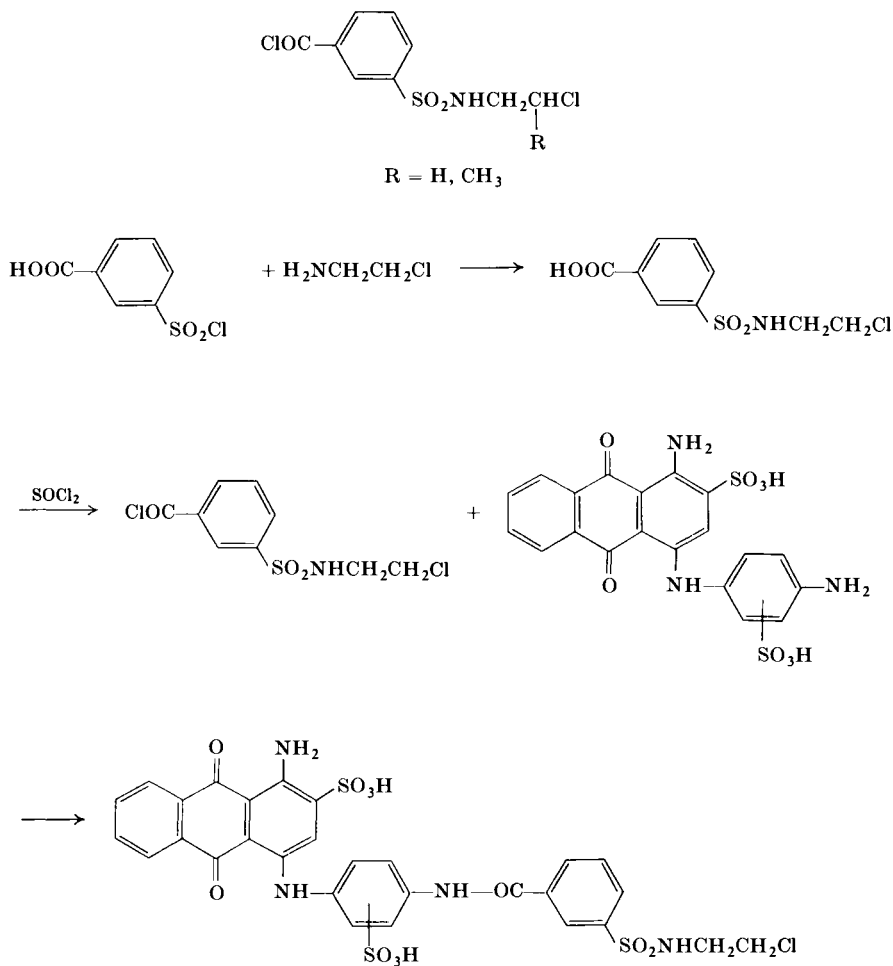


¹⁷⁷ BASF, *DAS* 1,210,506 (6.7.1957).

¹⁷⁸ ICI, *BP* 847,142 (13.11.1957).

¹⁷⁹ BASF, *DAS* 1,066,682 (10.9.1957).

A particularly good method of synthesis is the acylation of dyestuffs of the azo,¹⁸⁰ anthraquinone,¹⁸¹ or tetrazaporphine¹⁸² ranges containing amino groups with aromatic carbonyl chloride sulfo- β -chloroalkyl-amides,¹⁸³ e.g.,



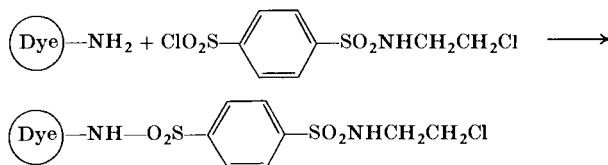
¹⁸⁰ BASF, DAS 1,083,957 (8.11.1957).

¹⁸¹ BASF, DAS 1,105,082 (31.8.1957).

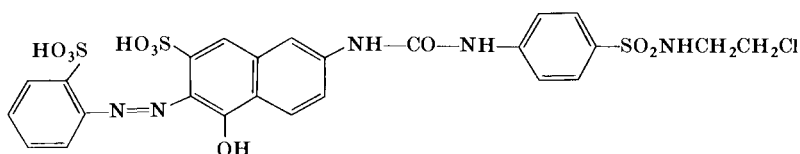
¹⁸² BASF, DAS 1,066,684 (8.11.1957).

¹⁸³ BASF, DAS 1,109,290 (31.10.1957).

The carbonyl chloride group can also be replaced by the chlorosulfonyl group to introduce the reactive residue into the amino dyestuff molecule.¹⁸⁴

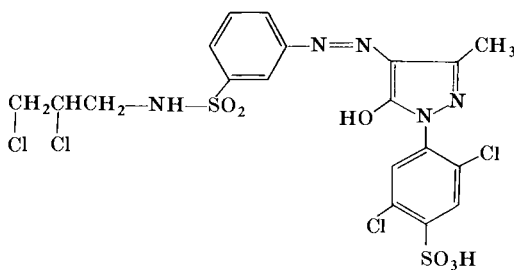


A further method consists in the linking of reactive amino compounds with the dyestuff molecules through carbamide¹⁸⁵ or urea bridges.¹⁸⁶



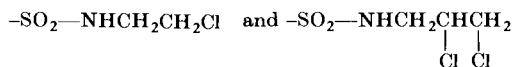
The fixation of fiber-reactive coupling components of this type and subsequent development of the reactive dyeing with diazo compounds possesses no technical importance.¹⁸⁷

β,γ-Dihalopropionylamides of Sulfonic Acids were claimed very widely as reactive groups by Sandoz¹⁸⁸ and then by ICI, especially for phthalocyanine dyes.¹⁸⁹ These dyestuffs, e.g., the yellow



are also suitable mainly for continuous processes.

Recently, the above-mentioned reactive groups



¹⁸⁴ BASF, *DAS* 1,085,627 (31.1.1958).

¹⁸⁵ BASF, *DAS* 1,085,626 (17.1.1958).

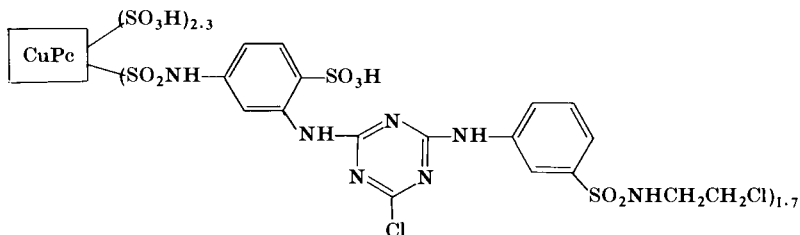
¹⁸⁶ BASF, *FP* 1,218,709 (14.1.1958).

¹⁸⁷ BASF, *BeP* 578,887 (24.5.1958); *GP* 1,154,790 (20.6.1959).

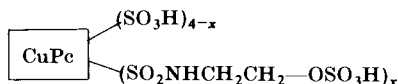
¹⁸⁸ S, *BeP* 589,628 (17.4.1959).

¹⁸⁹ S, *BeP* 597,143 (18.11.1959).

have frequently been described in bifunctional and polyfunctional reactive dyes with fixation yields exceeding 90%, which contain, in addition, a monochlorotriazine group also acting as a linking unit.^{69, 190, 191}

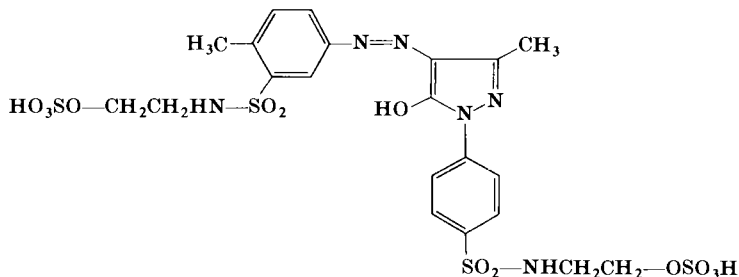


b. β -Sulfatoethylamides of Sulfonic Acids. In the years 1956–57 Ciba,^{174a} ICI,¹⁹² and BASF¹⁹³ claimed dyeing processes with, or the production of, dyestuffs which in addition to at least one acid, water-solubilizing group ($-\text{SO}_3\text{H}$, $-\text{COOH}$) contained at least once the reactive group $-\text{SO}_2-\text{NHCH}_2\text{CH}_2-\text{OSO}_3\text{H}$, e.g.,



$$x \cong 1-2$$

Bayer also developed dyes which contained no water-solubilizing substituents other than the reactive sulfato groups.¹⁹⁴



Yellow

¹⁹⁰ BASF, *FP* 1,228,601 (10.6.1958); ICI, 1,256,161 (4.3.1959); E. Koboyashi, *JP* 15,003/67 (26.12.1963).

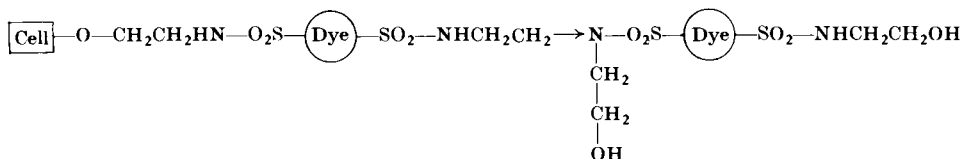
¹⁹¹ ICI, *FP* 1,439,996; 1,429,819 (7.4.1964); *BP* 1,118,785 (13.11.1964); *FP* 1,463,288 (8.1.1965); *EGP* 56,878 (15.7.1966); *FP* 1,546,109 (29.11.1966).

¹⁹² ICI, *DAS* 1,091,259 (14.12.1956).

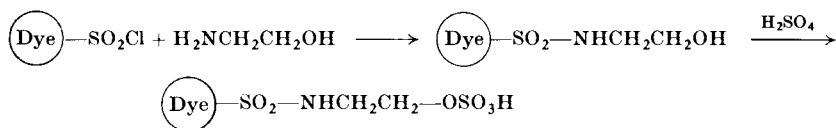
¹⁹³ BASF, *DAS* 1,098,123 (21.12.1957).

¹⁹⁴ FBy, *BeP* 569,439 (15.7.1957).

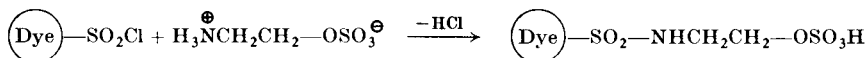
Products of this type have been marketed as Levafix dyestuffs since 1958. They are unsuitable for dyeing from a long liquor, but give very high fixation yields and excellent wet-fastness properties when dyeings on cellulosic fibers are steamed or fixed in dry heat in the presence of alkalis. This is due to the presence of several reactive groups, to the additional mutual reactivity of the dyestuff molecules at the sulfonamide nitrogen atoms, for example,



and to the pigmentation caused by splitting out of the mobile, water-solubilizing sulfato residues in the alkaline medium.¹⁴⁶ These reactive groups can be introduced through the dyestuff- β -hydroxyethylsulfonamides (obtained from chlorosulfonyl compounds and ethanolamine) by esterification with sulfuric acid.¹⁹⁵



Another method is the condensation of the chlorosulfonyl dyestuff with the β -aminoethanol half-ester of sulfuric acid obtained in crystalline form from ethanolamine and sulfuric acid by splitting out of water on heating,¹⁹⁶ so that the required products are obtained directly.¹⁹⁵

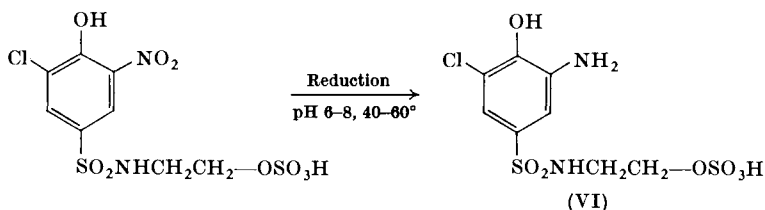


At temperatures between 40° and 60° and at pH 6–8, the β -sulfatoethylaminosulfonyl group is stable, so that corresponding nitro compounds can be reduced to the amines under these conditions.¹⁹⁷

¹⁹⁵ FBy, *DAS* 1,116,846 (31.1.1958); Gy, *BeP* 580,407 (7.7.1958); FBy, *BeP* 604,814 (11.6.1960); 615,208 (16.3.1961).

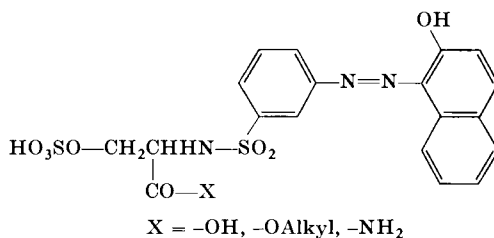
¹⁹⁶ H. Wenker, *Am. Soc.* **57**, 2328 (1935); P. A. Leighton, W. A. Perkins and M. L. Renquist, *ibid.* **69**, 1540 (1947).

¹⁹⁷ FBy, *DAS* 1,109,702 (6.11.1957).



The aminophenol derivative (VI) containing a reactive group is suitable, for example, as a diazo component for the synthesis of reactive metal complex dyes.

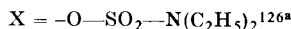
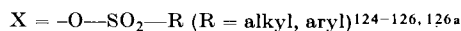
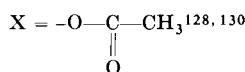
A variant of the β -sulfatoethylsulfonamide reactive residue is the group described by Sandoz with a carboxylic acid function in the β -position to the mobile group.¹⁹⁸



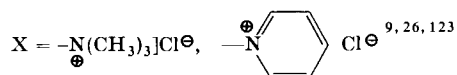
c. Other β -Substituted Ethylsulfonamides. In numerous patents, reactive groups of the type



are included in the general formula and, in part, are described as follows:



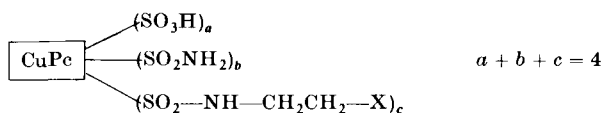
More interesting technically are the more reactive systems containing cationic mobile groups, such as



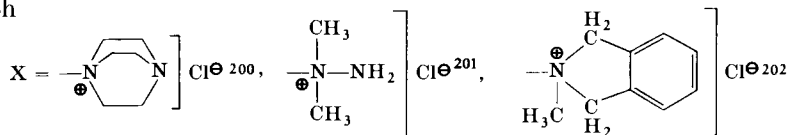
¹⁹⁸ S, *BeP* 643,924 (22.2.1963).

¹⁹⁹ CIBA, *BeP* 620,899 (31.7.1961); *FP* 1,331,001 (2.8.1961); *BeP* 621,243 (10.8.1961).

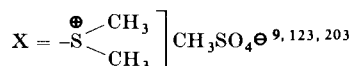
and, in particular, phthalocyanine dyes of the type



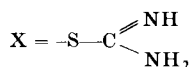
with



The β -sulfonium group also mentioned



has no practical importance because of the odor of the sulfur compounds released during the reaction with cellulose. The isothiuronium group



is also mentioned as a mobile group in the β -position.¹²³

A special position is occupied by the β -thiosulfatoethylamides of sulfonic acids.



This dyestuff group (e.g., the copper phthalocyanine derivative Inthion Brilliant Blue I5R), which has been developed intensively by Farbwerke Hoechst, reacts in the dyeing of cellulose not with the hydroxyl groups of the material, but in presence of Na_2S by polycondensation at room temperature with itself.²⁰⁴

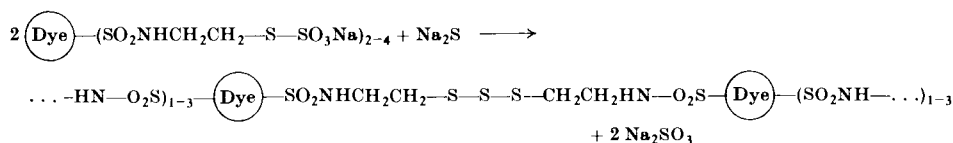
²⁰⁰ ICI, *FP* 1,334,557 (3.7.1961).

²⁰¹ ICI, *FP* 1,359,483 (15.5.1962).

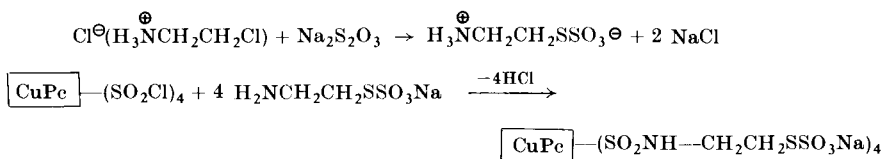
²⁰² ICI, *BP* 1,015,401 (27.5.1963).

²⁰³ FH, *BeP* 638,182 (3.10.1962); Fran, *FP* 1,519,829 (23.2.1967).

²⁰⁴ K. Schimmelschmidt, Hoffmann, H., and Baier, E., *Angew. Chem.* **74**, 975-977 (1962); *Chem. Ber.* **96**, 38-47 (1963); FH, *BeP* 699,915 (14.6.1966).

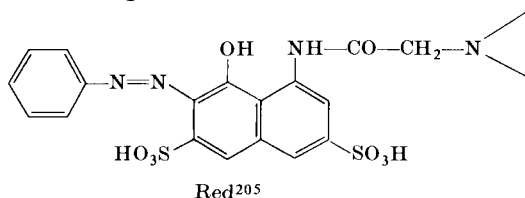


The production of dyestuffs of the Inthion type, which contain several thiosulfate groups in the molecule without further water-solubilizing groups, can be carried out, for example, in the following way²⁰⁴:

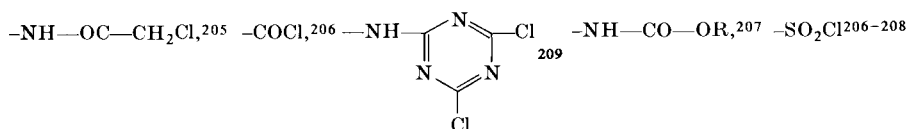


16. Ethyleneimine Derivatives

As previously mentioned, β -substituted ethylamine derivatives (see Section A,13) and β -substituted ethylamides of sulfonic acids (Section A,15) react with the fiber in an alkaline medium through an ethyleneimine intermediate stage. Since 1957, however, water-soluble reactive dyes already containing an ethyleneimine residue in the molecule have been described, for example,



They are generally produced by condensation of suitable functional groups with ethyleneimine, for example,



²⁰⁵ CIBA, *FP* 1,205,384 (10.4.1957).

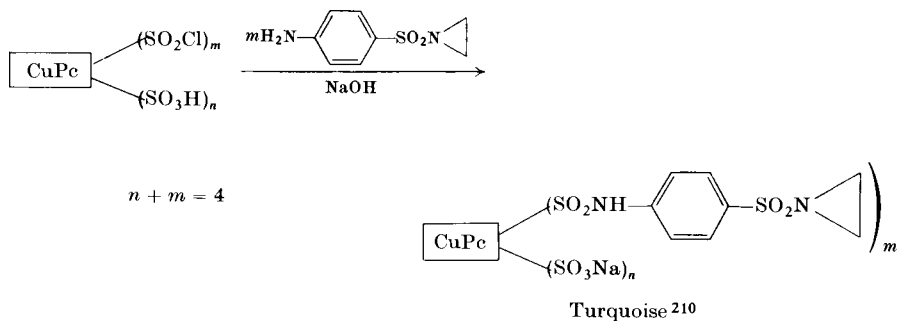
²⁰⁶ IC, *USP* 3,297,677 (17.10.1960).

²⁰⁷ S, *FP* 1,217,337 (23.12.1957).

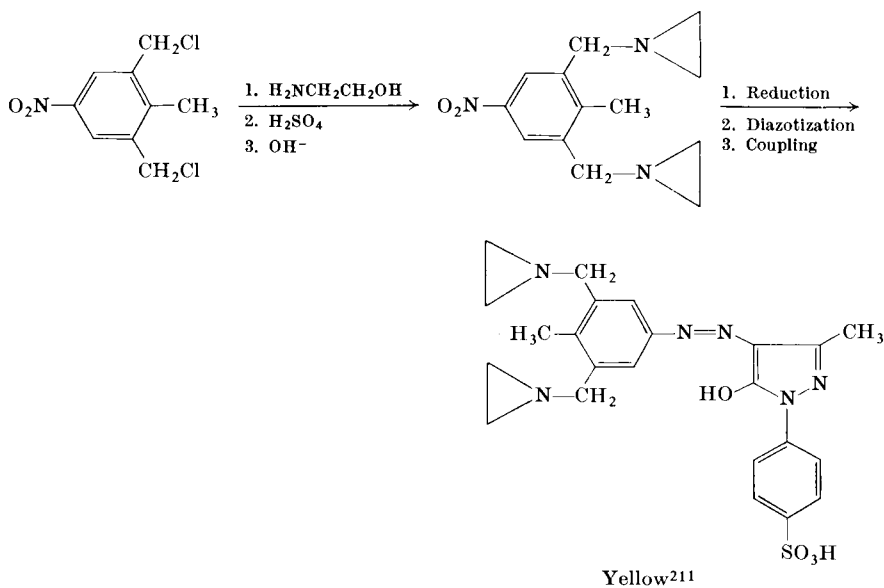
²⁰⁸ S, *FP* 74,695 (addition to *FP* 1,217,337) (23.12.1957).

²⁰⁹ K. Matsui, *JP* 11,442/63 (16.8.1960).

while intermediate products containing ethyleneimine groups can also be used.²¹⁰



Synthesis sometimes also proceeds through the corresponding β -substituted ethylamine derivatives.

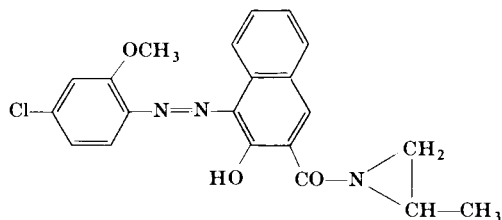


Ethyleneimine dyes are best fixed on cellulosic fibers in dry heat in an alkaline or slightly acid medium [e.g., in the presence of $\text{Zn}(\text{BF}_4)_2$ ²¹¹], in which case they give dyeings with very good wet-fastness properties.

²¹⁰ K. Matsui, *J P* 1,954,166 (23.12.1963).

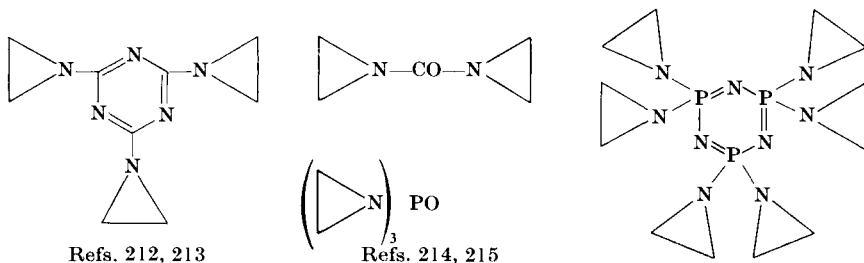
²¹¹ G, *BeP* 641,606 (31.12.1962).

They have, however, attained no technical importance in this field nor in the fixation of water-insoluble types, such as²⁰⁶



on synthetic fibers.

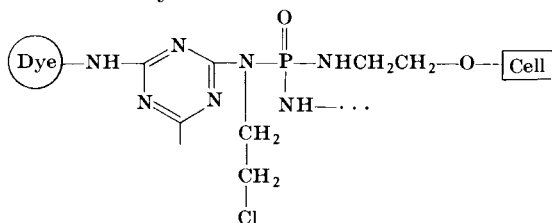
Finally, a few patents must be mentioned in which polyfunctional cross-linking agents, such as



are described.

While BASF links dyestuffs containing reactive hydrogen atoms (>NH , -OH , etc.) through tris(ethylencimino)-*s*-triazine to the cellulosic fiber,²¹² Allied Chemical also adds diisocyanates to the same cross-linking agent and uses as dyestuffs water-soluble 1:1 metal complexes (containing HO groups linked by a coordinate bond²¹³).

Aziridinyl compounds together with vinyl sulfone²¹⁴ and halotriazine²¹⁵ reactive dyes can also be fixed on cellulose by heating for a short time at $130\text{--}160^\circ$, since they react with the fiber and function as a bridge between fiber and reactive dyestuff.



²¹² BASF, *BeP* 613,442 (4.2.1961); 631,190 (18.4.1962); 631,585 (28.4.1962).

²¹³ NAC, *USP* 3,295,916 (4.6.1962).

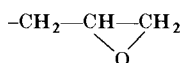
²¹⁴ USA-Secretary of Agriculture, *USP* 3,197,269 (23.11.1962).

²¹⁵ USA-Secretary of Agriculture, *USP* 3,084,017 (24.8.1960).

At the same time, fabrics dyed as described possess increased creaseproof and fireproof properties.

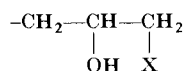
17. Epoxide Derivatives and Their Precursors

The group (VII)



(VII)

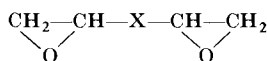
X = Cl, Br



(VIII)

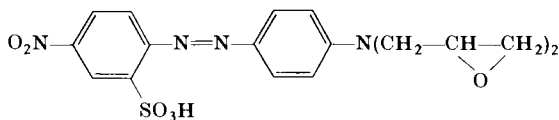
and its precursor (VIII) are nearly always mentioned together, since (VII) is produced from (VIII) by the action of alkalis, i.e., under the conditions of application to cellulose.

Dyestuff intermediates containing the residues (VII) and (VIII)^{147, 216} and also bifunctional and polyfunctional cross-linking agents of the type

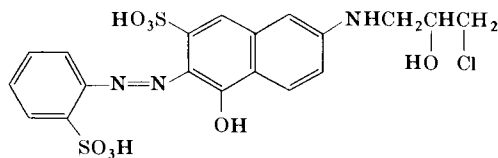


X = direct linkage, —O—, —N—, etc.
 $\begin{array}{c} | \\ \text{R} \end{array}$

for water-soluble azo dyes containing amino groups^{148, 217} were claimed at a very early date. From 1957, Ciba, BASF, and Bayer have also claimed dyestuffs into which the groups (VII) or (VIII)



Ref. 218



Ref. 218

are already incorporated.^{218–220}

The reactive residues (VII) or (VIII) can be introduced into the dyestuffs in several ways.

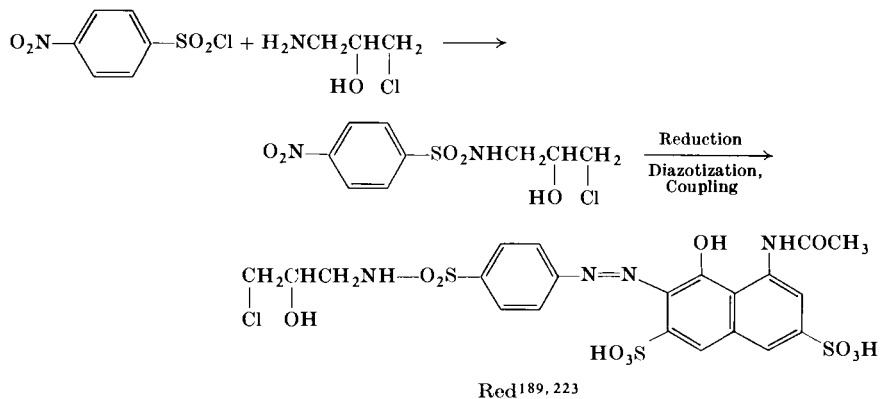
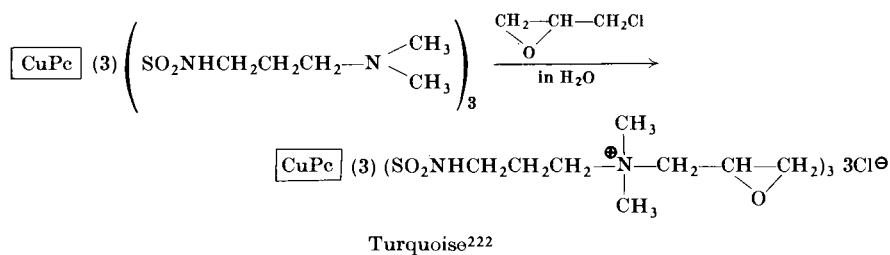
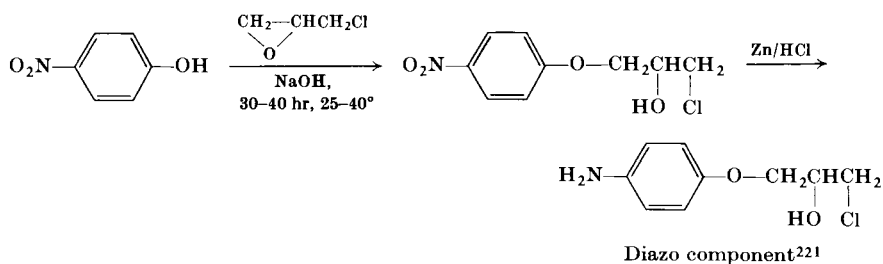
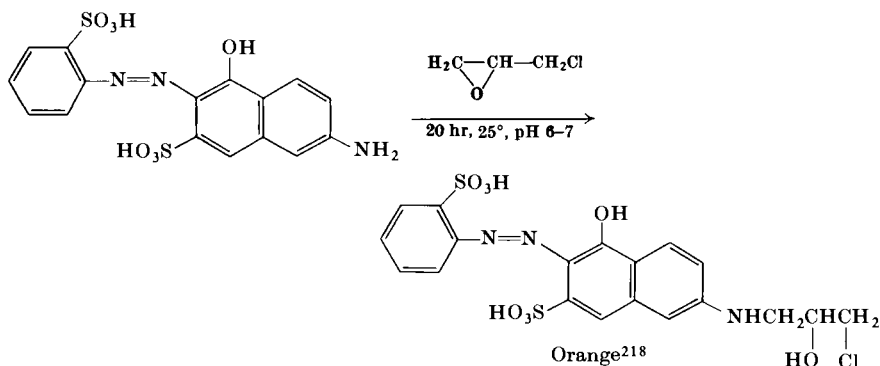
²¹⁶ ICI, *FP* 1,228,545 (19.5.1959); Kutkevichus, S. J., Lakstauskas, J., and Pesite, M., *RP* 165,669 (27.4.1962).

²¹⁷ CIBA, *BeP* 570,896 (4.9.1957); *FP* 1,496,902 (20.10.1965).

²¹⁸ CIBA, *BeP* 571,463; 571,464 (25.9.1957).

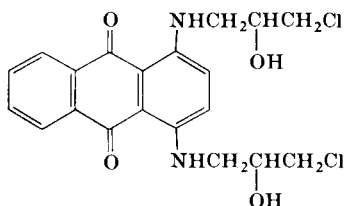
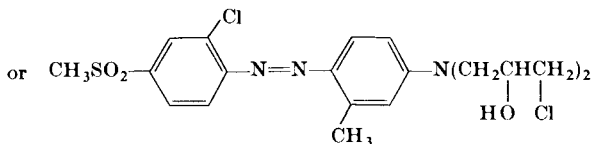
²¹⁹ BASF, *BeP* 585,004 (29.11.1958); 585,005 (2.12.1958).

²²⁰ FBy, *BeP* 572,411 (28.10.1957).

Red^{189, 223}²²¹ ICI, *BeP* 578,746 (19.5.1958); Kharkov Polytechnic, *RP* 191,713 (25.10.1965).²²² FBy, *FP* 1,280,838 (24.12.1959).²²³ ICI, *BeP* 581,359 (1.11.1957); *USP* 3,152,860 (29.12.1961).

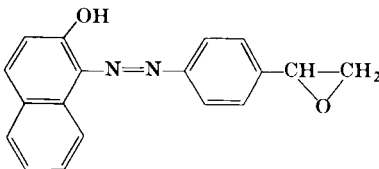
Although water-soluble cellulose-reactive dyes of this type give dyeings with very good wet-fastness properties after padding and fixation in steam or dry heat in the presence of alkali, their reactivity is nevertheless insufficient for the exhaustion process. Moreover, it is not easy to find brilliant and lightfast structures. They were therefore not successful in practice.

On the other hand, disperse dyes for polyamide fibers (Procinyd dyes, ICI), such as

Blue²²⁴Scarlet²²⁵, see ¹⁴⁵

have achieved technical importance. In this case, because of the stability required when dyeing at the boil and also because the amino groups present in polyamide fiber are more nucleophilic, the reactivity of the groups (VII) and (VIII) —somewhat too low for cellulose—is exactly right.

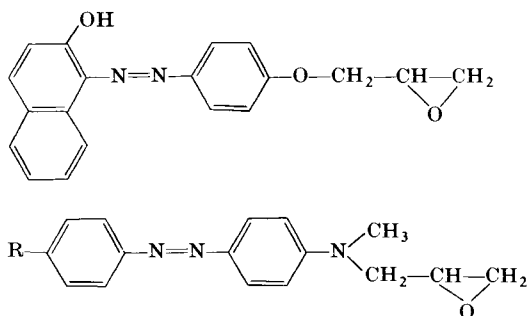
The somewhat different speed at which, depending on the bridge link, the epoxide ring is opened with alkali iodides in aqueous dioxane was studied by Hopff and Lienhard in the dyestuffs²²⁶



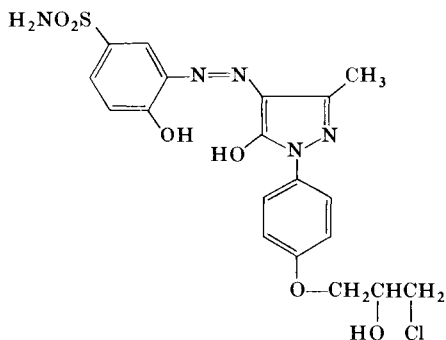
²²⁴ ICI, *BeP* 571,739 (4.10.1957); *BP* 875,105 (8.5.1959); *FP* 1,465,924 (26.1.1965).

²²⁵ ICI, *BeP* 571,740; 571,742 (4.10.1957); *BP* 868,468 (4.9.1958); 875,451 (8.5.1959).

²²⁶ H. Hopff and P. Lienhard, *Helv. Chim. Acta* **45**, 1742–1749 (1962).

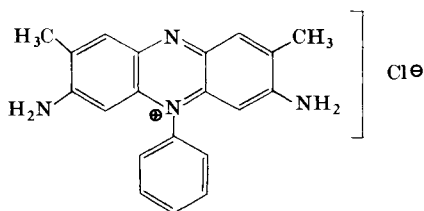


The epichlorohydrin or epoxide group is also suitable for the reactive dyeing of wool. ICI developed systematically 1:2 chrome or cobalt complexes in which the reactive groups are bound to the dyestuff through $-O-$ or $-S-$, e.g., in the orange 1:2 chrome complex of the dye²²⁷



or through $-NR-$ ²²⁸ or $-SO_2-$ ²²⁹.

For silk, the basic dye obtained by condensation of the amino groups of the safranine



with epichlorohydrin (10 hr, 60°) is considered suitable.²³⁰

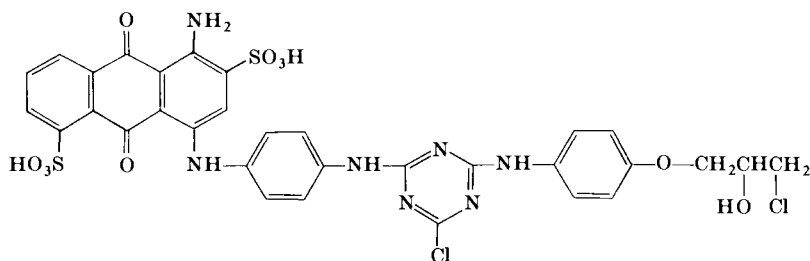
²²⁷ ICI, *BeP* 609,775 (3.11.1960).

²²⁸ ICI, *BeP* 609,774 (3.11.1960).

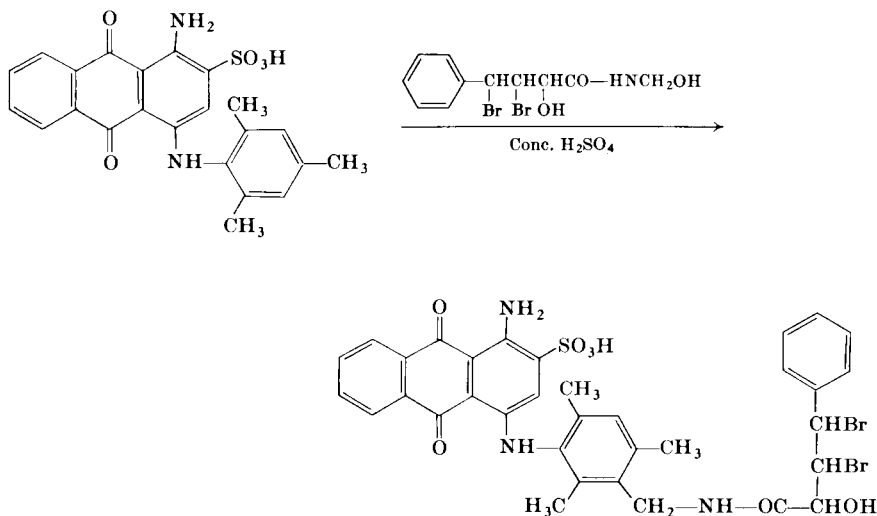
²²⁹ ICI, *BeP* 592,884 (13.7.1959).

²³⁰ L. P. Kovshina and A. A. Kharkharov, *RP* 154,340 (26.3.1962).

Recently ICI has combined heterocyclic reactive groups with groups (VII) or (VIII) to attain a maximum fixation yield under all conditions of application.^{190, 191, 231}

Blue²³¹

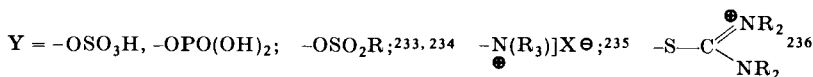
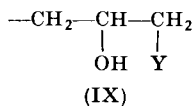
A special variant of the bromohydrin group (VIII) is found in the wool dyestuffs of Sandoz.²³²



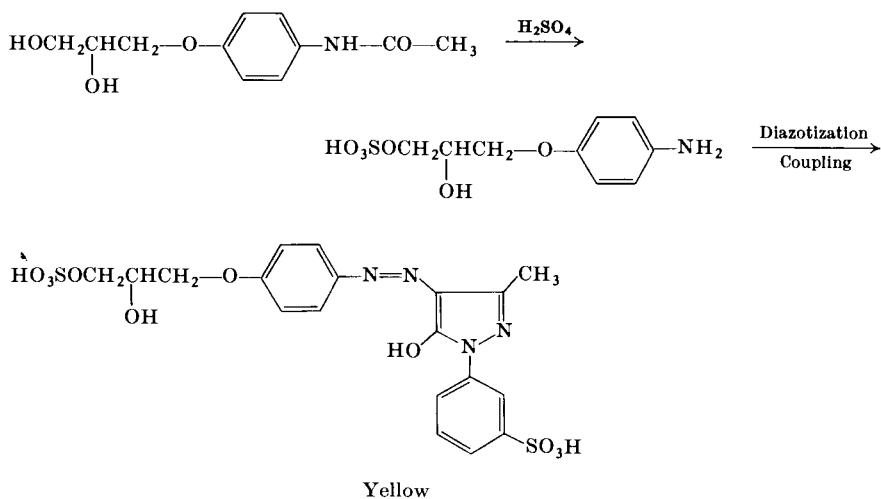
In addition to halohydrins (VIII), alcohols (IX) substituted in the α -position by other mobile groups (Y) are also epoxide precursors or reactive groups.

²³¹ ICI, *FP* 1,487,628 (23.7.1965); 1,495,035 (23.8.1965); *BP* 1,086,996 (23.8.1965).

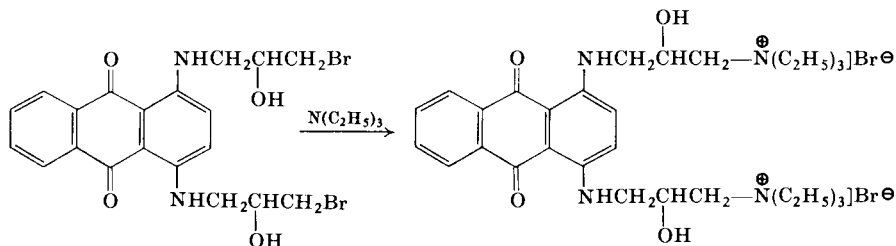
²³² S, *BeP* 630,205 (30.3.1962).



Dyes containing these residues are obtained, for example, by esterification of the appropriate β,γ -dihydroxypropyl compounds with sulfuric acid.²³³



or by quaternization of the halohydrins (VIII) with aliphatic or heterocyclic tertiary amines²³⁵



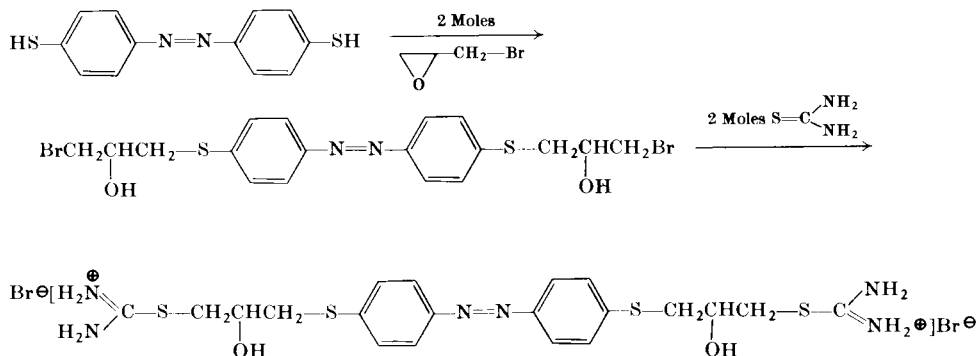
²³³ BASF, *BeP* 596,945 (14.11.1959).

²³⁴ BASF, *BeP* 585,006 (9.12.1958); 600,135 (17.2.1960); 600,634 (27.2.1960).

²³⁵ American Aniline Prod., Inc., *USP* 3,272,792 (18.12.1961); ICI, *FP* 1,363,433 (3.5.1962); Avdyunina, Z. P., Ersov, A. P., and Charcharov, A. A., *RP* 188,943 (25.9.1964).

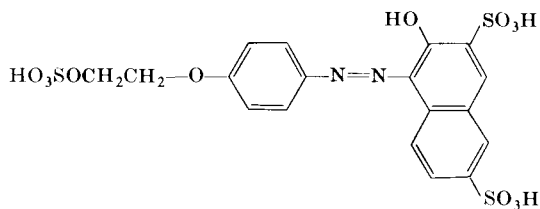
²³⁶ American Aniline Prod., Inc., *USP* 3,152,110 (18.12.1961).

or by condensation of bromohydrins with thiourea²³⁶

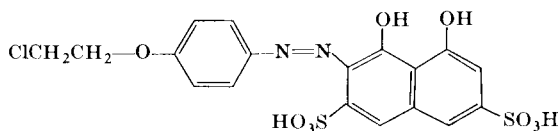


18. β -Substituted Ethers

One of the oldest reactive groups applied to cellulose from an aqueous phase is the β -substituted phenyl ethyl ether group²³⁷ used in 1952 by Guthrie in dyestuffs such as the red



or the purple

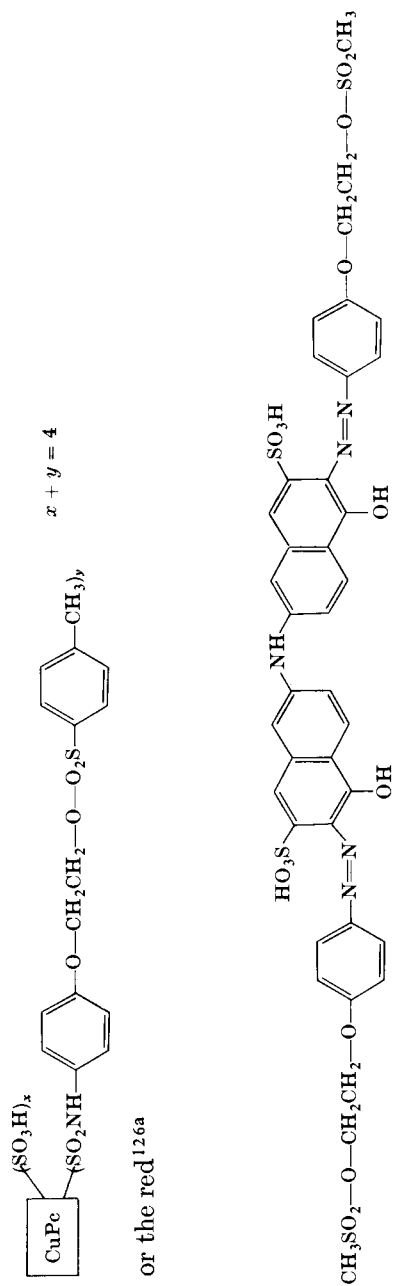


which gives somewhat lower fixation yields. It is well known that the reactivity of the halogen in β -halogenated ethers is lower than in β -haloamines. Sufficiently deep shades are therefore obtained only under very energetic conditions (20% caustic soda and fixation in dry heat for 2 hours at 120°), although very good wet-fastness properties are achieved.

Sandoz later described dyestuffs containing sulfoester mobile groups in the β -position, e.g., the turquoise²³⁸

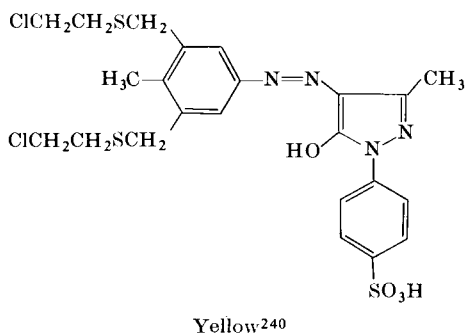
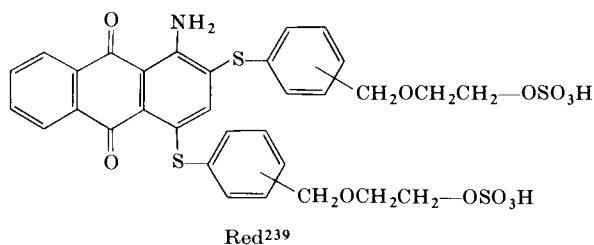
²³⁷ J. D. Guthrie, *Am. Dyestuff Repr.* **41**, 13 (1952).

²³⁸ S, *SP* 418,499 (23.10.1958).

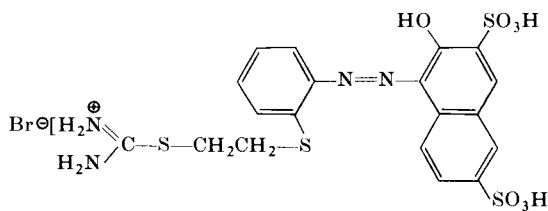


which can be dyed on viscose at 90° with trisodium phosphate, also from a long liquor.

The ether oxygen atom or the much stronger activating sulfur atom in the β -position can also be bound to a benzyl residue.



If an isothiuronium salt is present as a mobile group in the β -position, the dyestuffs may contain sulfo groups, e.g., as in²⁴¹



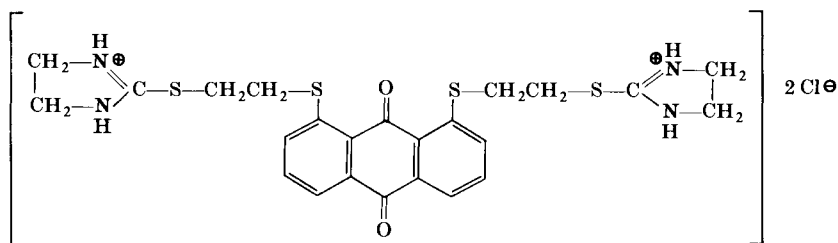
or they may be insoluble in water, so that the cationic reactive dyestuff owes its solubility only to the isothiuronium mobile groups.²⁴²

²³⁹ BASF, *FP* 1,229,749 (23.1.1958).

²⁴⁰ G, *USP* 3,169,822 (20.11.1961).

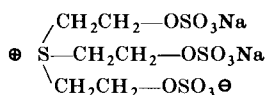
²⁴¹ American Aniline Prod., Inc., *USP* 3,152,109 (18.12.1961).

²⁴² American Aniline Prod., Inc., *USP* 3,152,108 (18.12.1961).

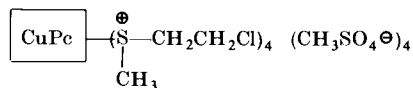


19. β -Substituted Ethylsulfonium Compounds

Tootal Broadhurst Lee Co. discovered that the sulfonium salt



cross-links with cellulose in an alkaline medium, "wash and wear" properties being conferred on the fiber.²⁴³ This product is marketed by ICI under the name Sulfix A. By *S*-alkylation of water-insoluble β -chloro(bromo)ethyl thioethers, cationic sulfonium dyestuffs such as the turquoise²⁴⁴

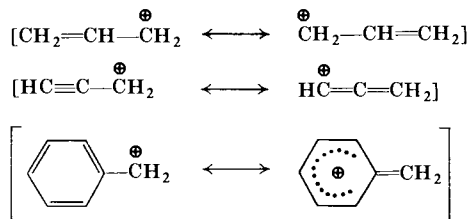


are obtained.

As with the β -substituted ethylammonium compounds, the fiber reaction in this case must also proceed from the activated methylene group in the α -position to the sulfonium sulfur.

20. Allyl, Propargyl, and Benzyl Derivatives

In all three carrier systems, the carbonium ion which remains after splitting out of the mobile group is stabilized mesomerically.²⁴⁵



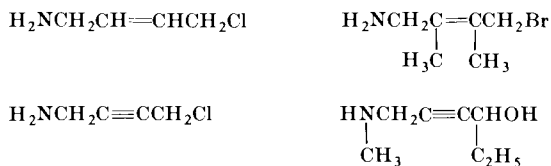
²⁴³ *Chem. Eng. News* **40**, 62-63 (1962).

²⁴⁴ AAP, USP 3,287,348 (30.4.1963).

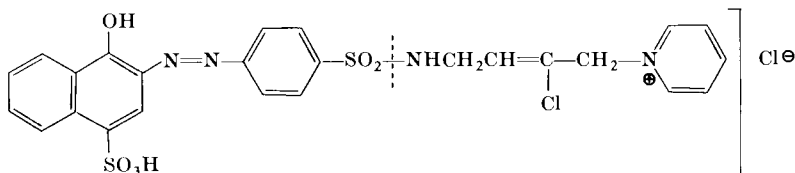
²⁴⁵ Kreutzkamp, N., and Meerwein, H., in Houben-Weyl, "Methoden der organischen Chemie," 4th ed., Vol. V, Part 4, p. 690. Thieme, Stuttgart, 1960.

Allyl and propargyl groups—particularly the corresponding chlorides—were developed intensively by BASF. The introduction of these residues can be achieved by the following methods:

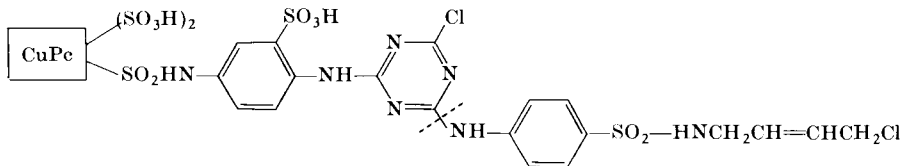
(1) Condensation of amines, such as



with dyestuffs or intermediate products containing carbonyl chloride, sulfonyl chloride, or imidochloride groups and, if necessary, subsequent esterification of the hydroxyl groups in the allyl position or quaternization of the halides with tertiary amines.



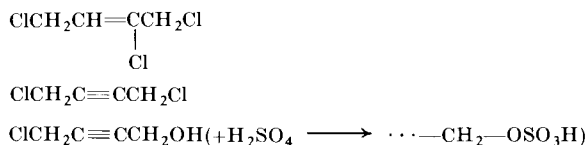
Ref. 246



Ref. 247

The reactive group $-\text{SO}_2\text{NH}-\text{CH}_2\text{C}\equiv\text{CCH}_2\text{Cl}$, which is particularly suitable for phthalocyanine dyestuffs, is used both in green mixtures²⁴⁸ and also in polyfunctional dyes together with other reactive groups.²⁴⁹

(2) Condensation of



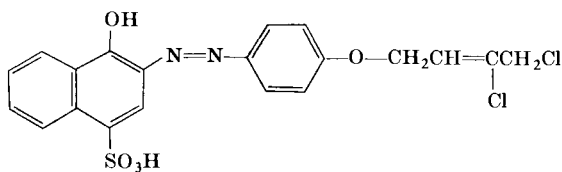
²⁴⁶ BASF, *BeP* 594,985 (16.9.1959); 599,139 (14.1.1960).

²⁴⁷ BASF, *BeP* 596,061 (15.10.1959).

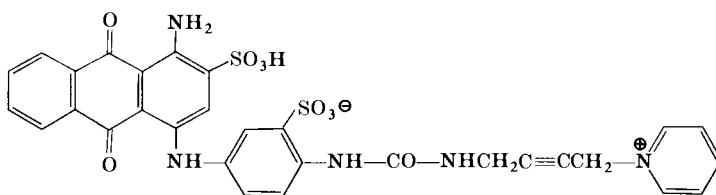
²⁴⁸ BASF, *BeP* 603,299 (30.4.1960).

²⁴⁹ BASF, *BeP* 628,728 (20.2.1963).

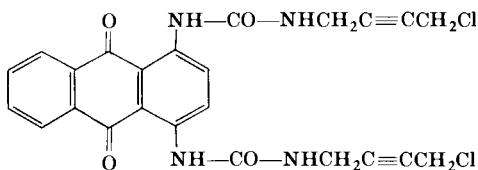
with phenolic $-\text{OH}$ or $-\text{SH}$ groups in dyestuffs²⁵⁰



(3) Condensation of dyestuffs containing amino groups with isocyanates, such as $\text{OCN}-\text{CH}_2\text{C}\equiv\text{CCH}_2\text{Cl}$ ²⁵¹

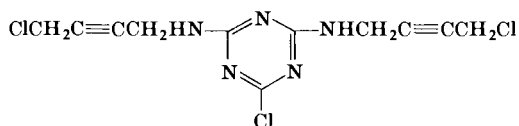


Blue for cellulose²⁵²



Red-violet for polyamides²⁵²

Colorless, polyfunctional cross-linking agents for two-component dyeing processes are obtained from cyanuric chloride and 1-amino-4-chlorobutylene-2.²⁵³



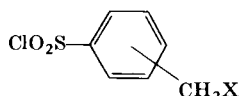
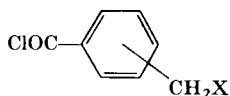
²⁵⁰ BASF, *BeP* 613,286 (1.2.1961).

²⁵¹ BASF, *BeP* 613,865 (14.2.1961); *GP* 1,208,020 (18.3.1961).

²⁵² BASF, *BeP* 618,415 (3.6.1961).

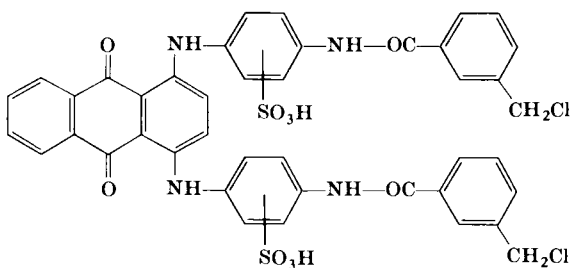
²⁵³ BASF, *BeP* 631,290 (21.4.1962).

Benzyl derivatives as reactive groups were described mainly by BASF and Sandoz.²⁵⁴⁻²⁵⁷ Either amino dyestuffs are acylated with halomethylbenzoyl chlorides or halomethylbenzenesulfonyl chlorides

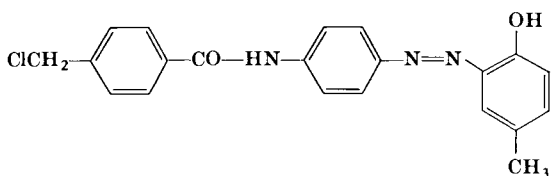


X = Cl, Br

giving water-soluble cellulose-reactive dyes²⁵⁵ or reactive disperse dyes for polyamide fibers,²⁵⁶

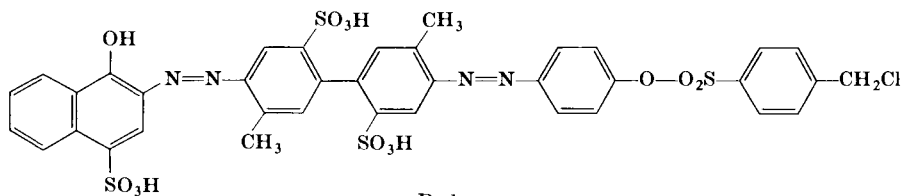


Green



Yellow

or else, starting with dyestuffs containing a phenolic hydroxyl or mercapto group, the corresponding esters, which are particularly suitable for wool and polyamide fibers, are obtained.



Red

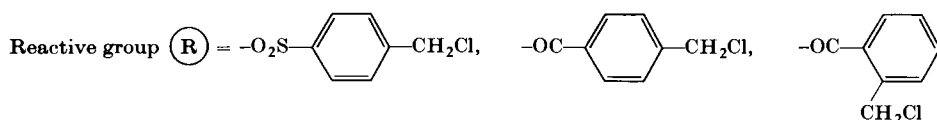
²⁵⁴ BASF, *DAS* 1,054,059 (3.5.1957).

²⁵⁵ BASF, *BeP* 594,074 (14.8.1959); 594,263 (20.8.1959); S, *BeP* 595,186 (23.9.1959); BASF, *BeP* 595,342 (26.9.1959).

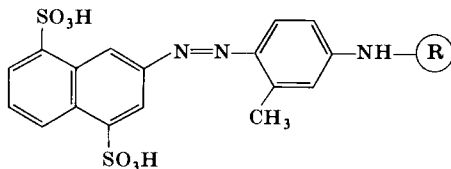
²⁵⁶ S, *BeP* 595,296 (23.9.1959).

²⁵⁷ S, *BeP* 602,581 (20.4.1960).

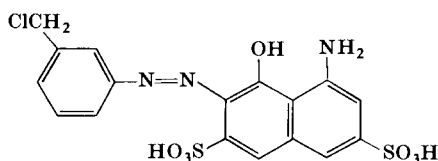
Japanese authors determined in the sequence



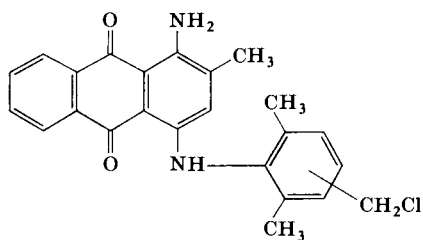
a decreasing reactivity with cellulose in dyestuffs such as²⁵⁸



If the benzyl halides contain amino groups, they can be used as diazo components for the synthesis of reactive dyes.²⁵⁹

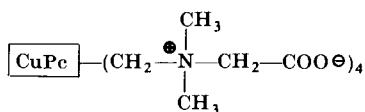


These amines can also be used for the direct synthesis of disperse dyes for the dyeing and printing of polyamide fibers.²⁶⁰



Blue

While reactive dyes containing benzyl halide groups have attained no technical importance, water-soluble copper phthalocyanine derivatives of the type



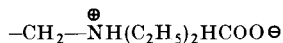
²⁵⁸ Manabe, O., Konishi, H., and Hiyama, H., *J. Soc. Org. Syn. Chem., Japan* **21**, 632-635 (1963).

²⁵⁹ G, *USP* 3,301,846 (31.12.1962).

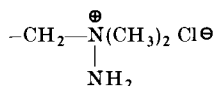
²⁶⁰ S, *SP* 8,591/60 (27.7.1960).

are available.²⁶¹ In an alkaline medium, they react partly with the fiber, splitting off dimethylaminoacetic acid, and are converted partly into insoluble pigments, similar in principle to the Alcian Blues of ICI, producing in this manner fast blue dyeings.

In this connection, mention must be made of a number of patent applications which describe phthalocyanine or vat dyes²⁶⁴ likewise containing aminomethylene groups, e.g.,²⁶²



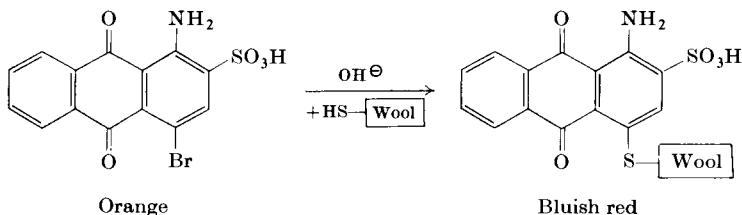
or hydrazinomethylene groups such as²⁶³



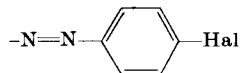
These dyestuffs are, however, taken up by cellulose direct from acid solution without reacting with the fiber.

B. AROMATIC CARRIER SYSTEMS

In 1938—long before the technical value of the reactive dyes was recognized—GAF discovered that a deep bluish red dyeing with very good wet-fastness properties is obtained when wool is dyed from an acetic acid bath with the dyestuff intermediate “bromaminic acid” and then aftertreated for 1 hour at 80° in an alkaline liquor containing 4 g/liter of NaHCO₃. The following fiber reaction, *inter alia*, must take place, representing simultaneously the formation of a dye.²⁶⁵



In this patent, dyestuffs are also mentioned with a halogen atom activated through the azo bridge



²⁶¹ BASF, *BeP* 611,907 (22.12.1960).

²⁶² BASF, *FP* 1,382,633; 1,389,716 (15.2.1963); Sterling Drug Inc., *BeP* 698,845 (23.5.1966).

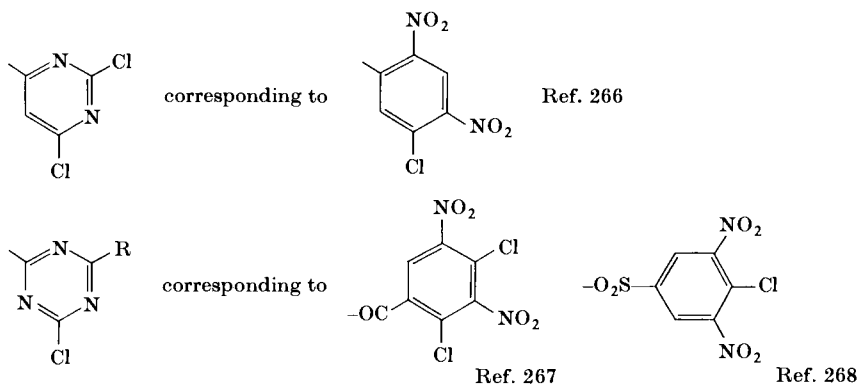
²⁶³ S, *BeP* 638,438 (12.10.1962).

²⁶⁴ BASF, *FP* 1,386,760 (6.3.1963).

²⁶⁵ G, *USP* 2,232,892 (8.6.1938).

as a reactant for wool, gelatin, and other nitrogen-containing materials.

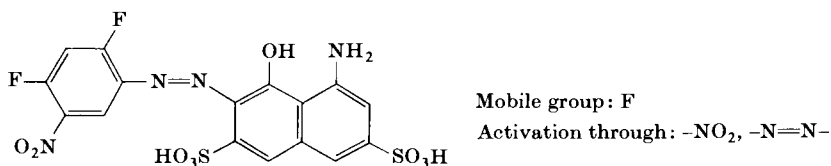
Due to the equivalence of the groups $\text{N}=\text{C}$ and $\text{O}_2\text{N}-\text{C}=\text{N}$ with regard to the activation of halogen atoms in the *o*- or *p*-position in heteroaromatic or aromatic rings, the next step after discovery of the halotriazine and halopyrimidine reactive groups was to test the analogous carbocyclic systems for their suitability.



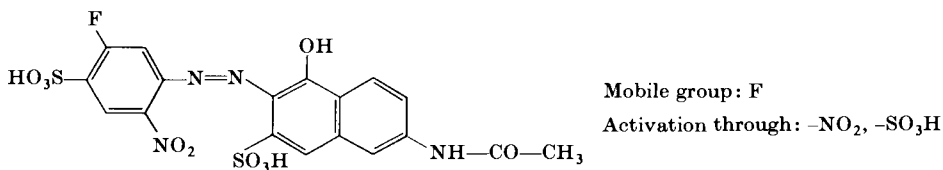
In the years 1959–63, nine firms described reactive dyes of this type.

Depending on the type of linkage between the aromatic reactive group and the dyestuff, and also on the kind of activating negative substituents and the kind of mobile groups, the following types can be distinguished:

(1) Halonitroanilines as diazo components:



Pad-steam fixation with NaOH/NaCl gives reddish navy blue²⁶⁹



Orange²⁷⁰

²⁶⁶ Acna, *BeP* 617,711 (71.5.1961).

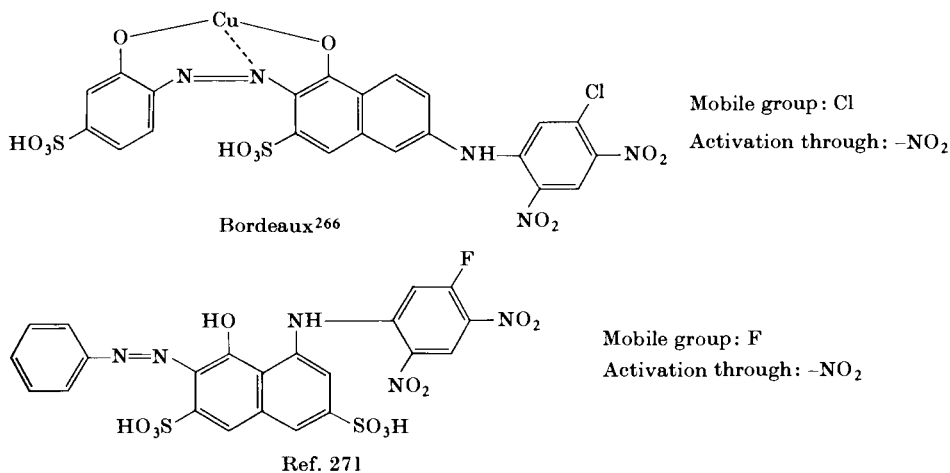
²⁶⁷ MCI, *JP* 9,810/64 (29.3.1961).

²⁶⁸ ICI, *FP* 1,271,328 (16.9.1959).

²⁶⁹ ICI, *BP* 882,001 (16.9.1959).

²⁷⁰ K. Matsui *et al.*, *J. Soc. Org. Syn. Chem. Japan* **24**, No. 2, 132–136 (1966).

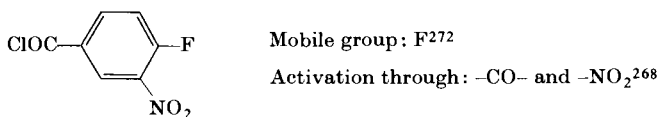
(2) Condensation of amino dyestuffs with 4,6 dinitro-1,3-dihalo-benzene:



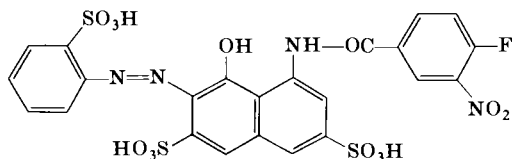
(3) Acylation of dyes containing amino groups with aromatic carboxylic or sulfonic halides which in addition to the activating -CO- or -SO₂- group in the *o*- or *p*-position to the mobile group contain a further negative substituent:

Mobile groups: halogen
Further negative substituent: -NO₂

Most interesting in this case is probably the readily available



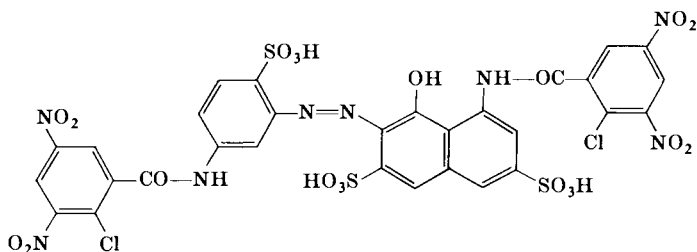
giving dyestuffs such as the brilliant red,^{268, 272}



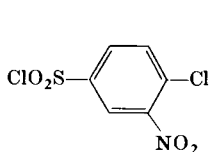
²⁷¹ MCI, *JP* 317/66 (5.3.1963).

²⁷² FBy, *BeP* 615,614 (27.3.1961).

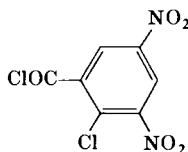
Dyestuffs such as the bluish red



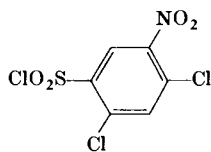
Further reactive acylating components are, for example,



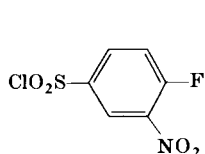
Refs. 268, 272, 274, 275



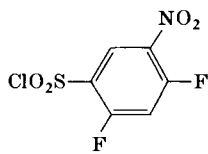
Ref. 267



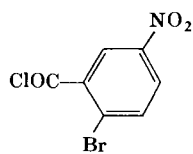
Ref. 277



Refs. 268, 272, 275, 276



Ref. 277



Ref. 278

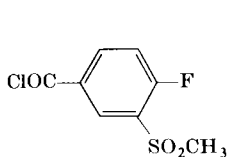
Further negative substituent: $-\text{SO}_2\text{CH}_3$

²⁷⁴ CIBA, *FP* 1,274,098 (2.12.1959).

²⁷⁶ IC, *FP* 1,412,060 (31.10.1963).

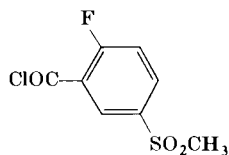
²⁷⁷ K. Matsui *et al.*, *J. Soc. Org. Syn. Chem. Japan* **23**, No. 2, 161-165 (1965).

²⁷⁸ CFM, *FP* 1,291,280 (4.6.1960).

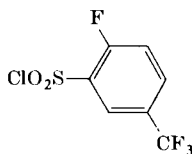


Refs. 279, 280

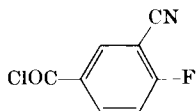
Mobile groups: halogen

Further negative substituent: $-\text{CF}_3$ 

Refs. 280, 281

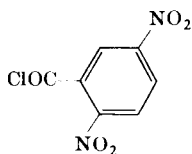


Ref. 281

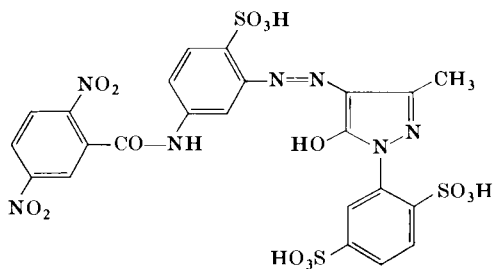


Ref. 279

Mobile groups: halogen

Further negative substituent: $-\text{CN}$ 

Ref. 282, see 278

Mobile groups: $-\text{NO}_2$, $-\text{SO}_2\text{CH}_3$ Further negative substituent: $-\text{NO}_2$, $-\text{CN}$, $-\text{SO}_2\text{CH}_3$ e.g., in the greenish yellow²⁸²

Dyestuffs of this type containing pyridinium mobile groups are also described.²⁸³

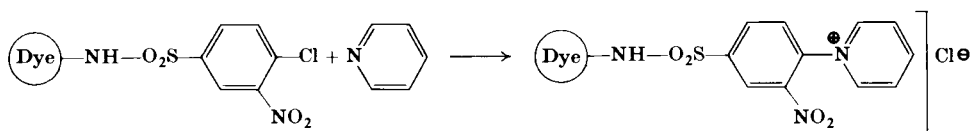
²⁷⁹ CFM, *FP* 1,304,825 (2.11.1960).

²⁸⁰ Gy, *BeP* 627,437 (24.1.1962); 628,424 (14.2.1962).

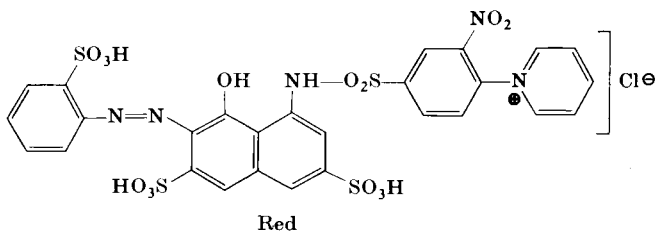
²⁸¹ K. Matsui *et al.*, *J. Soc. Org. Syn. Chem. Japan* **21**, No. 9, 713–718 (1963).

²⁸² Gy, *BeP* 625,941 (12.12.1961).

²⁸³ ICI, *BP* 978,162 (7.2.1962).



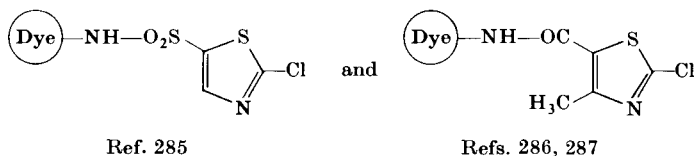
e.g.,



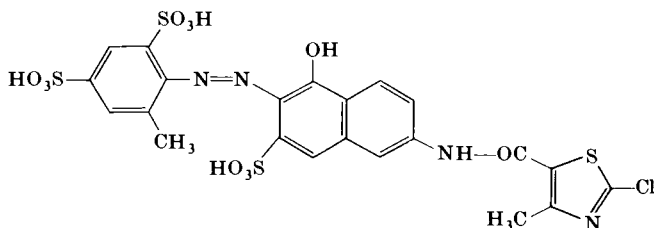
C. HETEROCYCLIC CARRIER SYSTEMS

1. Five-Membered Heterocycles

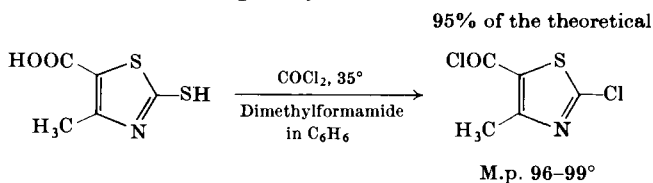
According to Albert,²⁸⁴ five-membered heterocycles are “ π -excess heterocycles,” i.e., the nucleophilic substitution of halogen and other mobile groups is much more difficult. Only when double-bonded nitrogen atoms attracting π -electrons are present in the ring, are anionic mobile groups attached to five-membered heterocycles sufficiently mobile to show the required fiber reactivity. Halogen is especially activated in the 2-position of thiazole (see ref. 284); in 1960–62 certain firms developed dyestuffs of the type



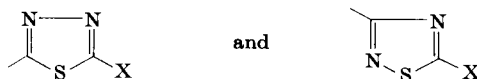
e.g., the orange

²⁸⁴ A. Albert, “Chemie der Heterocyclen,” p. 219, Verlag Chemie, Weinheim, 1962.²⁸⁵ Fran, *BeP* 611,736 (26.12.1960).²⁸⁶ FBy, *BeP* 624,259 (31.10.1961).²⁸⁷ BASF, *BeP* 630,929 (11.4.1962).

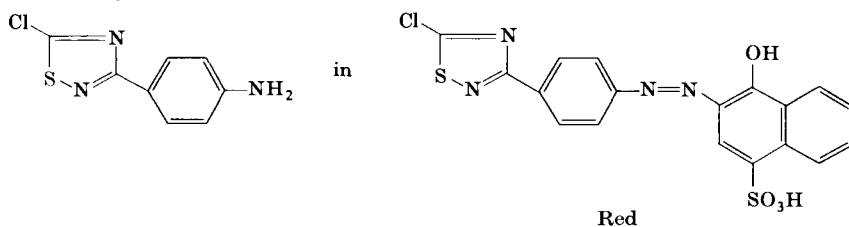
suitable for printing on cellulosic fibers. A new synthesis of these reactive components has been developed by BASF.²⁸⁸



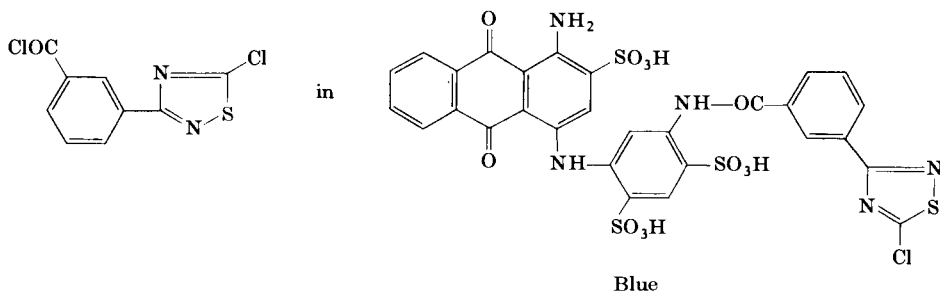
The groups



are also mentioned in BeP 630,929 (BASF)²⁸⁷ (X = residue split off as anion). Later, 3-phenyl-5-chlorothiadiazoled-(1,2,4) derivatives, in particular, e.g., the diazotizable amine²⁸⁹



or carbonyl and sulfonyl chlorides,²⁹⁰ such as



were developed as reactive groups.

The readily available 3,5-dichloro-4-cyanoisothiazole produced according to a synthesis discovered by Hatchard²⁹¹ from malonodinitrile and carbon disulfide by chlorination can be converted into its carbonyl chloride, a useful reactive component.²⁹²

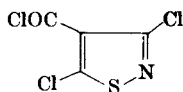
²⁸⁸ BASF, DAS 1,187,620 (31.7.1963).

²⁸⁹ BASF, BeP 671,510 (28.10.1964).

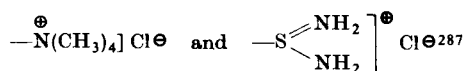
²⁹⁰ BASF, BeP 660,635 (5.3.1964).

²⁹¹ W. R. Hatchard, *J. Org. Chem.* **29**, 660 (1964).

²⁹² FBy, BeP 666,863 (17.7.1964).

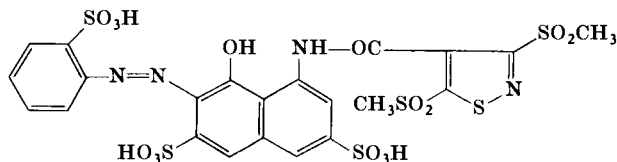


In addition to halogen, mention is made of $-\text{SO}_3\text{H}$, $-\text{SO}_2\text{H}$, $-\text{SH}$,²⁸⁵ strongly negative substituted phenoxy or thiophenoxy groups,²⁸⁶ $-\text{SCN}$, $-\text{SSO}_3\text{H}$, and

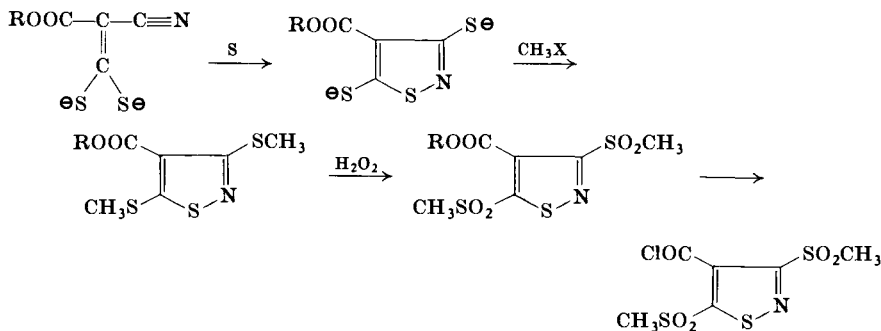


as mobile groups attached to the thiazole or thiadiazole carrier.

Of technical importance, however, are only the mobile sulfonyl groups, as described by Farbenfabriken Bayer in general attached to five-membered heterocycles,²⁹³ but in particular to the isothiazole system²⁹²; brilliant, rapidly fixed reactive dyestuffs are obtained, e.g., the red



Synthesis of the reactive component is achieved in the following manner from cyanoacetic ester, carbon disulfide, and sulfur (as an oxidizing agent), based on work done by Hatchard.²⁹⁴



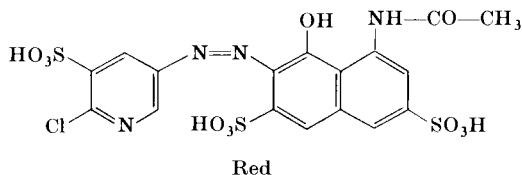
2. Pyridine Derivatives

With only one double-bonded ring nitrogen atom, pyridine is a low-activating carrier system. To be sufficiently reactive at least for

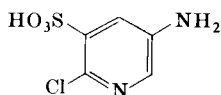
²⁹³ FBy, *FP* 1,467,293 (28.12.1964).

²⁹⁴ W. R. Hatchard, *J. Org. Chem.* **29**, 665 (1964).

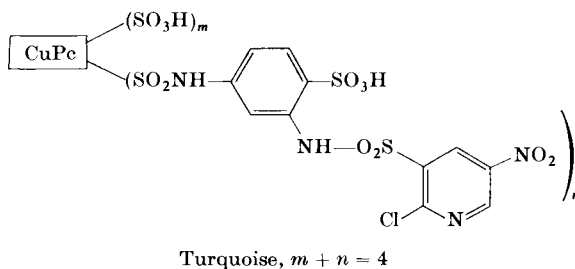
fixation in dry heat or in steam, further negative substituents are required in the *o*- or *p*-position to the mobile halogen,²⁹⁵ for example,



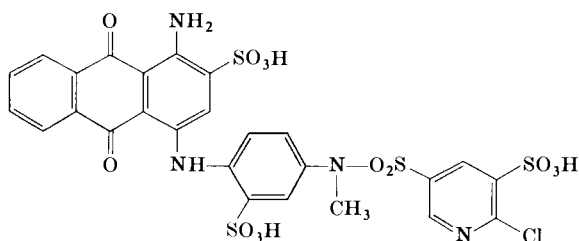
produced by diazotization of



and coupling to *N*-acetyl-H acid, or the turquoise



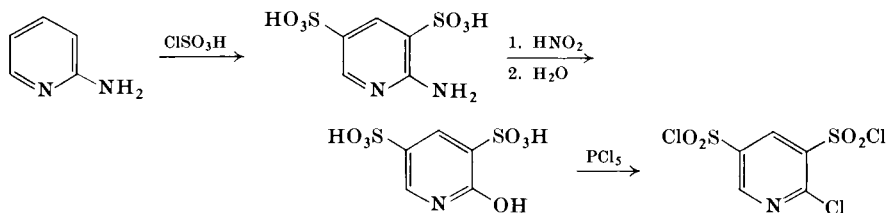
The dulling of the shade observed in dyes containing sulfonylamino bridges ($\text{(Dye)}-\text{NH}-\text{SO}_2-$ reactive group) as a result of dissociation of the sulfonamide hydrogen is avoided by *N*-alkylation.²⁹⁶



Francolor claims a new reactive component synthesized from 2-aminopyridine.²⁹⁶

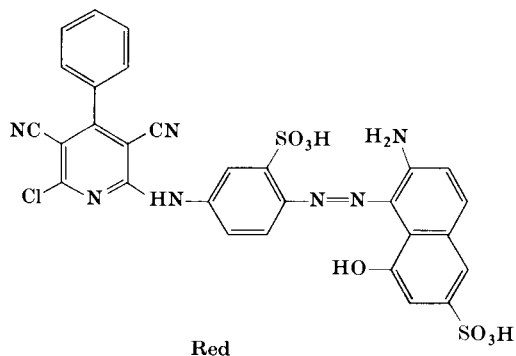
²⁹⁵ Fran, *FP* 1,420,406 (8.8.1964).

²⁹⁶ Fran, *FP* 88,352 (24.6.1965).

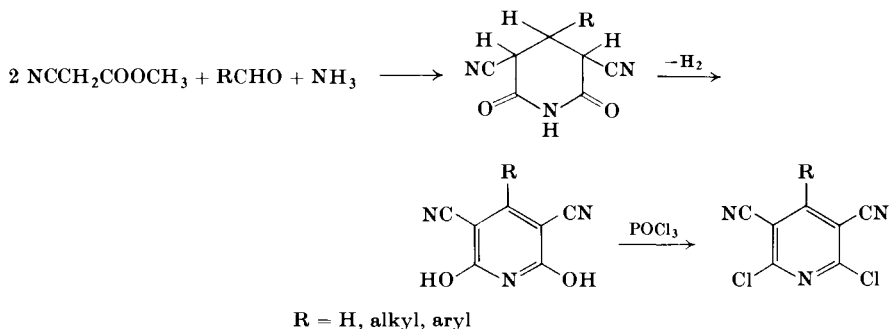


(After reaction of one chlorosulfonyl group with the amino dyestuff the second is hydrolyzed.)

By condensation of amino dyestuffs with 3,5-activated 2,6-dichloropyridine derivatives, easily fixed reactive dyes are obtained which are similar to the halodiazinylamino or halotriazinylamino dyestuffs and whose reactivity increases rapidly with rising temperature.^{297, 298}



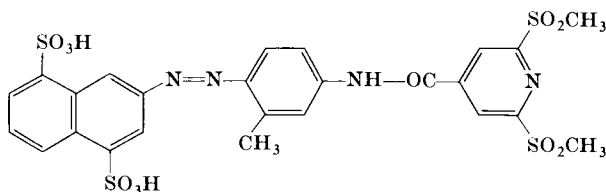
These 4-substituted 3,5-dicyano-2,6-dichloropyridines are obtained by the following method²⁹⁷:



²⁹⁷ M. Russocki and J. Mielicki, *Ind. Chim. Belge* **33**, No. 5, 449-454 (1968).

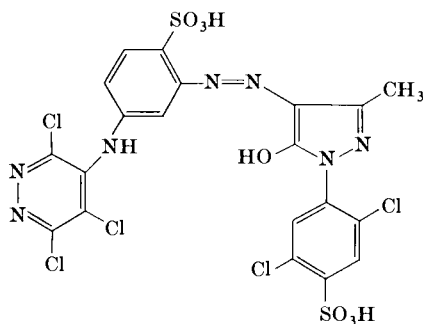
²⁹⁸ Institut Przemystie Organicznego, *BeP* 692,073 (30.12.1966).

Dyestuffs produced from 2,6-bis(methylsulfonyl)pyridine-4-carbonyl chloride, as described by Farbenfabriken Bayer, are considered particularly reactive.²⁹⁹



3. Pyridazine Derivatives

Dyestuffs containing chloropyridazine groups are suitable for the printing and continuous dyeing of cellulosic fibers with subsequent fixation in dry heat or in steam. Tetrachloropyridazine, which is easily obtained from dichloromaleic hydrazide on an industrial scale, can be condensed in an aqueous alcoholic medium with 1,3-diaminobenzene-4-sulfonic acid; after diazotization and coupling, e.g., the brilliant yellow³⁰⁰



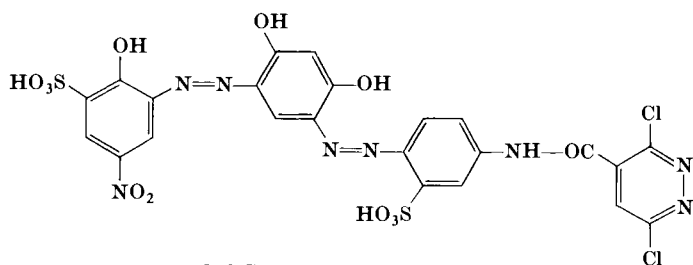
is obtained. When the chloropyridazine ring is bound not through the inactivating imino bridge, but through those bridge links which exert an electron-withdrawing influence on the heterocycle, the reactivity increases to such an extent that the dyestuffs are also suitable for dyeing from a long liquor.^{301, 302}

²⁹⁹ FBy, *BeP* 673,573 (10.12.1964).

³⁰⁰ CIBA, *BeP* 604,068 (23.5.1960).

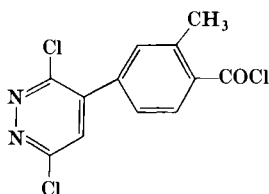
³⁰¹ CFM, *FP* 1,403,233 (2.7.1963); *BP* 1,064,020 (5.12.1964).

³⁰² CIBA, *FP* 1,541,028 (25.8.1966).

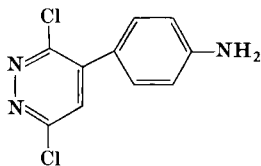


1:2 Co complex of ref. 301

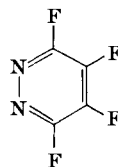
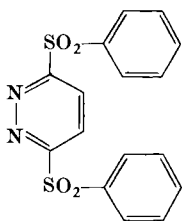
Further reactive components of this type are³⁰²



or the diazotizable amine.



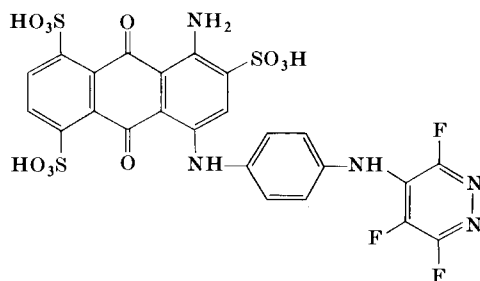
Farbenfabriken Bayer introduced sulfonyl groups³⁰³ and fluorine³⁰⁴ as activating mobile groups into the reactive components to replace activating bridge links.



³⁰³ FBy, *DP* 6,516,117 (10.12.1964).

³⁰⁴ FBy, *BeP* 713,141 (7.4.1967).

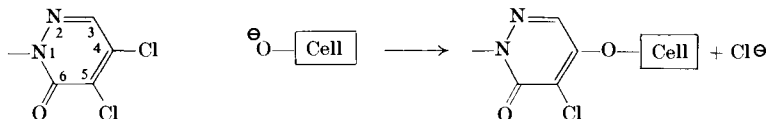
In this way, rapidly fixed printing dyestuffs, such as the bluish green



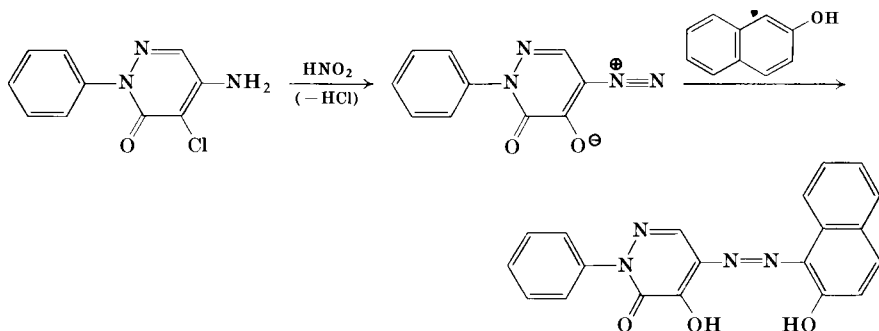
were synthesized.³⁰⁴

4. Pyridazone Derivatives

This reactive group, which has achieved technical importance in Primazin-P dyestuffs, was developed exclusively by BASF and described comprehensively by this firm in 1965.³⁰⁵ Contrary to the other technically important heterocyclic reactive groups, the 5-pyridazone substituted on nitrogen atom 1 is not an aromatic nitrogen-heterocycle; its 4,5-dihalo derivatives react in the 4-position as vinylogous carbonyl halides³⁰⁵:



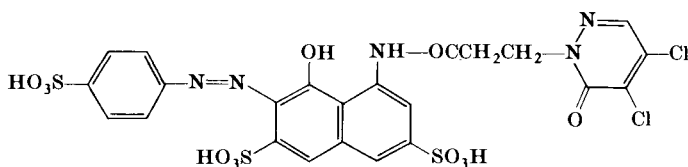
As the diazotizing and coupling capacity of 1-phenyl-4-amino-5-chloro-6-pyridazone shows, this system also has, in many cases, a certain aromatic character.³⁰⁶



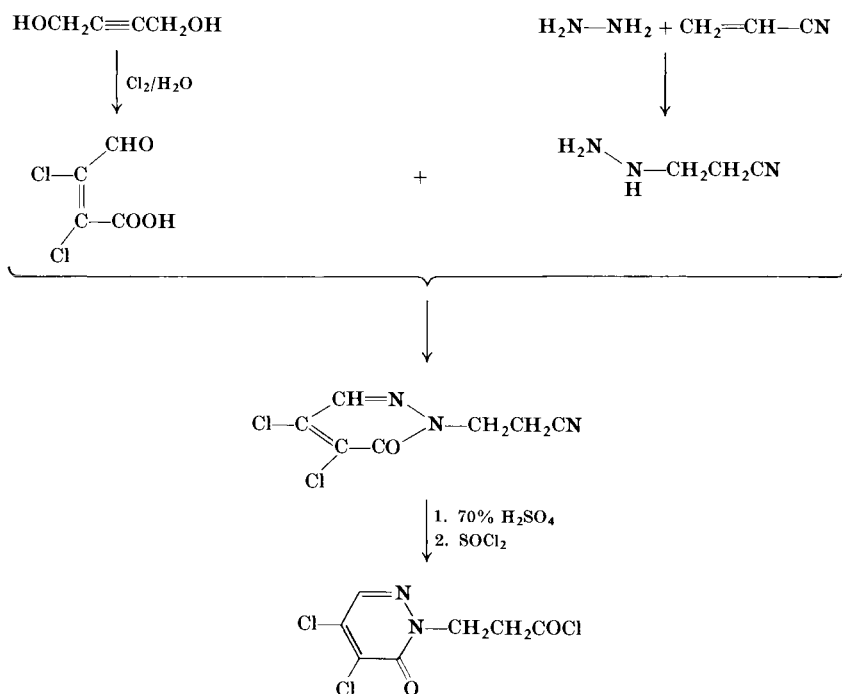
³⁰⁵ H. R. Hensel and G. Lützel, *Angew. Chem.* **77**, 303-308 (1965).

³⁰⁶ K. Dury, *Angew. Chem.* **77**, 282-290 (1965).

The commercial production of the reactive component on which Primazin-P dyestuffs, e.g., the brilliant red^{305, 307}



are based, is accomplished by starting with 2-butyne-1,4-diol obtained from Reppe chemistry, through mucochloric acid and cyclization with β -hydrazinopropionitrile.³⁰⁵⁻³⁰⁸



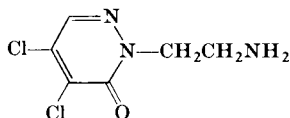
Thanks to the aliphatic bridge link between dyestuff and dichloropyridazone group, the unfixed residues of Primazin-P dyestuffs³⁰⁷ can easily be rinsed clear in textile printing.

The solubility and brilliance of shade are also improved by the intermediate aliphatic link.³⁰⁵

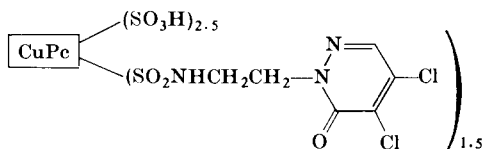
³⁰⁷ BASF, *DAS* 1,193,623 (18.8.1960); *BeP* 636,895 (7.8.1963); *FP* 1,499,615 (6.11.1965).

³⁰⁸ BASF, *BeP* 591,996 (23.6.1959).

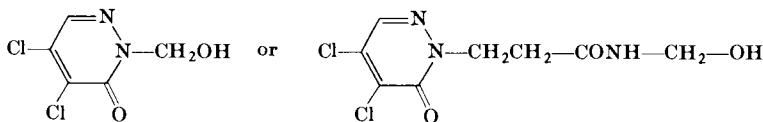
The following derivatives of 1-alkyl-4,5-dichloro-6-pyridazones are also suitable for the introduction of this reactive group into dyestuffs:



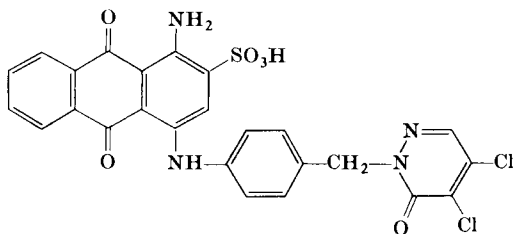
Refs. 305, 309



Turquoise



Ref. 305



According to Tscherniac-Einhorn

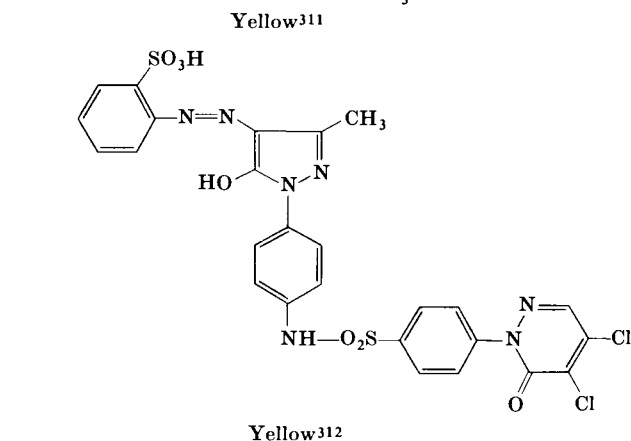
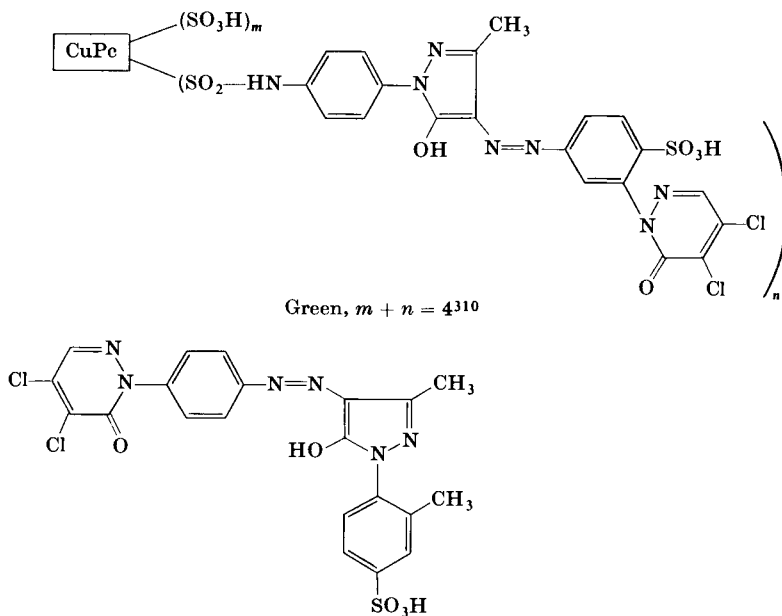
Linking of the dichloropyridazone ring to the dyestuff through functional groups such as $-N=N-$, and, $-NH-$,^{310, 311} or $-SO_2Cl$ and $-COCl$ ^{311, 312} at the 1-phenyl residue gives reactive dyes whose solubility does not quite attain commercial requirements.

³⁰⁹ BASF, *USP* 3,256,275 (14.2.1961); *BeP* 613,990 (16.2.1961).

³¹⁰ BASF, *DAS* 1,123,065 (17.8.1959); 1,130,096 (29.4.1960); 1,150,478 (4.5.1960).

³¹¹ BASF, *BeP* 592,281 (25.6.1959).

³¹² BASF, *BeP* 599,598 (29.1.1960).



As mobile groups attached to 6-pyridazone, only chlorine and the still more reactive bromine are mentioned; however, mucobromic acid required for the synthesis of 4,5-dibromo derivatives is too expensive for industrial application.³⁰⁵

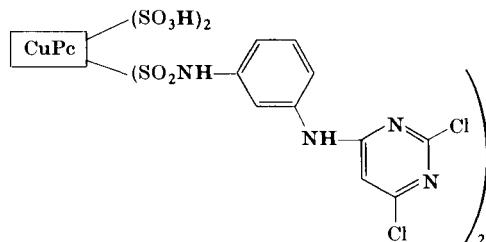
5. Pyrimidine Derivatives

In addition to *s*-triazine, pyrimidine is technically the most important heterocyclic carrier system; at present, four reactive ranges on this basis

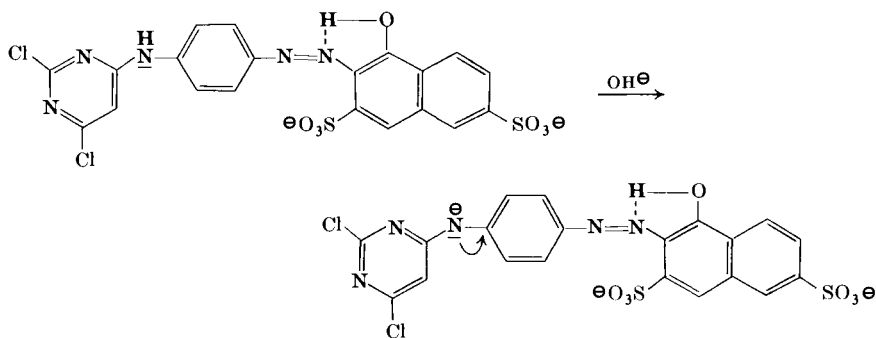
are available for cellulosic fibers—Drimaren (Sandoz), Reacton and Reactofil (Geigy), and Levafix P dyestuffs (Bayer).

Depending on the bridge link, substituents, and mobile groups, pyrimidine permits with regard to the properties attained in application (reactivity, ease of rinsing clear, standard of fastness properties of the dyestuffs) an even wider range of variations than *s*-triazine, which leads essentially to highly reactive dyes and whose less active mono-amino-monohalogen stage gives dyeings whose stability to hydrolysis doesn't attain this of pyrimidyl—cellulose bonds.

a. Chloro (and Bromo)-pyrimidines Linked through Imino Bridges.
i. Dichloropyrimidylamino dyestuffs. The suitability of the reactive dyes, e.g., the turquoise



produced by reaction of 2,4,6-trichloropyrimidine with water-soluble dyestuffs containing amino groups for the dyeing and printing of cellulosic fibers, was first recognized in 1956 by ICI³¹³ and also, independently, by BASF,³¹⁴ Sandoz,³¹⁵ and Bayer.³¹⁶ A dulling of the shade results from this direct linkage of the acid and, in the alkaline medium, dissociated³¹⁷ dichloropyrimidylamino group to the chromophore system.



³¹³ ICI, *DAS* 1,088,460 (4.9.1956); *BeP* 578,177 (27.4.1959).

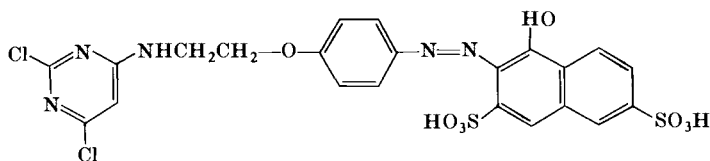
³¹⁴ BASF, *FP* 1,194,043 (5.4.1957).

³¹⁵ S, *BeP* 572,994 (21.11.1957); 573,299 (29.11.1957); 586,635 (13.2.1959).

³¹⁶ FBy, *BeP* 572,973 (22.11.1957).

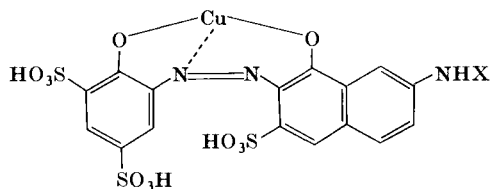
³¹⁷ H. Ackermann and P. Dussy, *Melliand Textilber.* **42**, 1167 (1961).

To prevent this, ICI introduced an aliphatic intermediate link between the dyestuff and the reactive group.³¹⁸



Brilliant red

ii. *Trichloropyrimidylamino dyestuffs*. The introduction of an electro-negative substituent—the simplest is chlorine—into the 5-position of 2,4,6-trichloropyrimidine increases the reactivity K_{cell} of the dyestuffs produced from it.³¹⁷



Rubine

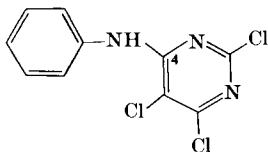
X	% Fixation, cold pad-batch process	$\frac{K_{\text{Cell}}^{30^\circ} \times 10^5 (\text{sec}^{-1})}{0.2 \text{ N NaOH}}$
	63	0.7
	75	2.0

In model tests, Ackermann and Dussy^{318a} obtained from aniline and tetrachloropyrimidine in aqueous acetone at 40–50° a homogeneous

³¹⁸ ICI, BP 952,620 (24.8.1959).

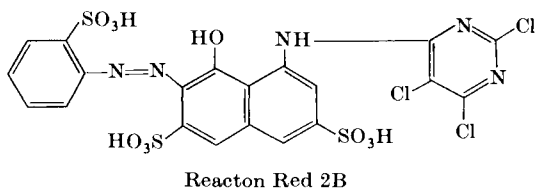
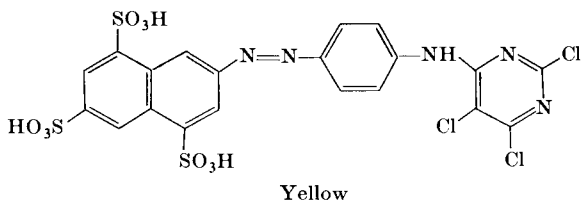
^{318a} H. Ackermann and P. Dussy, *Helv. Chim. Acta* **45**, 1683–1698 (1962).

product which, because of its physical properties and chemical reactions, was identified as 4-phenylamino-2,5,6-trichloropyrimidine.

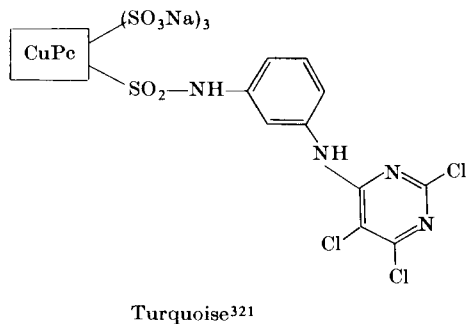


Also in the reaction with amino dyestuff molecules the chlorine atom in the 4-position of tetrachloropyrimidine reacts selectively.

Geigy³¹⁹ and Sandoz³²⁰ claimed almost simultaneously water-soluble trichloropyrimidinylamino reactive dyes, such as



or



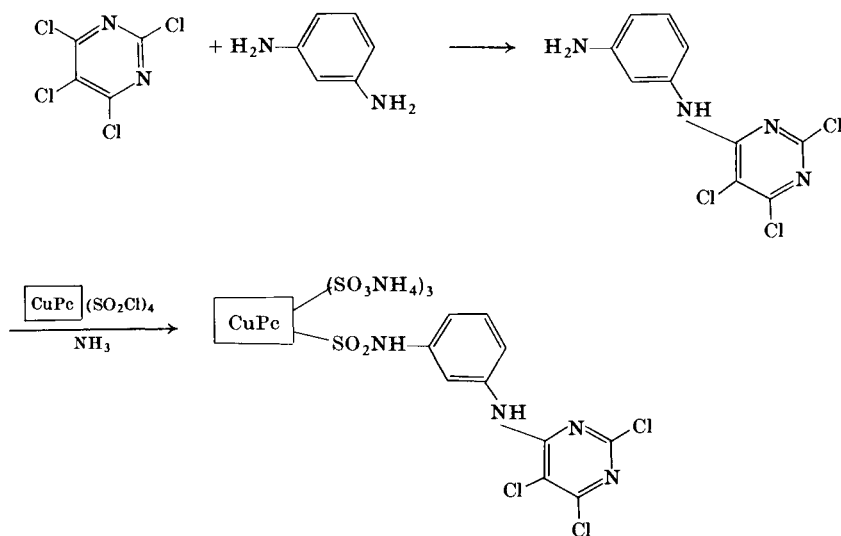
³¹⁹ Gy, *BeP* 578,933 (23.5.1958).

³²⁰ S, *BeP* 578,742 (28.5.1958); *SP* 399,623 (28.5.1958).

³²¹ S, *SP* 440,509 (28.8.1961).

and in 1959 marketed them together under the names Reacton³²² (Geigy) and Drimaren dyestuffs³²³ (Sandoz). This technically important group of cellulose-reactive dyes can be applied at 95° from a long liquor. Because of the ease of removal of unfixed dyestuff, the high stability of the alkaline printing pastes, and the negligible splitting of the fiber-dyestuff bond during fixation in steam, this group is particularly suitable for textile printing and continuous dyeing. Moreover, owing to the equally stable bond between cellulose and the pyrimidine ring in an alkaline or acid medium, this dyestuff group possesses outstanding wet-fastness properties.³²⁴

The above-mentioned turquoise dyestuff is best produced according to a patent of Sandoz³²¹ by stirring *m*-phenylenediamine in aqueous sodium bicarbonate solution with tetrachloropyrimidine for 48 hours at room temperature, giving the mono-condensation product 3-[2',4',5'-trichloropyrimidyl-(6')-amino]aniline, which is subsequently reacted with a mole of copper phthalocyanine-3,3',3'',3'''-tetrasulfonyl chloride first for 3 hours at 0–20° and pH 7.5–8 and then for 12 hours at 20–22° in ammoniacal solution.



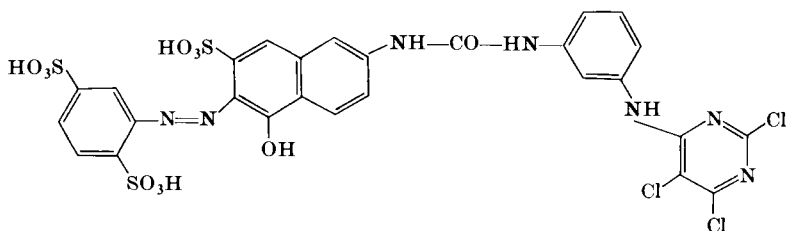
After dissolving with caustic soda, clarification, and salting out, the dyestuff with the above formula is produced.

³²² H. Schumacher, *Melliand Textilber.* **41**, 1548–1554 (1961).

³²³ M. Capponi, E. Metzger, and A. Giamava, *Am. Dyestuff Repr.* **50**, 505–515 (1961).

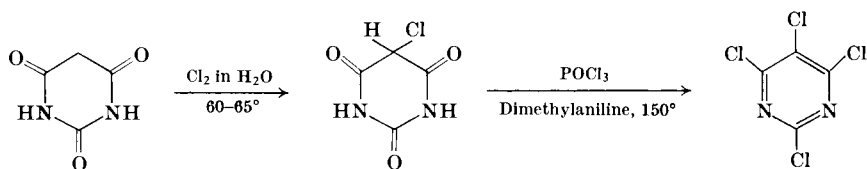
³²⁴ J. Benz, *J. Soc. Dyers Colourists* **77**, 734–740 (1961).

Geigy developed the Reacton S dyes which are particularly recommended in the exhaustion process, e.g., by introduction of an arylurea group.³²⁵

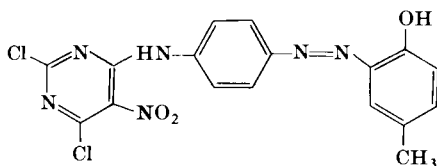


Orange

Sandoz discovered a technically advantageous tetrachloropyrimidine synthesis proceeding through 5-chlorobarbituric acid.³²⁶



iii. *Chloropyrimidylamino dyestuffs with other negative substituents in the 5-position.* Water-insoluble dichloro-5-nitropyrimidylamino dyestuffs, e.g., the yellow



were recommended by ICI³²⁷ and Sandoz³²⁸ for the dyeing of polyamide fibers—if required, with an alkaline aftertreatment. Cellulose dyes of this type, such as³²⁹

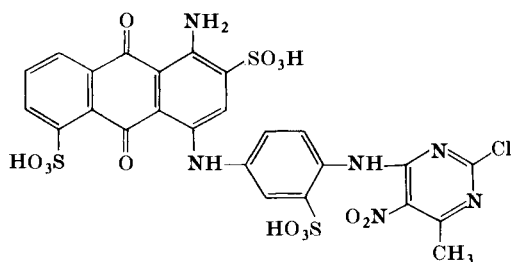
³²⁵ Gy, *SP* 460,205 (17.3.1961).

³²⁶ S, *BeP* 590,251 (6.5.1959).

³²⁷ ICI, *BP* 822,948 (30.1.1957).

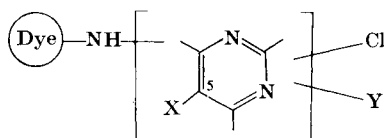
³²⁸ S, *BeP* 585,384 (18.12.1958).

³²⁹ ICI, *BP* 891,601 (28.4.1959).



Greenish blue

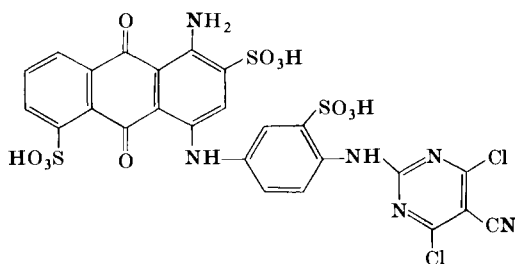
are activated in such a manner that they react with cellulose under much milder conditions than trichloropyrimidylamino derivatives, although the fiber bond formed is also split so easily that they are unsuitable for practical application. Sandoz³³⁰ and ICI³³¹ claimed halopyrimidine dyestuffs which can also carry other negative groups (X) in the 5-position.



Y = Cl, H, alkyl, -COOR

X = -NO₂; -CN; -COOH; -SO₃H; -CONH₂; -SO₂NH₂; haloalkyl,
e.g., -CH₂Cl; -CH₂COOH

In the greenish blue³³¹

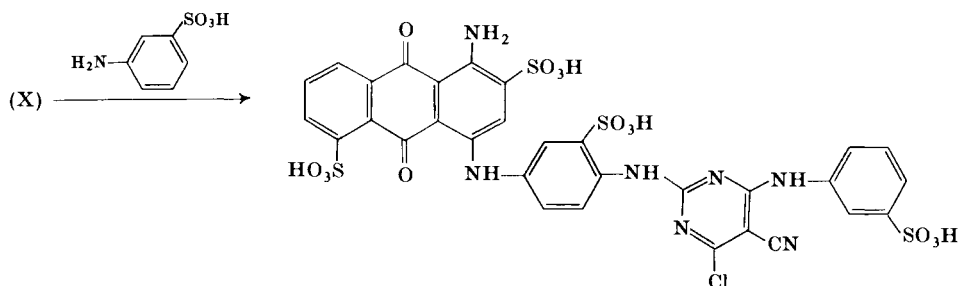


(X)

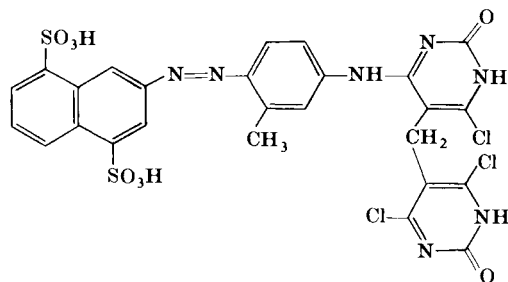
³³⁰ S, *BeP* 589,889 (27.4.1959); 589,972 (29.4.1959); *SP* 419,385; 420,414 (31.7.1959).

³³¹ ICI, *BeP* 592,748 (23.10.1959).

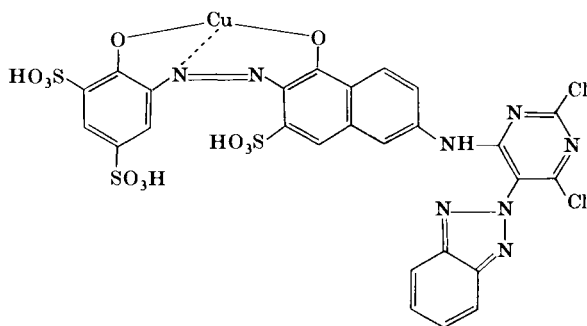
a chlorine atom can be substituted by NH_3 or an amine, giving dyestuffs with still sufficient reactivity.³³²



5-Substituents of a particular type are present in the dyestuffs synthesized by GAF³³³ from 5,5'-methylenebis(chloropyrimidine)³³⁴



and the 5-aryltriazolyl derivatives of Geigy.³³⁵



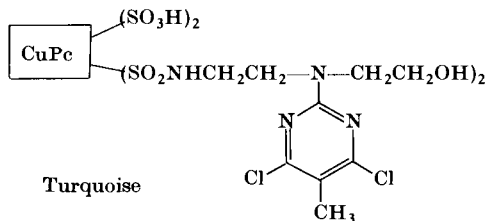
³³² ICI, *FP* 80,328/1,265,518 (12.9.1960).

³³³ G, *USP* 3,232,926 (31.12.1962).

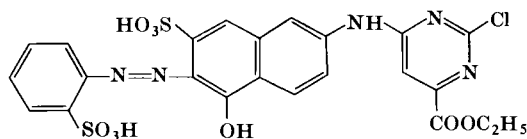
³³⁴ H. Gysling and G. Schwarzenbach, *Helv. Chim. Acta* **32**, 1501 (1949).

³³⁵ Gy, *FP* 1,402,553 (30.7.1963).

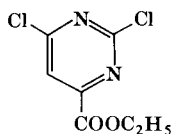
iv. *5-Alkylchloropyrimidylamino dyestuffs*. 5-Methyl-2,4,6-trichloropyrimidine was used by Geigy as a reactive component for azo³³⁶ and phthalocyanine dyes.³³⁷



v. *Halopyrimidylamino dyestuffs with a negative substituent in the 6-position*. For the synthesis of such dyestuffs, e.g., the orange

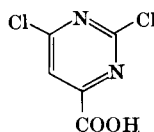


the reactive components, for example,



Ref. 338

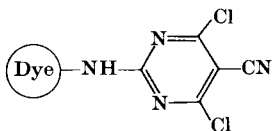
or



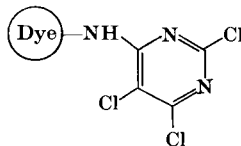
Ref. 339

are suitable.

vi. *Halopyrimidylamino dyestuffs with other mobile groups in addition to halogen*. If dihalo- or trihalopyrimidylamino dyestuffs, such as



or



e.g., (Dye) = 2-Naphthylamine-4,8-disulfonic acid \rightarrow *m*-Toluidine

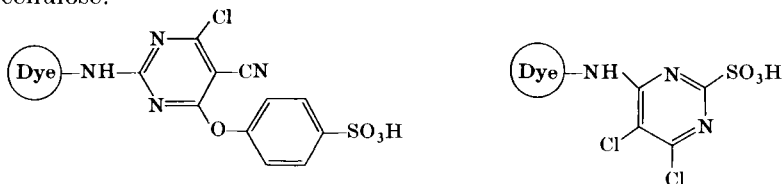
³³⁶ Gy, *BeP* 578,932 (23.5.1958).

³³⁷ Gy, *FP* 1,227,999 (26.6.1958).

³³⁸ S, *SP* 452,078 (30.4.1959).

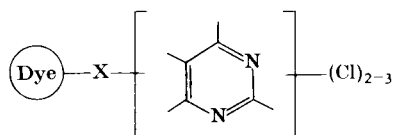
³³⁹ S, *SP* 364,062 (30.4.1959).

are reacted with phenolsulfonic acids³⁴⁰ or with alkali sulfites,³⁴¹ a chlorine atom is replaced by the sulfophenoxy residue or the sulfo group, which are themselves mobile groups capable of nucleophilic substitution by cellulose.

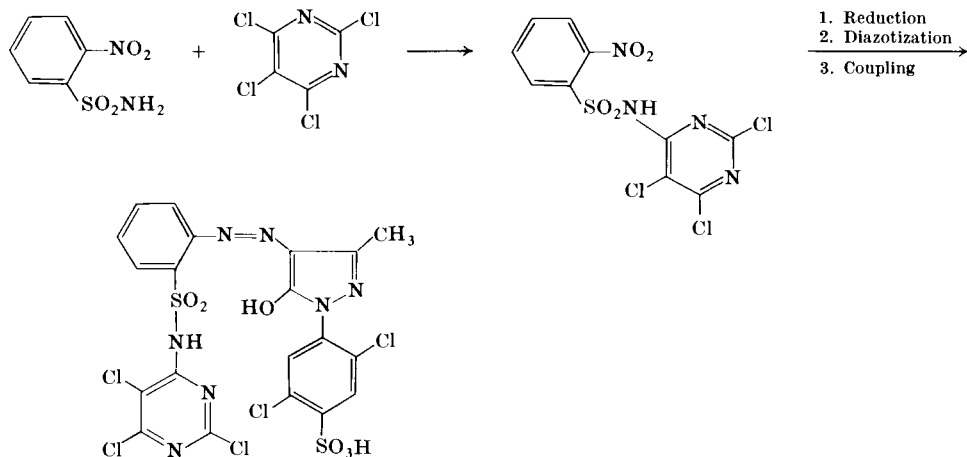


The increased water solubility of the dyes achieved in this way may sometimes be an advantage, but the instability of the sulfo group attached to the pyrimidine ring is a disadvantage, since it slowly splits out as SO_2 .

b. Chloro and Bromo pyrimidines Linked through other Bridge Members (X). The general structure of these dyes is



i. Chloropyrimidylaminosulfonyl dyestuffs ($X = -\text{SO}_2\text{NH}-$). Sulfonamide groups can be acylated, for example, with tetrachloropyrimidine, which in this way may also be introduced into dyestuffs.³⁴²

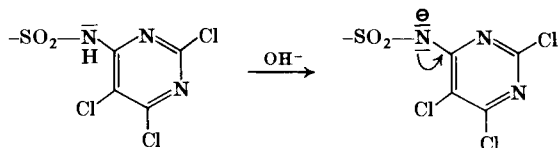


³⁴⁰ ICI, *FP* 1,283,172 (24.8.1959).

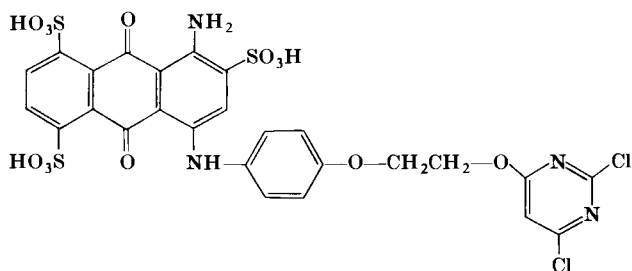
³⁴¹ ICI, *BeP* 594,355 (24.8.1959).

³⁴² S, *BeP* 591,770 (12.6.1959).

The chloropyrimidylaminosulfonyl group is so acidic that it is largely dissociated in the alkaline medium required for the fiber reaction, resulting in an inactivation of the reactive system.



ii. *Chloropyrimidyloxy (or thio) dyestuffs* ($X = -O-$ or $-S-$). Both phenolic³⁴³⁻³⁴⁷ and alcoholic³⁴³⁻³⁴⁸ hydroxyl groups (or mercapto groups) in dyestuffs or dyestuff intermediates can be condensed smoothly in an aqueous or aqueous acetone medium in the presence of acid-binding agents with 2,4,6-trichloropyrimidine,^{343, 348} 2,4-dichloropyrimidine or 2,4-dichloro-6-methylpyrimidine,^{344, 345, 348} 2,4,5,6-tetrachloropyrimidine^{348, 349} or chloropyrimidine derivatives with negative groups in the 5-position ($-\text{NO}_2$, $-\text{CN}$, $-\text{COOH}$, $-\text{CONH}_2$, $-\text{SO}_3\text{H}$, $-\text{SO}_2\text{Cl}$, $-\text{SO}_2\text{NH}_2$).^{346, 347} Because the oxygen bridge is more electronegative than the imino bridge and, in contrast to the latter, is not dissociated in the alkaline medium, it shows a less marked inactivation of the reactive group, i.e., dyestuffs of this type, for example,



Bluish green³⁴³

³⁴³ S, *BeP* 573,301 (29.11.1957).

³⁴⁴ S, *SP* 363,748 (24.12.1958).

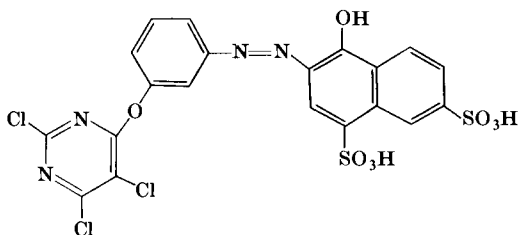
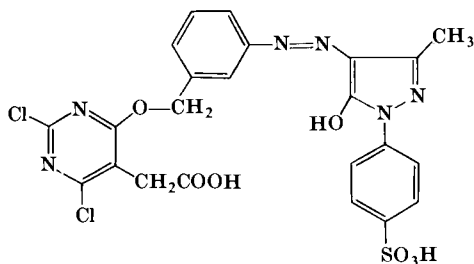
³⁴⁵ S, *SP* 364,856 (24.12.1958).

³⁴⁶ S, *SP* 419,386 (31.7.1959).

³⁴⁷ S, *SP* 419,387 (31.7.1959).

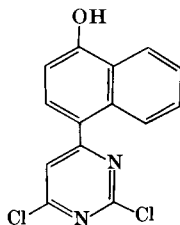
³⁴⁸ S, *BeP* 603,752 (27.4 1961).

³⁴⁹ S, *SP* 401,304 (27.7.1961).

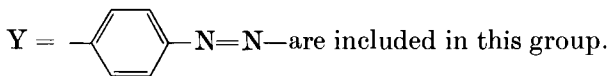
Red³⁴⁹Yellow³⁴⁸

are more reactive than halopyrimidylamino derivatives.

iii. *Chloropyrimidyl dyestuffs with direct linkage between chloropyrimidine and dyestuff* ($X = \text{direct linkage}$). Naphthols condense with chloropyrimidines in the presence of Friedel-Crafts catalysts to form fiber-reactive coupling components,³⁵⁰ e.g., 1-naphthol and 2,4,6-trichloropyrimidine give

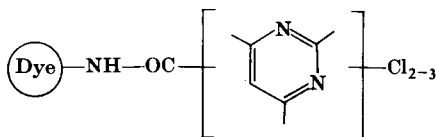


iv. *Reactive dyes from carbonyl chlorides of chloropyrimidyl derivatives and dyestuffs containing amino groups* ($X = -NH-OC-Y-$). Dyes with $Y = \text{direct linkage}$, $Y = \text{alkyls}$, $Y = \text{aryls}$, and $Y = \text{aralkyls}$, and



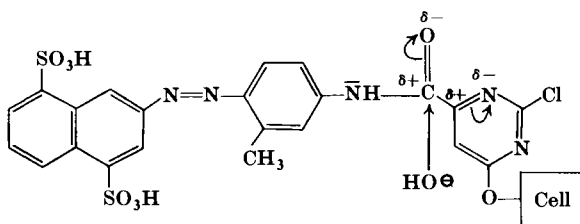
³⁵⁰ ICI, BP 1,028,922 (1.3.1962).

(a) *Chloropyrimidylcarbonyl chlorides* (Y = direct linkage) as *reactive components*. The introduction of a carbonyl group between the chloropyrimidyl residue and the amino group of the dyestuff offers two



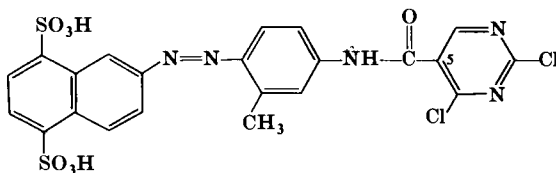
advantages over chloropyrimidylamino dyes: Firstly, an activation through the electron-attracting carbonyl group replaces inactivation through the imino bridge, i.e., the dyestuffs are much more reactive. They dye cellulose partly at room temperature from a long liquor. Secondly, more brilliant shades are obtained when the pyrimidyl residue is not bound directly to the auxochrome.

On the other hand, a disadvantage is that the electron-attracting effect of the pyrimidine system on the carbonyl group results in an unstable carbamide bridge liable to hydrolysis, and therefore in dyeings with poor fastness to washing.



Yellow³⁵¹

This effect is least evident in the relatively electron-rich 5-position of pyrimidine, for which reason dyestuffs such as the yellow³⁵²

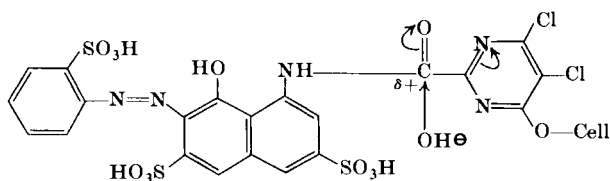


³⁵¹ Gy, *BeP* 587,308 (6.2.1959); CIBA, *BeP* 593,840 (7.8.1959).

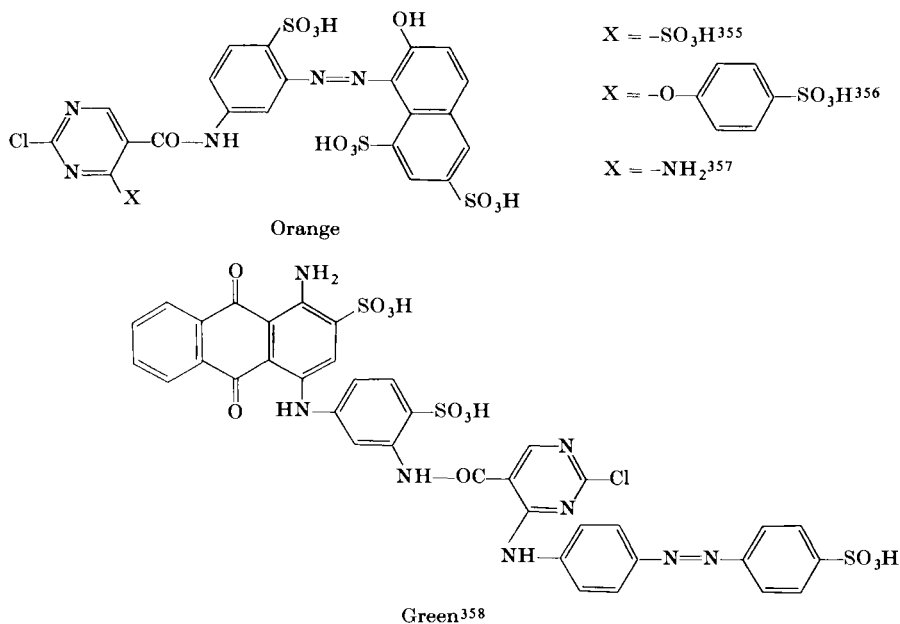
³⁵² Gy, *BeP* 644,495 (1.3.1963); S, *BeP* 645,855 (9.5.1963); *FP* 1,385,660 (13.12.1962); 1,567,844 (8.6.1967).

combine high reactivity with technically useful fastness to washing of the dyeings (Reactofil dyestuffs, Geigy).

From 4,5,6-trichloropyrimidine-2-carbonyl chloride³⁵³ dyestuffs are obtained which react very quickly with cellulose at room temperature, but whose carbamide bridge is so unstable that it is generally split when the dyeing is washed at the boil in an alkaline liquor.³⁵⁴



In 2,4-dichloropyrimidoyl-(5)-amino dyestuffs, one of the two chlorine atoms (presumably the one in the 4-position) can be replaced by a sulfo group,³⁵⁵ a phenoxy or thiophenoxy group,³⁵⁶ or by an amino substituent—possibly a further dyestuff molecule,^{357, 358} while maintaining the cellulose reactivity.



³⁵³ FBy, *BP* 1,202,026 (25.3.1968).

³⁵⁴ Farbenfabriken Bayer AG, unpublished work.

³⁵⁵ Gy, *SP* 464,395 (28.2.1964).

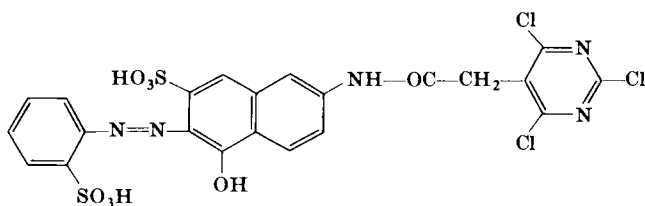
³⁵⁶ Gy, *SP* 464,396 (28.2.1964).

³⁵⁷ Gy, *SP* 464,397 (28.2.1964).

³⁵⁸ S, *FP* 86,540 (4.10.1963).

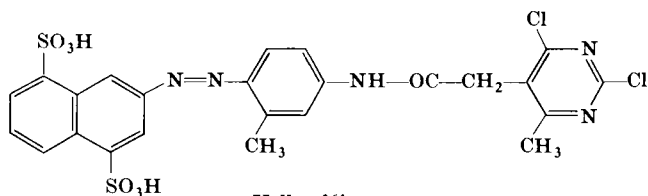
2,4-Dichloropyrimidine-5-(or 6-) carbonyl chlorides are produced by condensation of urea with oxymethylenemalonic ester or oxalacetic ester and treatment of the hydroxypyrimidine carboxylic acids with halogenating agents such as PCl_3 , PCl_5 , POCl_3 , SOCl_2 , etc.³⁵⁹

(b) *Carbonyl chlorides linked through bridge members, $-\text{Y}-$, with the chloropyrimidyl residue as reactive components ($\text{Y} = \text{alkyls, aryls, aralkyls}$). 2,4,6-Trihydroxypyrimidyl-(5)-acetic acid, produced from ethane-1,1,2-tricarboxylic ester and urea, is converted with chlorinating agents into 2,4,6-trichloropyrimidyl-(5)-acetyl chloride. Reactive dyes synthesized with this product, e.g., the orange*

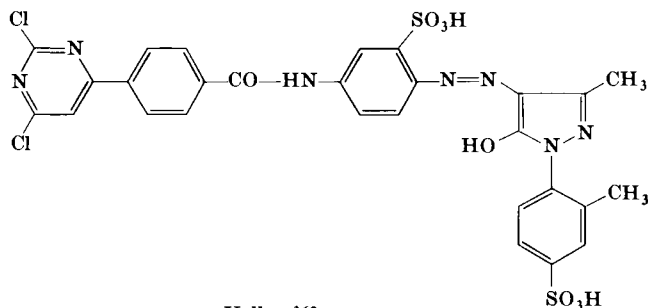


are very reactive and give dyeings and prints with good fastness to washing.³⁶⁰

Separation of the carbonyl group from the pyrimidine ring through an intermediate link, $-\text{Y}-$, always leads to carbamide bridges which are more stable to hydrolysis.



Yellow³⁶¹



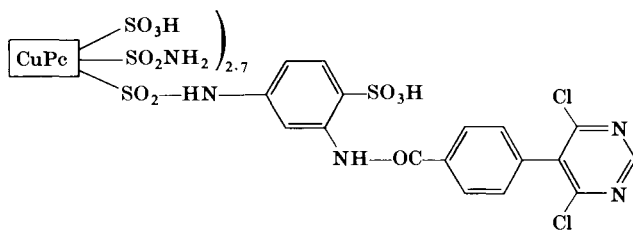
Yellow³⁶²

³⁵⁹ CIBA, *BeP* 593,588 (31.7.1959).

³⁶⁰ S, *BeP* 594,856 (16.10.1959).

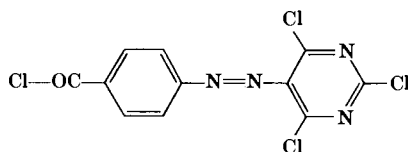
³⁶¹ S, *FP* 1,473,449 (11.3.1965).

³⁶² BASF, *BeP* 644,765 (6.3.1963).

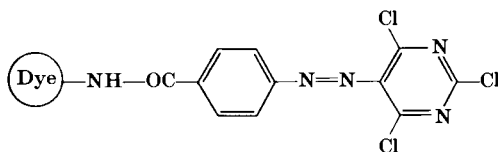
Turquoise³⁶³

(c) *Chloropyrimidylazobenzene derivatives* ($Y = \text{—}\text{C}_6\text{H}_4\text{—N=N—}$) An

original type of chloropyrimidine dyestuff was developed by Francolor,³⁶⁴ who coupled, for example, diazotized 4-aminobenzoic acid with barbituric acid and obtained from this product with POCl_3 the reactive component

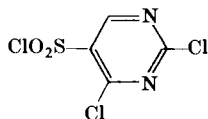


In the dyestuffs



the electron-attracting azo bridge in the 5-position exerts a strong activation on the trichloropyrimidine system.

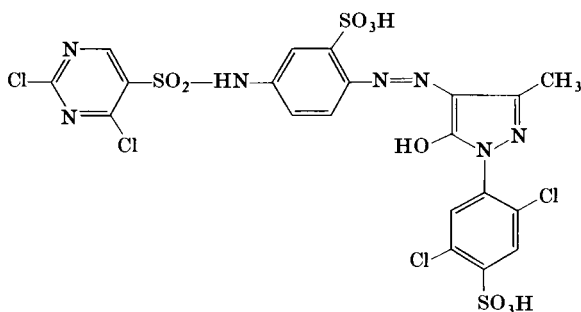
v. *Reactive dyes from sulfonyl chlorides of chloropyrimidyl derivatives and dyestuffs containing amino groups* ($X = \text{—NH—O}_2\text{S—}$). Uracil can be chlorosulfonated in the 5-position and then converted with $\text{POCl}_3/\text{PCl}_5$ into the reactive component



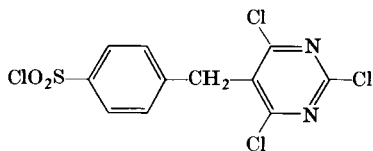
³⁶³ CIBA, *BeP* 703,535 (7.9.1966).

³⁶⁴ Fran, *FP* 1,367,542 (22.5.1963).

from which dyestuffs of the type

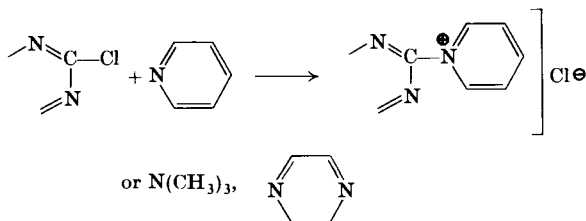


were synthesized.³⁶⁵ Also in this case, intermediate linkages, e.g., $-\text{CH}_2-$, can be introduced between the chlorosulfonyl group and the chloropyrimidyl residue, resulting in reactive components, such as³⁶⁶



c. Pyrimidines with Mobile Groups other than Chlorine (and Bromine).

i. Pyrimidines with quaternary ammonium groups. In 1959, ICI discovered that derivatives of less reactive chloro heterocycles, such as monochlorotriazinylamino and also dichloro- and trichloropyrimidinyl-amino dyestuffs react smoothly with 1 mole of tertiary amine in aqueous solution, forming stable ammonium salts whose cellulose reactivity is considerably higher than that of the chlorine products on which they are based.³⁶⁷



³⁶⁵ CIBA, *BeP* 596,940 (13.11.1959).

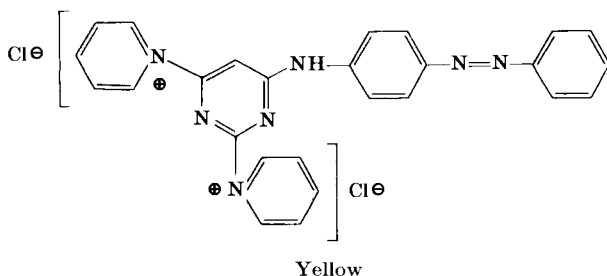
³⁶⁶ S, *BeP* 665,839 (26.6.1964).

³⁶⁷ ICI, *FP* 1,271,347 (24.9.1959); *BeP* 595,299 (24.9.1959).

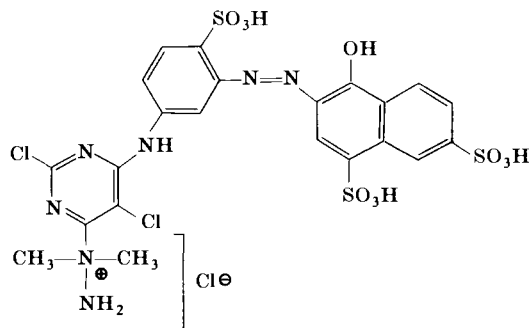
It was soon recognized that small, nonstoichiometric additions of such quaternized dyestuffs or intermediate products suffice for the activation of chlorotriazine and chloropyrimidine dyestuffs since in the cellulose reaction the catalytic tertiary amine is constantly liberated.³⁶⁸

Mobile ammonium groups have attained no technical importance except in the monochlorotriazine range.

Cellulose-reactive dyestuffs free from sulfo groups which owe their water solubility only to the mobile quaternary pyridinium groups are also described.³⁶⁹



Sandoz³⁷⁰ and, later, also ICI³⁷¹⁻³⁷³ used unsymmetrical dimethylhydrazine in this reaction. For example, reaction of 1 mole of unsymmetrical dimethylhydrazine with the corresponding trichloropyrimidylamino dyestuff at 40° in aqueous solution gives the acylhydrazonium dye



³⁶⁸ ICI, *BeP* 628,855 (26.2.1962).

³⁶⁹ American Aniline Prod., Inc., *USP* 3,152,113 (18.12.1961).

³⁷⁰ S, *FP* 1,331,981 (21.4.1961).

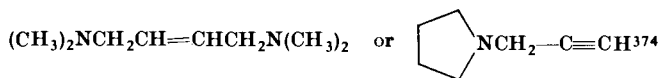
³⁷¹ ICI, *FP* 1,365,388 (15.5.1962).

³⁷² ICI, *FP* 1,364,736; 1,365,386; 1,365,387; 1,366,826 (15.5.1962); *BP* 974,136 (15.5.1962); *FP* 1,365,389; 1,370,185 (15.5.1962).

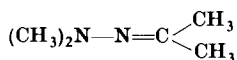
³⁷³ ICI, *FP* 1,370,128 (15.5.1962); S, *SP* 452,088 (29.11.1966); ICI, *FP* 1,365,385 (15.5.1962).

fixation of which is obtained on cellulosic fabric in the cold pad-batch process with soda ash after 6 hours. (The starting dyestuff requires caustic soda and a much longer time for complete fixation.)

In addition to special tertiary amines, e.g.,

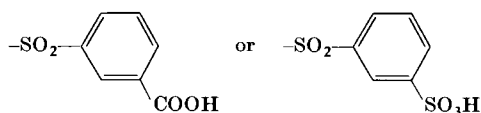


and special unsymmetrical dialkylhydrazines, such as $\text{H}_2\text{NN}(\text{CH}_2)_6$,³⁷⁵ hydrazones, e.g.,³⁷⁶



and also tetrazenes, e.g., $(\text{CH}_3)_2\text{N}-\text{N}=\text{N}-\text{N}(\text{CH}_3)_2$,³⁷⁷ are also described as catalysts for chloropyrimidylamino dyestuffs.

ii. *Pyrimidines containing mobile sulfonyl groups.* In 1963, Geigy mentioned alkylsulfonyl residues as possible mobile groups attached to pyrimidine-5-carboxylic acid derivatives,³⁵² and Cassella claimed aliphatic and heterocyclic carrier systems (*inter alia*, pyrimidine) with mobile sulfonyl groups, such as



which also contain a further water-solubilizing residue.¹³³

Farbenfabriken Bayer developed on a wide scale more or less simultaneously heterocyclic six-membered rings with mobile sulfonyl groups, particularly 2-methylsulfonylpyrimidines^{303, 378} which are very easily produced, marketing their Levafix P dyestuffs obtained on this basis in 1966.

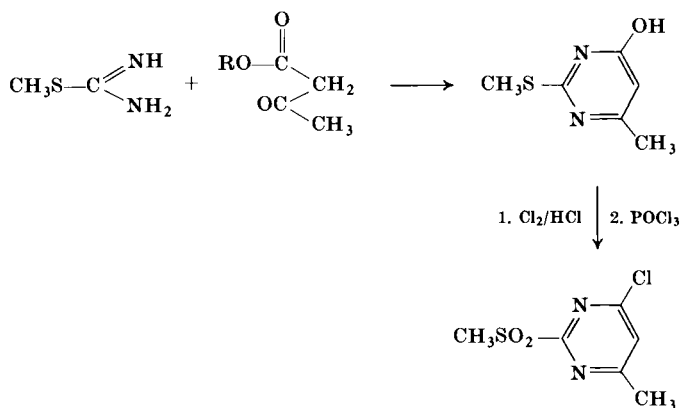
³⁷⁴ S, *BeP* 635,252 (10.8.1962).

³⁷⁵ S, *SP* 2,081/63 (7.9.1962).

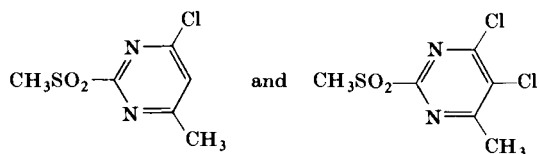
³⁷⁶ S, *BeP* 635,676 (31.8.1962); 635,897 (11.9.1962).

³⁷⁷ S, *BeP* 635,896 (4.9.1962).

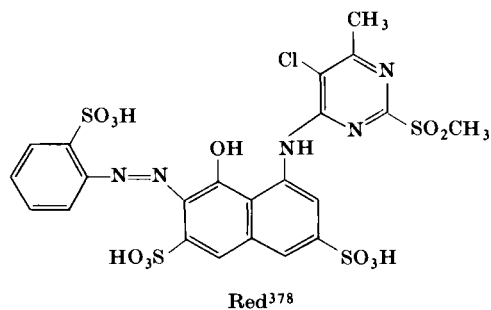
³⁷⁸ FBy, *BeP* 673,572; 673,573 (10.12.1964).



The reactive components

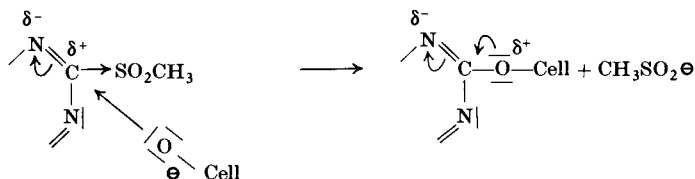


react with amino dyestuffs selectively at the chlorine atom in the 4-position, while the methylsulfonyl group is retained in the 2-position.

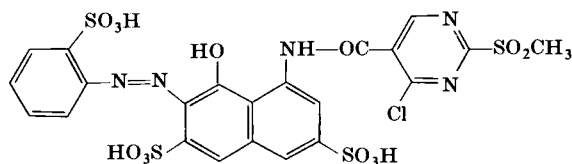


The commercial value of sulfonylpyrimidine dyestuffs is due to their high cellulose reactivity (in textile printing they are rapid-fixing types), combined with the stable fiber-dyestuff bond of the pyrimidine system. The reason for this combination of two properties which are opposed to each other in chloro heterocycles is the marked increase in the electrophilic character of the nuclear carbon atom through the sulfonyl group,

which disappears again in the cellulose reaction together with the mobile group.³⁷⁹

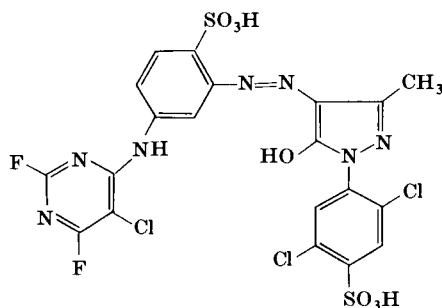


In addition to the technically important 2-methylsulfonylpyrimidyl-amino dyestuffs, derivatives of 2-methylsulfonylpyrimidine-4-³⁸⁰ and -5-carboxylic acid³⁸¹ are also described.



Brilliant red³⁸¹

iii. *Fluoropyrimidines*. The most recent group of cellulose-reactive pyrimidine compounds was discovered by Farbenfabriken Bayer^{382, 383} in 1966.



Thanks to the particularly strong electrophilicity of the reaction center through the mobile fluoro group, fluoropyrimidylamino dyestuffs are as

³⁷⁹ K. H. Schündehütte and K. Trautner, *Chimia (Aarau)* Suppl., p. 155 (1968).

³⁸⁰ FBy, DP 6,702,358 (16.2.1966).

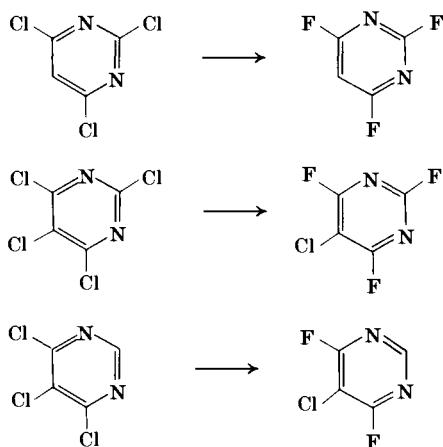
³⁸¹ FBy, DP 6,702,357 (16.2.1966).

³⁸² FBy, BeP 703,598 (10.9.1966).

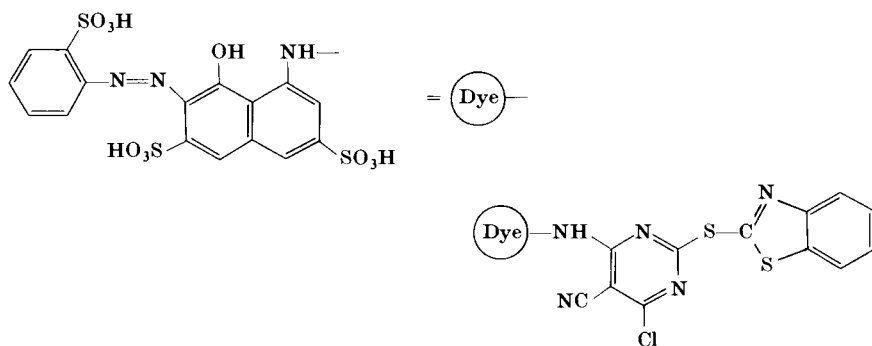
³⁸³ FBy, BeP 712,733 (25.3.1967).

reactive as dichlorotriazinylamino dyestuffs, i.e., they dye cellulose fibers at 30–40° from a long liquor and are fixed by steaming for 1 minute. In addition, they are particularly suitable for the dyeing of wool, on which they confer excellent wet-fastness properties. These technically very important dyestuffs were introduced into the market in 1970.

The new reactive intermediates are synthesized from the corresponding chloropyrimidines by halogen exchange with hydrofluoric acid or with alkali fluorides.³⁸⁴



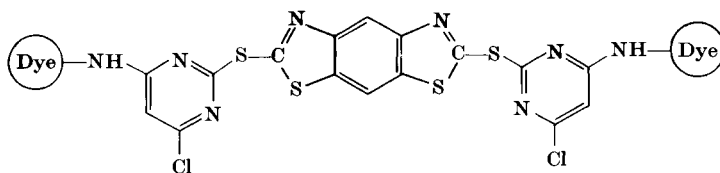
iv. Pyrimidines with other mobile groups. ICI also applied their systematic variations of the *s*-triazine mobile groups to pyrimidine. The following types, which have achieved no commercial importance up to the present, have been mentioned in patent applications:



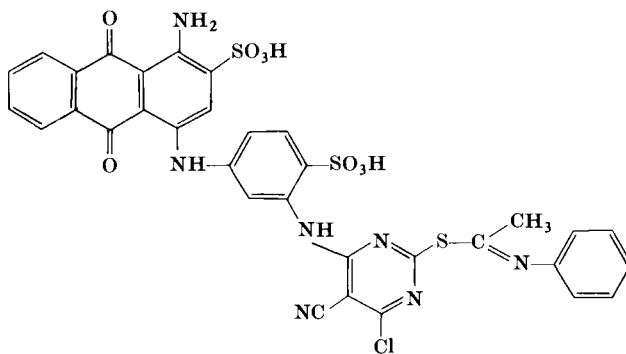
Ref. 385

³⁸⁴ FBy, BeP 706,987 (15.12.1966).

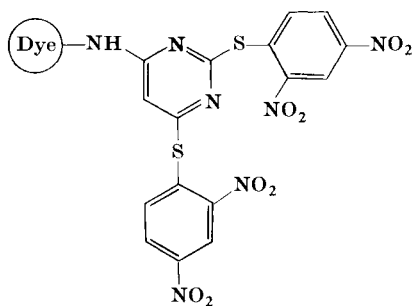
³⁸⁵ ICI, BeP 592,747 (8.7.1959).



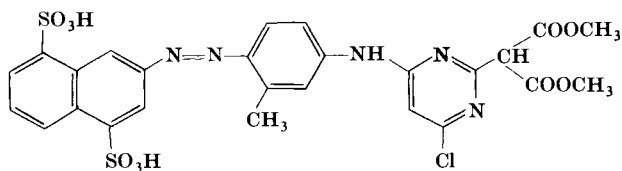
Ref. 386



Ref. 387



Ref. 388



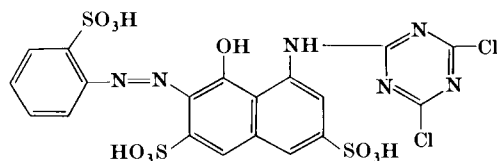
Ref. 389

³⁸⁶ ICI, *FP* 1,301,005 (14.7.1960).³⁸⁷ ICI, *BeP* 592,749 (31.12.1959).³⁸⁸ ICI, *FP* 1,286,998 (7.3.1960).³⁸⁹ ICI, *BeP* 610,754 (24.11.1960).

6. *s*-Triazine Derivatives

There are four types of *s*-triazine derivatives to be discussed: monohalo- and dihalo-substituted *s*-triazines, halo-substituted *s*-triazines with non-imino bridge links, and *s*-triazines with mobile groups other than halogen.

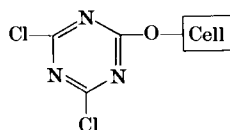
a. 2,4-Dihalo-s-triazinylamino-(6) Derivatives. i. Dichloro-s-triazinylamino derivatives. Rattee and Stephen of ICI recognized in 1954 that water-soluble dichlorotriazinylamino dyestuffs with a low affinity, such as the brilliant red



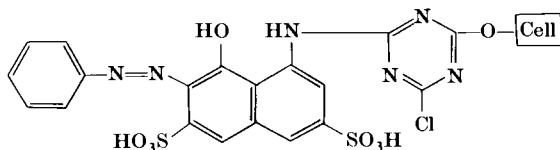
Procion Brilliant Red M-2BS

dye heavy shades on cellulosic fibers at room temperature from an aqueous alkaline solution with excellent wet-fastness properties, thereby discovering the first and—together with the monochlorotriazinylamino dyestuffs (Procion H and Cibacron dyestuffs)—even today, technically the most important group of cellulose-reactive dyestuffs.

This discovery was preceded by various unsuccessful attempts of other authors³⁹⁰ to produce reactive dyeings on cellulose from an aqueous liquor. In 1929–30 Haller and Heckendorn had already studied thoroughly the reaction of cyanuric chloride (and numerous other halogen heterocycles) dissolved in xylene with alkali cellulose, forming “immunized” cellulose derivatives of the type



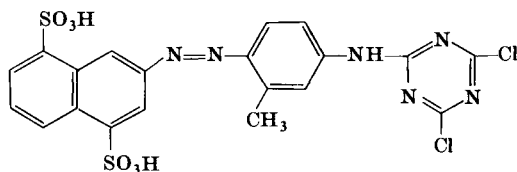
which could be dyed in a second reaction step with water-soluble amino dyestuffs with good wet-fastness properties.³⁹¹



³⁹⁰ G. Schroeter, *Ber.* **39**, 1559 (1906); IG, *USP* 1,567,731 (8.6.1925); J. D. Guthrie, *Am. Dyestuff Repr.* **41**, 13 (1952).

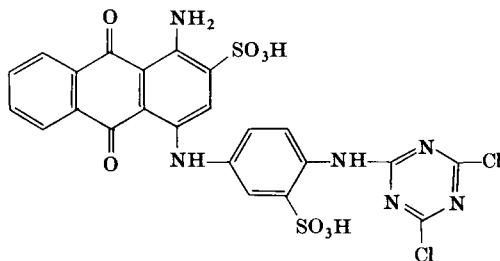
³⁹¹ CIBA, *USP* 1,886,480 (21.2.1930).

In their original patent applications dated 29.11.1954, ICI claim the dyeing and printing of cellulosic textiles with water-soluble azo³⁹² and anthraquinone dyestuffs³⁹³ containing a halo-*s*-triazinylamino group, the material first being padded with a neutral, aqueous solution of a dyestuff, such as the azo yellow



Procion Yellow M-RS

or the anthraquinone blue



Procion Blue M-3GS

and fixation then being obtained in 1 hour in a hot common salt solution containing alkali. For printing, ICI use a print paste which contains, in addition to the reactive dyestuff, urea, alginate thickening, and sodium bicarbonate, yielding the stronger alkaline soda ash required for the fiber reaction during subsequent steaming. In an "addition to" patent³⁹³ treatment with the acid-binding agent is undertaken before or simultaneously with application of the anthraquinone dyestuff.³⁹⁴ With the same priority ICI patented the dyestuff types corresponding to the first three Procion dyestuffs mentioned above, Yellow M-RS,³⁹⁵ Brilliant Red M-2BS,³⁹⁶ and Blue M-3GS,³⁹⁷ as well as Procion Brilliant Orange M-GS.³⁹⁸

³⁹² ICI, *BeP* 543,218 (29.11.1954).

³⁹³ ICI, *BeP* 543,219 (29.11.1954).

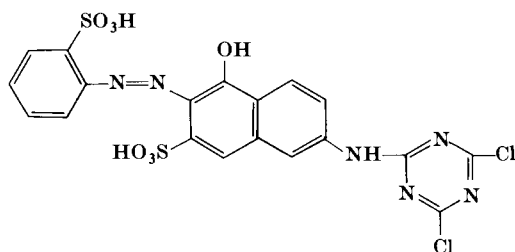
³⁹⁴ ICI, *BeP* 556,776 (18.4.1956).

³⁹⁵ ICI, *FP* 1,143,176 (29.11.1954).

³⁹⁶ ICI, *BeP* 543,214 (29.11.1954).

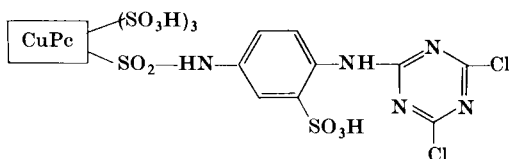
³⁹⁷ ICI, *BeP* 543,216; 543,217 (29.11.1954).

³⁹⁸ ICI, *DAS* 1,019,025 (29.11.1954).

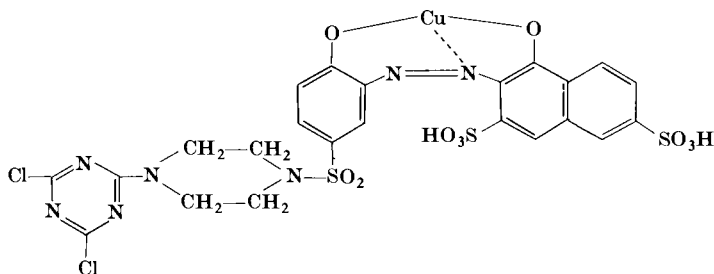


Procion Brilliant Orange M-GS

Subsequently, phthalocyanine derivatives, such as³⁹⁹



and, in certain cases, metal-containing azo dyestuffs with an aminoalkyl bridge between dyestuff and halo-*s*-triazinyl residue, such as⁴⁰⁰



were also claimed, as well as numerous other specific halo-*s*-triazinyl-amino dyes.

ICI also recognized the suitability of water-soluble dichloro-*s*-triazinylamino dyestuffs for dyeing⁴⁰¹ and printing⁴⁰² on natural and synthetic polyamide fibers, while Sandoz recommended disperse dyes for this application, such as the yellow⁴⁰³

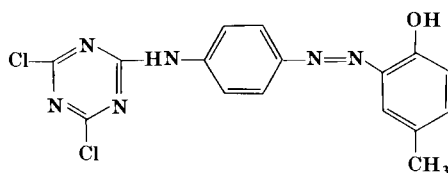
³⁹⁹ ICI, *BP* 805,562 (14.3.1956).

⁴⁰⁰ ICI, *BP* 929,426 (21.5.1959).

⁴⁰¹ ICI, *BP* 826,375 (7.3.1956).

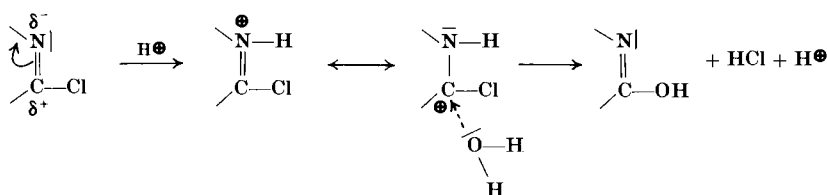
⁴⁰² ICI, *BP* 838,334 (7.3.1956).

⁴⁰³ S, *SP* 340,927 (2.6.1955); *Acna, BeP* 666,229 (2.7.1964).

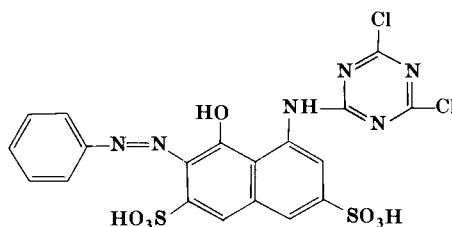


Acna claimed disperse dyes containing dichlorotriazine groups for the dyeing of basic-modified polypropylene fibers.⁴⁰³

Dichloro-*s*-triazinylamino dyestuffs dye cellulosic fibers from soda-alkaline, salt-containing, long liquors at 20–30° and therefore represent the most reactive commercial dyestuff group. This high reactivity nevertheless has disadvantages: During storage of the dyestuffs, hydrochloric acid separated by hydrolysis through protonation of the triazine, i.e., through Banks' acid catalysis, results in an autocatalytic acceleration of the further hydrolysis.

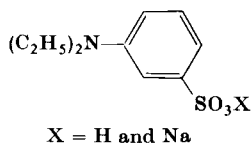


To obtain stable products with a good storage life ICI adds phosphate buffers,⁴⁰⁴ in the case of Procion Brilliant Red M-5BS



for example, at least 10% of a mixture of 7 parts of Na_2HPO_4 and 12.5 parts of KH_2PO_4 (pH 6–8).⁴⁰⁵

Mixtures of dialkylaminoarylsulfonic acids and their metal salts, e.g.,

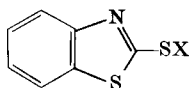


⁴⁰⁴ ICI, *BP* 838,335 (23.3.1956).

⁴⁰⁵ ICI, *BeP* 556,822 (20.4.1956).

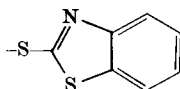
are also suitable as buffer substances for dichlorotriazinylamino dyestuffs.⁴⁰⁶

Print pastes can be stabilized⁴⁰⁷ by addition of sulfur compounds, such as



X = H, Na

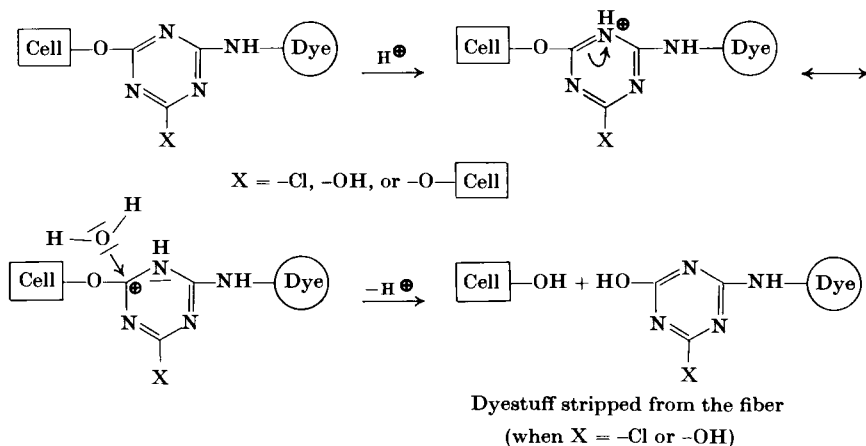
In this case, hydrolysis is suppressed by partial substitution of chlorine by the residue



which is also a mobile group capable of nucleophilic substitution by hydroxyl groups of the cellulose during steaming in the alkaline medium.

Cane sugar is suitable for the adjustment to standard strength of Procion M dyestuffs containing phosphate buffers.⁴⁰⁸

With the development of the Procion-alkali mixer in which the reactive dyestuff solution is mixed with alkali just before application to the fabric and only in the required amount, ICI took a further step towards overcoming the susceptibility to hydrolysis of the Procion M brands.⁴⁰⁹ Not only the dyestuffs but also the dyeings produced with them are subject to acid hydrolysis.⁴¹⁰



⁴⁰⁶ ICI, BP 842,933 (7.8.1957).

⁴⁰⁷ ICI, BP 877,028 (27.8.1959).

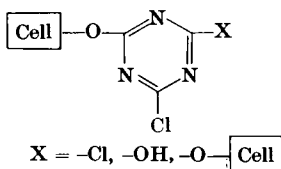
⁴⁰⁸ ICI, BP 909,215 (25.4.1960).

⁴⁰⁹ *Textile Mfr.* **86**, 161-162 (1960).

⁴¹⁰ I. D. Rattee, *Endeavour* **20**, 154 (1961).

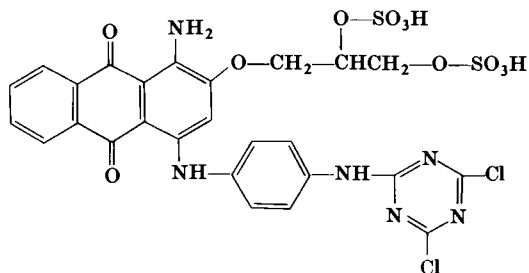
This splitting of the fiber-dyestuff bond takes place as a result of prolonged storage of the dyed fabrics in an acid industrial atmosphere or merely under the action of atmospheric carbonic acid. Although the small amount of dyestuff split off is easily removed during washing, bleeding may result from a mere moistening of the fabrics, e.g., red print on white ground.

After ICI had recognized the possibility of dyeing with dichlorotriazine dyestuffs, Ciba took up again the old principle of Haller and Heckendorn³⁹¹ and produced from cellulose derivatives of the type



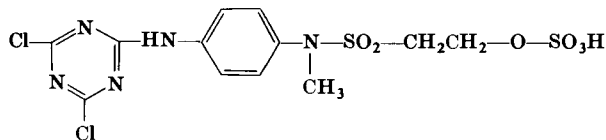
and primary or secondary mono- or diamines in aqueous solution at an increased temperature dyeings or dyestuff intermediates fixed to the fiber.⁴¹¹

BASF claimed dichlorotriazine dyestuffs containing no sulfo groups, but water-solubilized by esterification of hydroxyl groups with sulfuric acid or with benzoic acid *m*-sulfonyl chloride.⁴¹²



Blue

Polymers containing hydroxyl groups, such as polyvinyl alcohol, can be cross-linked with dichlorotriazinylamino compounds in an alkaline medium. Colored finishes are obtained on cellulosic fibers when dyestuffs of the Procion M type are used for this application.⁴¹³ Colorless cross-linking agents such as



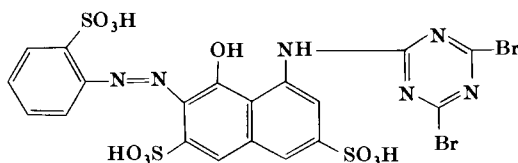
⁴¹¹ CIBA, *BeP* 580,715 (16.7.1958).

⁴¹² BASF, *FP* 1,212,162; 1,213,545 (31.8.1957); *DAS* 1,069,564 (8.1.1958).

⁴¹³ Gy, *FP* 1,320,443 (20.4.1961).

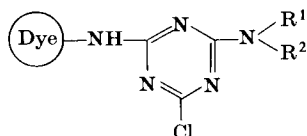
produce pigment-forming films with higher molecular weight polyhydroxy derivatives [Tylose, polyvinyl alcohol] when steamed in the presence of alkali.⁴¹⁴

ii. *2,4-Dibromo-s-triazinylamino-(6) derivatives*. ICI discovered that cyanuric bromide is also suitable for the synthesis of reactive dyestuffs.⁴¹⁵

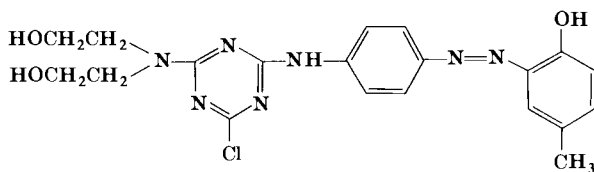


This reactive group has attained no technical importance up to the present.

b. *Monohalo-s-triazinylamino Derivatives*. Water-soluble 2-chloro-4-aminotriazinylamino-(6) dyestuffs of the type



have considerable importance as Cibacron and Procion H dyestuffs, particularly for the printing and continuous dyeing of cellulosic fibers; as disperse dyes (Procinyl dyestuffs, ICI), they are suitable for the dyeing of polyamide fibers with good wet-fastness properties.⁴¹⁶



Procinyl Yellow GS

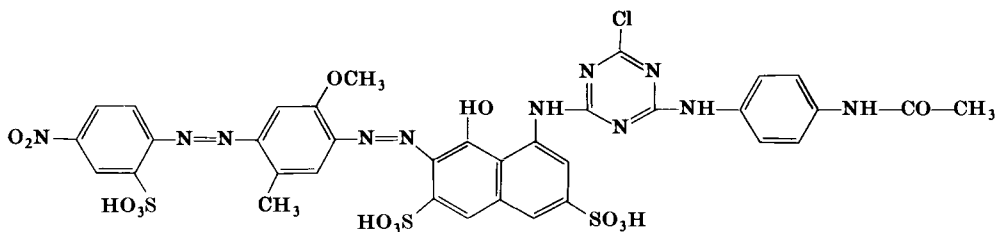
Since the end of the 1920s, Ciba had marketed certain direct dyestuffs containing a monochloro-*s*-triazinyl residue in the molecule, e.g., Chlorantine Fast Blue 8G.

⁴¹⁴ FH, DAS 1,165,542 (21.2.1962).

⁴¹⁵ ICI, BP 838,342; 838,343; 838,344; 838,345 (13.3.1957).

⁴¹⁶ ICI, FP 1,177,851 (15.6.1956); BP 802,935 (15.6.1956); BeP 558,433 (15.6.1956);

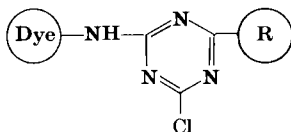
I. Ya. Kalontarov, S. B. Dawidjanz, and E. M. Krjukowa, RP 159,906 (17.10.1962).



Immediately after the original discovery by ICI that fast shades can be produced on cellulose with chlorotriazinylamino dyestuffs from an aqueous alkaline bath, forming a chemical bond, Ciba therefore turned its attention to the development⁴¹⁷ and application⁴¹⁸ of particular monochlorotriazinylamino dyes for reactive dyeing. This work led to the development of many Cibacron and Procion H dyestuffs, applied at 80°, which the two firms marketed together in 1957.

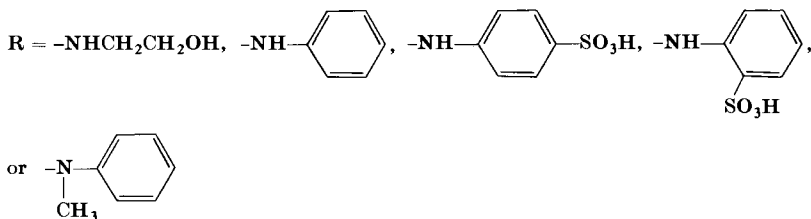
In addition to monochloromonoamino-*s*-triazinylamino compounds, monochloromonoalkoxy- and monochloroaryloxy-*s*-triazinyl compounds are also claimed in the original manufacturing patents of Ciba.⁴¹⁷

The *monochloro-s-triazinylamino group*



permits by variation of the residue R, which presents no technical difficulties, the development of a wide range of dyestuffs with different reactivities, affinities, and solubilities.

i. 2-Chloro-4-amino-s-triazinylamino-(6) dyestuffs. Cibacron and Procion H dyestuffs, as well as the Procion Supra brands, which bear two reactive groups in every molecule, contain not only free amino groups ($R = -NH_2$), but also substituted amino groups

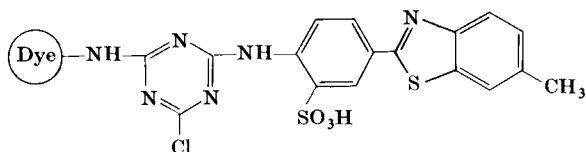


⁴¹⁷ CIBA, *BeP* 559,945 (10.8.1956); 560,105 (17.8.1956); 560,734 (12.9.1956); 560,791; 560,793; 560,794 (14.9.1956).

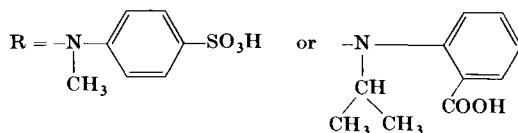
⁴¹⁸ CIBA, *DAS* 1,057,242 (27.1.1956); *BeP* 559,944 (10.8.1956).

which are generally introduced in a second step by reaction of the original dichlorotriazinylamino dyestuffs with ammonia or with the corresponding amine in an aqueous medium at 20–50° (see ref. 417). An alkylamino group produces a stronger inactivating effect on the chlorine atom than an amino or an arylamino group, while the inactivating effect of a dialkylamino group is too strong for practical purposes. Similar to the *N*-methylaniline residue, a sulfo group in the ortho position to the imino bridge reduces the affinity of the reactive dyestuff. In this way, the influence of the dyestuff (e.g., high affinity and association tendency, i.e., sensitivity to salt in the case of J-acid derivatives) can be compensated in such a manner that all the dyestuffs of a range possess similar reactivity, solubility, and affinity.

Specific amino substituents R or types of such substituents are described in numerous patents. A substituent which increases the affinity considerably is, for example, dehydrothiotoluidinesulfonic acid.⁴¹⁹



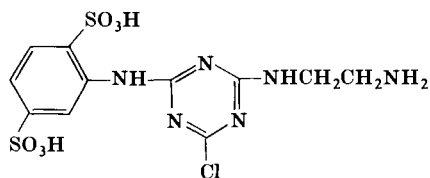
On the other hand, the affinity is reduced by *N*-alkylaminobenzene sulfonic or carboxylic acids, which are therefore incorporated particularly into printing dyestuffs. In this connection, it is significant that in addition to an increased water solubility they also ensure an improved stability (resistance to hydrolysis) in the alkaline print paste.⁴²⁰



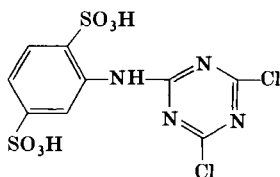
Aliphatic bridge links between large direct dyestuff molecules (e.g., copper phthalocyanines) and the reactive group reduce the affinity and improve solubility and diffusion. An intermediate product which gives technically valuable reactive turquoise brands on condensation, for example, with copper phthalocyanine sulfonyl chloride is

⁴¹⁹ CIBA, *BeP* 561,999 (29.10.1956).

⁴²⁰ CIBA, *BeP* 607,714 (1.9.1960).

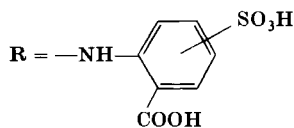
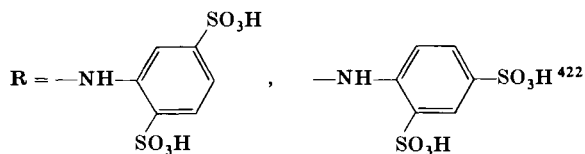
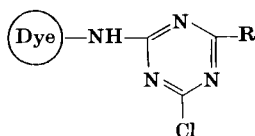


It is obtained by reaction of

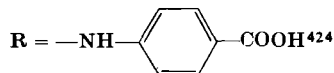


with monoprotonated ethylenediamine at pH 6.5–7.5 and 25–45°. ⁴²¹

Specific water-solubilizing and, in certain cases, affinity-reducing substituents (–R) are listed below.



Particularly good stability in print paste ⁴²³

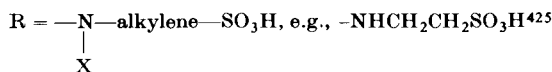


⁴²¹ CIBA, *BeP* 586,371 (10.1.1959).

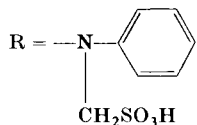
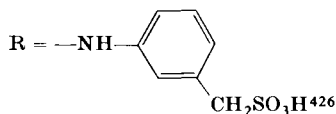
⁴²² ICI, *BP* 1,008,841 (15.3.1961).

⁴²³ ICI, *BeP* 610,586 (23.11.1960); 632,873 (28.5.1962).

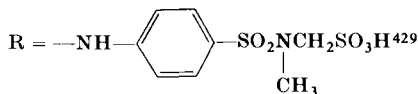
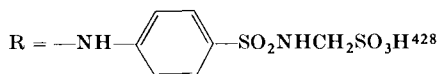
⁴²⁴ ICI, *BeP* 664,754 (20.8.1964).



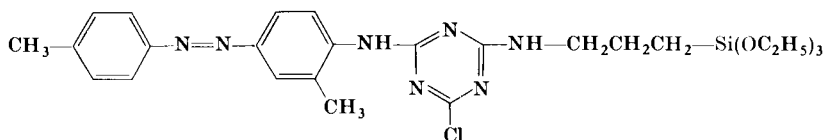
X = H, alkyl



Reacna dyestuffs⁴²⁷



Through the amino substituents all kinds of properties can be conferred on the dyestuff. Introduction of an aminoalkylalkoxysilane group gives not only cellulose-reactive dyestuffs, but also products which are suitable for the coloring of glass fibers.⁴³⁰



ii. 2-Chloro-s-triazinylamino-(6) dyestuffs with other 4-substituents bound through nitrogen. As Sandoz showed,⁴³¹ O-methylhydroxylamine, CH_3ONH_2 , reacts with dichlorotriazinylamino dyestuffs at room temperature, yielding new, very reactive types of monochlorotriazine derivatives.

⁴²⁵ S, *BeP* 633,753 (17.8.1962).

⁴²⁶ CIBA, *BeP* 673,588 (11.12.1964).

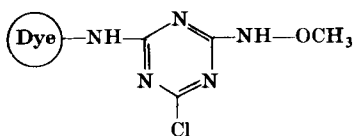
⁴²⁷ Acna, *BeP* 638,184 (4.10.1962); Montecatini Edison, *IT* 816,111 (15.10.1963); Acna, *BeP* 703,182 (29.8.1966).

⁴²⁸ Acna, *BeP* 644,639 (4.3.1963).

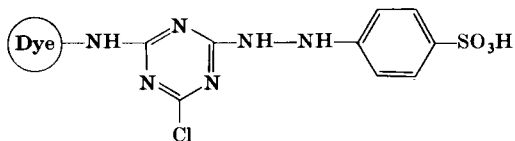
⁴²⁹ Acna, *BeP* 668,041 (10.8.1964).

⁴³⁰ UCC, *USP* 2,963,338 (12.10.1956).

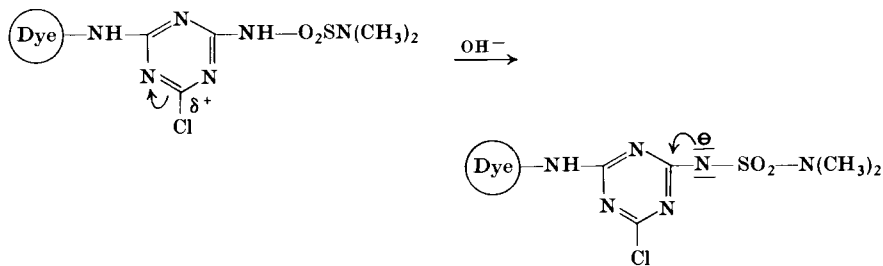
⁴³¹ S, *FP* 1,347,644 (23.2.1962); *BeP* 628,596 (28.2.1962).



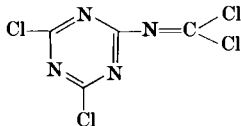
Hydrazine derivatives, e.g., phenylhydrazine sulfonic acids, react just as smoothly with dichlorotriazinylamino dyestuffs, forming⁴³²



While the basic hydrazine group reduces the reactivity of the triazine carbon atoms towards nucleophilic attack, thus reducing the reactivity of the dyestuff, introduction of a dimethylaminosulfonylamino residue [starting from $(\text{CH}_3)_2\text{N}-\text{SO}_2\text{NH}_2$]⁴³³ leads to monochlorotriazine dyestuffs which, in comparison with the Cibacron types, show an increased reactivity. If, however, the acid sulfonyltriazinylimino bridge dissociates in stronger alkaline medium, a marked inactivation of the chlorine atom takes place through the electron-donor effect of the anion.



A monochlorotriazine dyestuff type of particular interest from a chemical standpoint, but without any importance in industry, is obtained by starting with "tetrameric cyanogen chloride,"

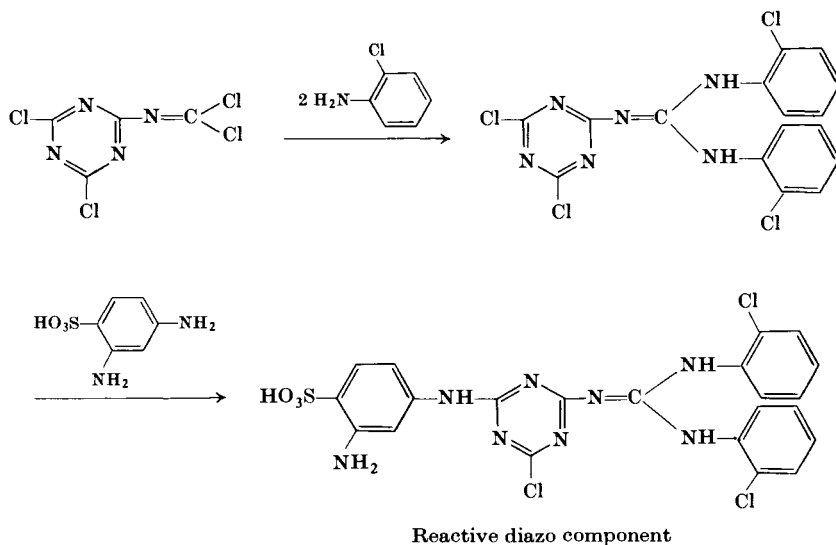


⁴³² Gemaco Sa., *FP* 1,257,428 (19.5.1960).

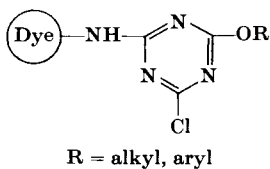
⁴³³ CFM, *BP* 1,044,244 (22.4.1964).

a by-product in the trimerization of cyanogen chloride to cyanuric chloride.⁴³⁴ This 2,4-dichloro-*s*-triazinyl-(6)-isocyanate dichloride has also become available recently by high-temperature chlorination of 2,4-dichloro-6-dimethylamino-*s*-triazine.⁴³⁵

For use as reactive component, both chlorine atoms of the isocyanate dichloride group, which are extremely reactive and susceptible to hydrolysis, must first be substituted; only then can the dyestuff residue be introduced by substitution of one of the two chlorine atoms on the triazine ring.⁴³⁴



iii. 2-Chloro-4-alkoxy(aryloxy)-*s*-triazinylamino-(6) dyestuffs. In the dyestuffs,

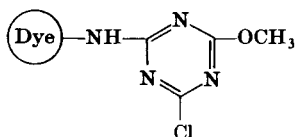


because of the less basic character of the group -OR, the chlorine atom is less inactivated than in the monochloromonoamino-*s*-triazinylamino dyestuffs (Cibacron and Procion H brands).

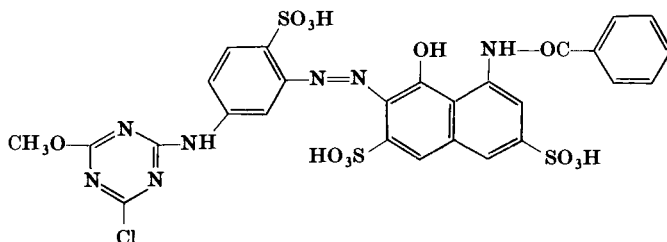
⁴³⁴ Gy, BeP 607,353 (10.7.1959); FP 1,270,873 (28.9.1959).

⁴³⁵ E. Kühle, B. Anders, and G. Zumach, *Angew. Chem.* **79**, 675 (1967).

Although this type of very reactive dyestuff has been developed since 1956 almost simultaneously by ICI^{436, 437} and Ciba,^{437, 438} (R = -CH₃, -C₆H₅, -C₆H₄-SO₃H, etc.) it was not until 1968 that Ciba marketed the rapidly fixed Cibacron Pront range for textile printing on this basis.

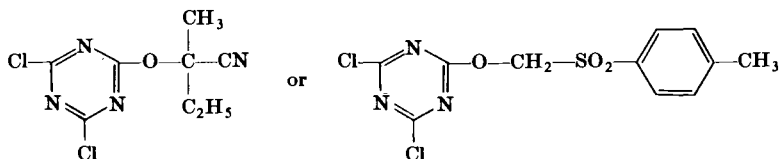


Methoxydichlorotriazine, which is easily produced from cyanuric chloride and methanol in the presence of water and sodium bicarbonate, condenses, for example, with 1,3-diaminobenzene-4-sulfonic acid at 20–30°, forming 1-[2'-chloro-4'-methoxytriazinyl-(6')]-amino-3-amino-benzene-4-sulfonic acid, from which after diazotization and coupling with benzoyl H-acid the brilliant red



is obtained.⁴³⁷

The intrinsically slight inactivation of the chlorine by the alkoxy group is further decreased in the alkyl residue by negative substituents which weaken the basicity of the oxygen. This effect was utilized by Acna, who converted cyanuric chloride with cyanohydrins (produced *in situ* from ketone + KCN)⁴³⁹ or with α -hydroxymethyl sulfones⁴⁴⁰ into



⁴³⁶ ICI, BP 803,473 (20.1.1956); BP 558,390 (15.6.1956); BP 843,985 (10.4.1958); 948,969 (4.12.1961).

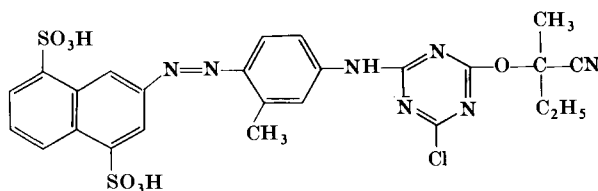
⁴³⁷ CIBA, DAS 1,105,541 (29.6.1956).

⁴³⁸ CIBA, DAS 1,100,207 (29.6.1956); 1,128,939 (12.9.1956).

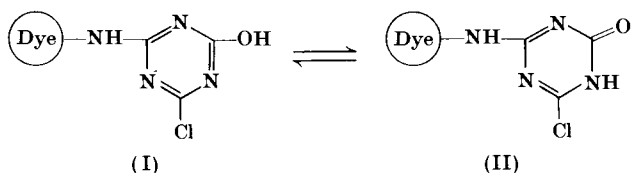
⁴³⁹ Acna, BeP 647,119 (26.4.1963); IT 830,521 (28.4.1964).

⁴⁴⁰ Acna, BeP 678,155 (22.3.1965); GE 1,806,394 (31.10.1967).

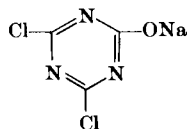
and from these components synthesized highly reactive monochloro-triazine dyestuffs, such as the yellow



Also noteworthy are the 2-chloro-4-hydroxy-s-triazinylamino-(6) dyestuffs

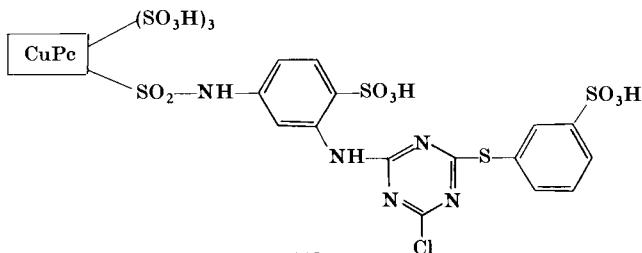


which not only occur in the hydrolysis of dichlorotriazine dyestuffs (Procion M brands), but can also be produced by acylation of amino dyestuffs with the stable aqueous solution of the sodium salt of 2,4-dichloro-6-hydroxy-s-triazine.⁴⁴¹



In contrast to the methoxychlorotriazine derivatives, dyestuffs of this type react very slowly. They exist mainly in the tautomeric lactam form (II).

iv. 2-Chloro-4-alkylthio(arylthio)-s-triazinyl-(6)-amino dyestuffs. In dichlorotriazine dyestuffs, a chlorine atom is substituted very easily by the residue of a mercaptan or thiophenol, yielding very reactive, less substantive products.

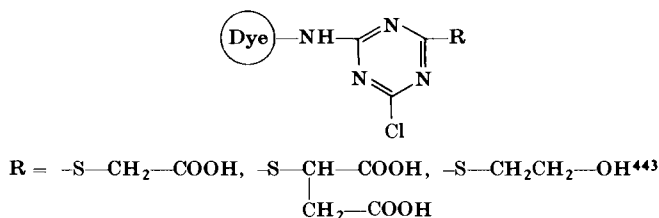


Ref. 442

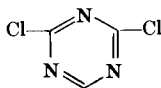
⁴⁴¹ CIBA, *FP* 1,229,750 (20.2.1958); *BeP* 587,713 (18.2.1959).

⁴⁴² ICI, *BeP* 570,101 (7.8.1957).

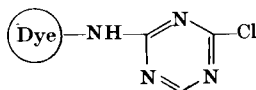
or



v. 2-Chloro-s-triazinylamino-(6) dyestuffs with hydrogen or a carbon substituent in the 4-position. 2,4-Dichloro-s-triazine

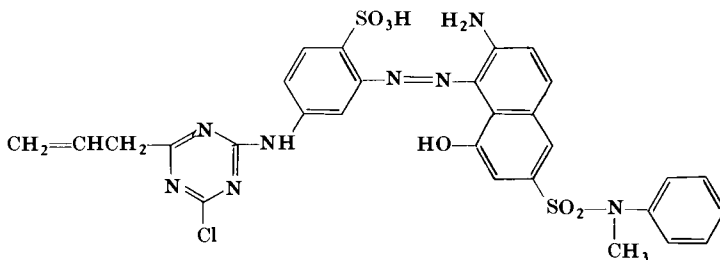


obtained under pressure by mixed trimerization of 2 moles of cyanogen chloride and 1 mole of hydrocyanic acid is suitable for synthesis of dyes of the type⁴⁴⁴



which can be applied to cellulose, for example, by the cold pad-batch process.

2-Methyl-4,6-dichloro-s-triazine, 2-phenyl-4,6-dichloro-s-triazine, and their derivatives were already used by Ciba in 1955 as reactive components in monosulfoazo dyestuffs for wool.⁴⁴⁵

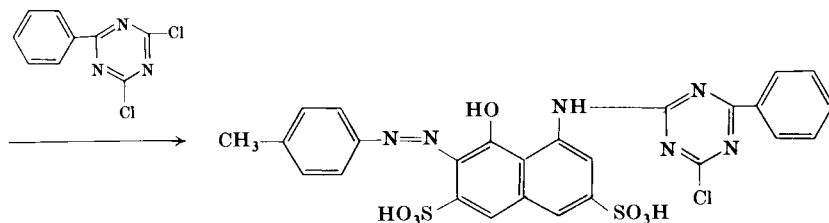


⁴⁴³ CIBA, *BeP* 570,494 (21.8.1957); 570,524 (22.8.1957).

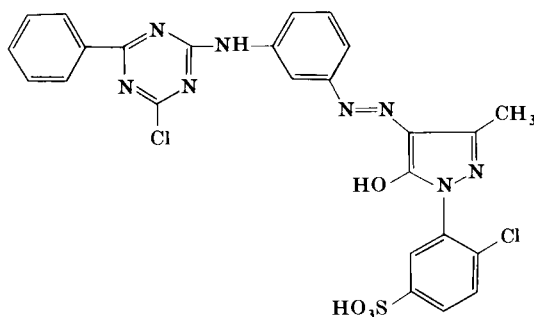
⁴⁴⁴ CIBA, *BeP* 592,148 (23.6.1959).

⁴⁴⁵ CIBA, *BeP* 547,708 (10.5.1955).

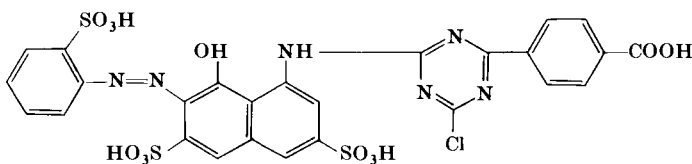
They can be condensed with amino dyestuff at 30–40° and pH 6.5–7 in aqueous solution without any difficulty.⁴⁴⁶



BASF developed reactive dyestuffs thoroughly, especially from 2-phenyl-4,6-dichloro-*s*-triazine and its derivatives, available from vat dyestuff chemistry.^{412, 447, 448}



Ref. 448



Ref. 447

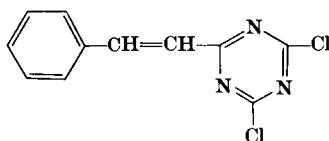
At the Organic Intermediates and Dyes Research Institute in Rumania, V. J. Mur and co-workers investigated 2-styryl-4,6-dichloro-*s*-triazine⁴⁴⁹

⁴⁴⁶ CIBA, *SP* 349,013 (11.4.1956).

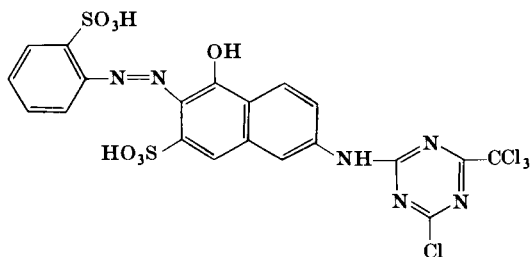
⁴⁴⁷ BASF, *FP* 1,213,653; 1,213,654 (11.10.1957); *DAS* 1,100,587; 1,067,404 (12.10.1957).

⁴⁴⁸ BASF, *BeP* 628,251 (15.2.1962).

⁴⁴⁹ Mur, V. J. and Krasnovskaja, L. S., Scientific Research Institute of Organic Intermediates and Dyes, Rumania, *RP* 182,821 (29.7.1963); 192,214; 192,820 (27.5.1965).

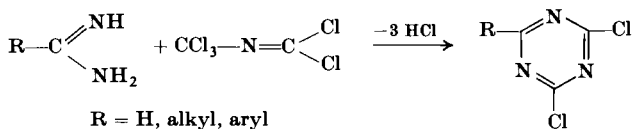


and 2-trichloromethyl-4,6-dichloro-*s*-triazine⁴⁵⁰ as reactive components for monochlorotriazine dyestuffs. The strong electron-attracting trichloromethyl group activates the chlorine atom in dyestuffs such as



to such an extent that they attain approximately the reactivity of dichlorotriazine dyestuffs. On the other hand, since the trichloromethyl group reduces the affinity considerably, the fixation yield on cellulosic fibers is lower than that of the Procion M types.

The 2,4-dichloro-*s*-triazine derivatives with a carbon substituent in the 6-position discussed in this section were until recently, particularly in the 6-alkyl range, not readily available, e.g., only by Grignard reactions. Farbenfabriken Bayer discovered a good method of synthesis in the reaction of corresponding amidines with trichloromethyl isocyanate dichloride, easily obtained by high-temperature chlorination of dimethylcarbamic chloride.⁴⁵¹



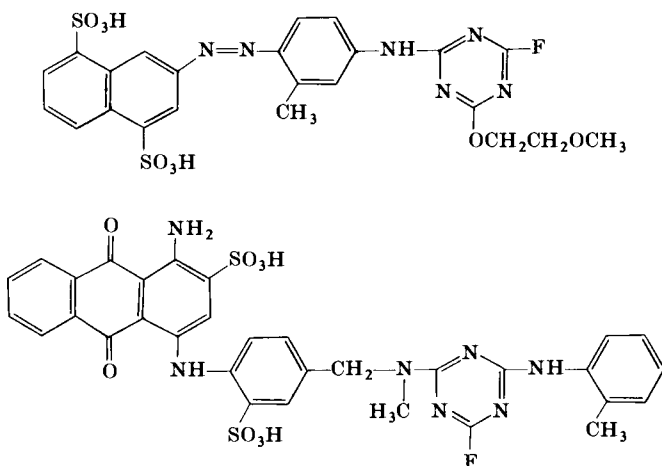
vi. 2-Fluoro-4-substituted-s-triazinylamino-(6) dyestuffs. Not until recently were cyanuric fluoride⁴⁵² and other fluorotriazine derivatives synthesized by Farbenfabriken Bayer and tested for their suitability as

⁴⁵⁰ V. J. Mur *et al.*, Scientific Research Institute of Organic Intermediates and Dyes, Rumania, *RP* 191,714 (10.8.1964).

⁴⁵¹ FBy, *GP* 1,178,437 (22.12.1962).

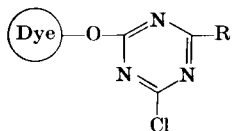
⁴⁵² FBy, *GP* 1,044,091 (26.4.1957); 1,076,696 (21.8.1957); 1,126,875 (27.8.1957).

reactive components. The 2-fluoro-4-alkoxy- and -4-alkylamino-s-triazinylamino-(6) derivatives, in particular, proved to be valuable dyestuffs which combine the high reactivity of the dichlorotriazine dyestuffs with the very good wet-fastness properties of the monochloro types.⁴⁵³



Ref. 454

c. *Products with Bridge Links other than the Imino Group between Halo-s-triazine Residue and Dyestuff.* Cyanuric chloride and its mono-substitution products condense smoothly with water-soluble^{455, 456} or water-insoluble⁴⁵⁷ dyestuffs containing acylatable hydroxyl groups, forming products of the type



which are suitable as reactive dyestuffs not only for cellulose⁴⁵⁵ and wool,⁴⁵⁶ but also for polyamide fibers.⁴⁵⁷

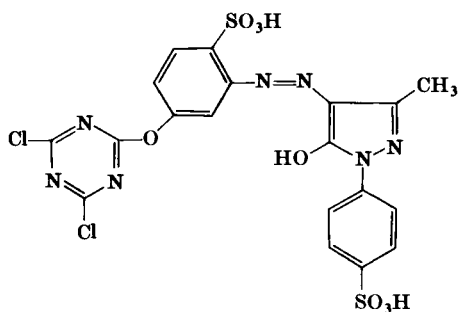
⁴⁵³ FBy, *BeP* 713,937 (19.4.1967).

⁴⁵⁴ FBy, *BeP* 716,013; 716,014 (2.6.1967).

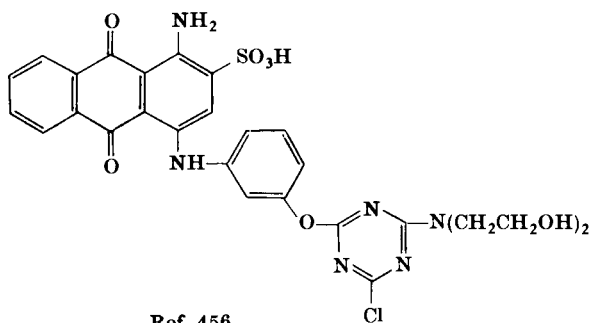
⁴⁵⁵ CIBA, *FP* 1,207,925 (30.7.1957).

⁴⁵⁶ CIBA, *BeP* 604,518 (2.6.1960).

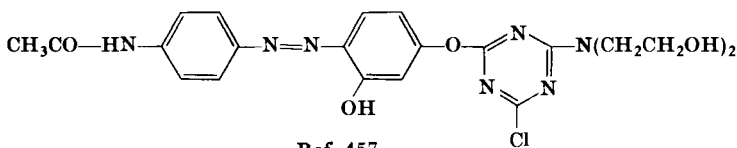
⁴⁵⁷ S, *BeP* 596,341 (23.10.1959).



Ref. 455

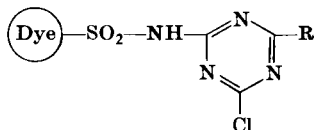


Ref. 456



Ref. 457

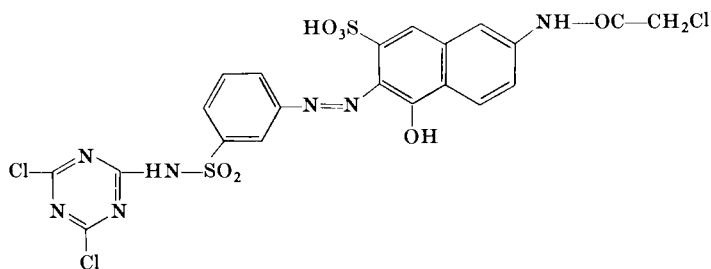
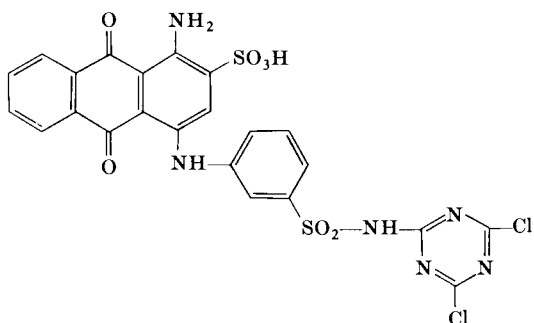
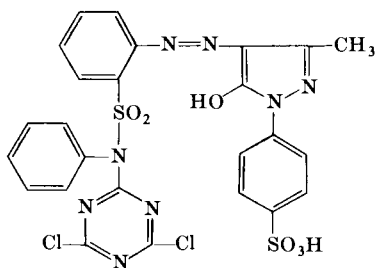
i. Halotriazinylaminosulfonyl dyes.



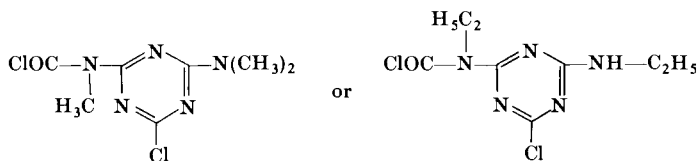
Similar to phenols, primary or secondary sulfonamide groups can also be acylated smoothly with cyanuric chloride and its derivatives, for example, at pH 11.5 and 0–5°. Reactive dyestuffs suitable both for cellulosic fibers⁴⁵⁸ and wool⁴⁵⁹ are obtained.

⁴⁵⁸ FBy, *BeP* 572,015 (14.10.1957); *GP* 1,419,169 (15.4.1959); ICI, *FP* 1,352,275 (11.1.1962).

⁴⁵⁹ FBy, *BeP* 606,081 (23.7.1960); *GP* 1,419,565 (21.12.1960); *BeP* 661,236 (21.3.1964).

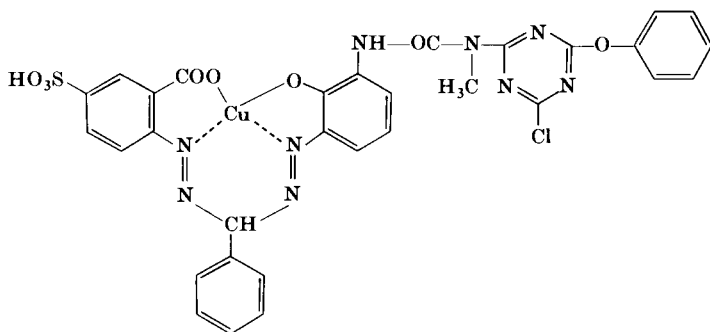
Brilliant orange⁴⁵⁸Brilliant blue⁴⁵⁸Yellow⁴⁵⁹

ii. *Dyes with a urea bridge between halotriazine residue and dyestuff.* Almost simultaneously, Geigy, Bayer, and Sandoz used as reactive components halo-*s*-triazinylcarbamic chlorides, such as



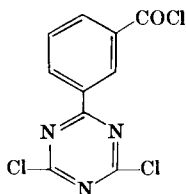
which are easily obtained by phosgenation of the corresponding 2,4-diamino-6-chloro-*s*-triazine.⁴⁶⁰

The dyestuffs synthesized in this way are somewhat more reactive than corresponding types with the stronger inactivating imino bridge.

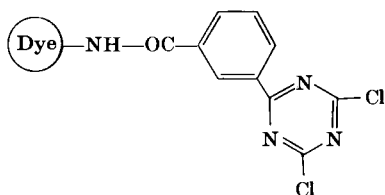


Blue

*iii. Halo-*s*-triazinylbenzoyl chlorides as reactive components.* American Cyanamid used compounds such as



for the acylation of amino dyestuffs. In this case, the carbonyl chloride group reacts selectively so that reactive dyes of the type



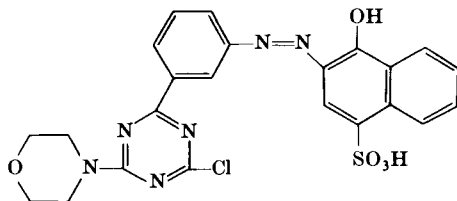
are obtained.⁴⁶¹

*iv. Halo-*s*-triazine groups bound directly to the chromophore system.* 2-Phenyl-4-chloro-6-amino-*s*-triazine with a diazotizable amino group

⁴⁶⁰ Gy, *BeP* 650,328 (10.7.1963); FBy, *BeP* 656,629 (4.12.1963); S, *BeP* 661,080 (14.3.1964).

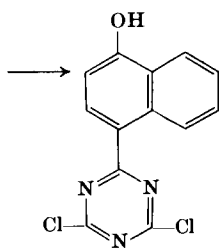
⁴⁶¹ CCC, *USP* 3,055,895 (22.12.1958).

in the phenyl nucleus was used by BASF as the reactive diazo component.⁴⁶² Dyestuffs such as the scarlet

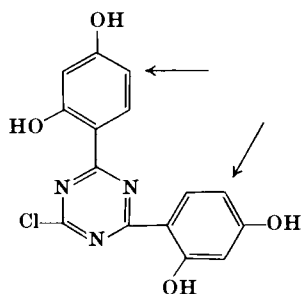


are not particularly reactive. They are fixed by the pad-steam process in the presence of caustic soda.

Naphthols and phenols condense under the conditions of the Friedel-Crafts reaction (AlCl_3 catalysis) with cyanuric chloride, forming reactive coupling components, such as

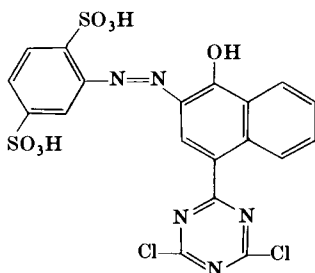


Refs. 463-465



Ref. 465

These were used to synthesize water-soluble cellulose dyestuffs, e.g.,



Yellowish red^{463, 464}

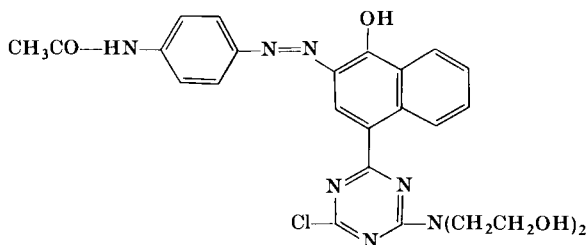
⁴⁶² BASF, *FP* 1,333,557 (14.9.1961).

⁴⁶³ ICI, *BP* 1,029,211 (1.3.1962).

⁴⁶⁴ ICI, *BP* 1,029,212 (1.3.1962).

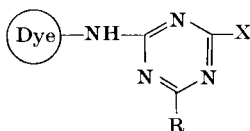
⁴⁶⁵ G, *USP* 3,293,238 (30.12.1963).

and also disperse dyestuffs for polyamide fiber, e.g.,



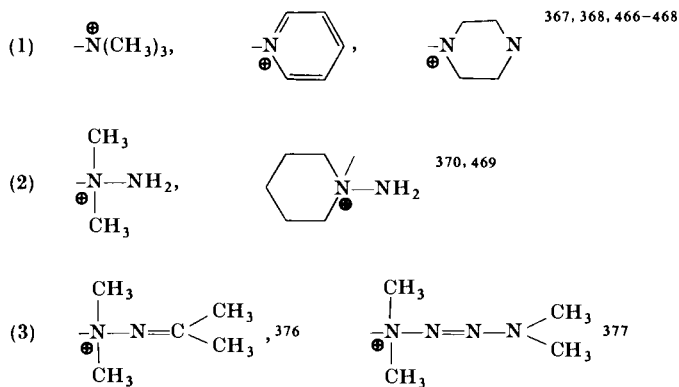
Red⁴⁶⁴

d. s-Triazine Derivatives with Mobile Groups other than Halogen. Of all carrier systems the mobile groups have been varied most widely in the technically important *s*-triazine system. Up to the present the following types have been described:



R = Any desired substituent, in most cases an amino group or identical with the mobile group X

X = Mobile group capable of nucleophilic substitution, e.g., the following groups:



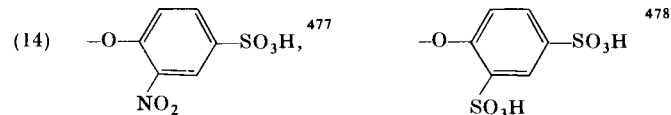
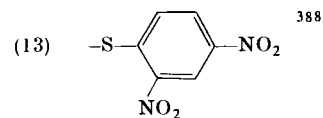
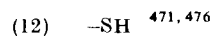
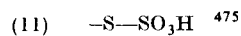
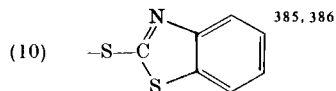
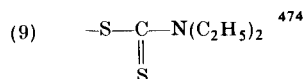
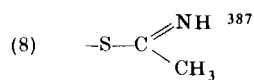
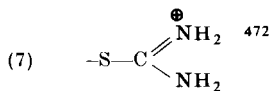
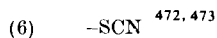
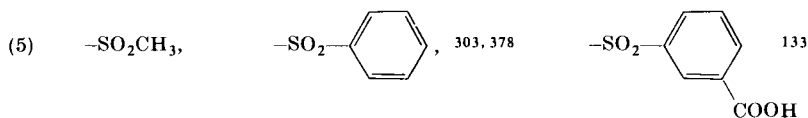
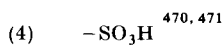
⁴⁶⁶ ICI, *BeP* 628,854 (25.2.1963).

^{466a} CIBA, *GP* 1,210,407 (8.12.1961).

⁴⁶⁷ ICI, *BP* 946,998 (10.8.1961); 1,005,240 (10.4.1963).

⁴⁶⁸ ICI, *BP* 1,012,625 (10.4.1963).

⁴⁶⁹ CIBA, *GP* 1,544,431 (14.9.1961).



⁴⁷⁰ ICI, *BeP* 563,439 (21.12.1956); CIBA, *SP* 354,875 (20.5.1957); S, *FP* 1,246,743 (11.11.1957).

⁴⁷¹ ICI, *FP* 1,471,782 (18.3.1965).

⁴⁷² Asahi Dye Mfg. Co., Ltd., *JP* 7,228 (12.10.1956); 18,183/64 (17.11.1961).

⁴⁷³ ICI, *DAS* 1,113,049 (12.2.1958); *USP* 3,127,232 (23.6.1961).

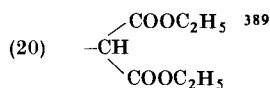
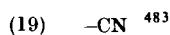
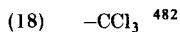
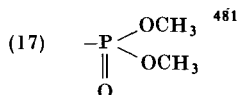
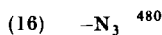
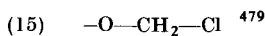
⁴⁷⁴ ICI, *DAS* 1,155,549 (11.3.1959); *BeP* 591,077 (21.5.1959).

⁴⁷⁵ MCI, *JP* 18,189/68 (1.5.1965).

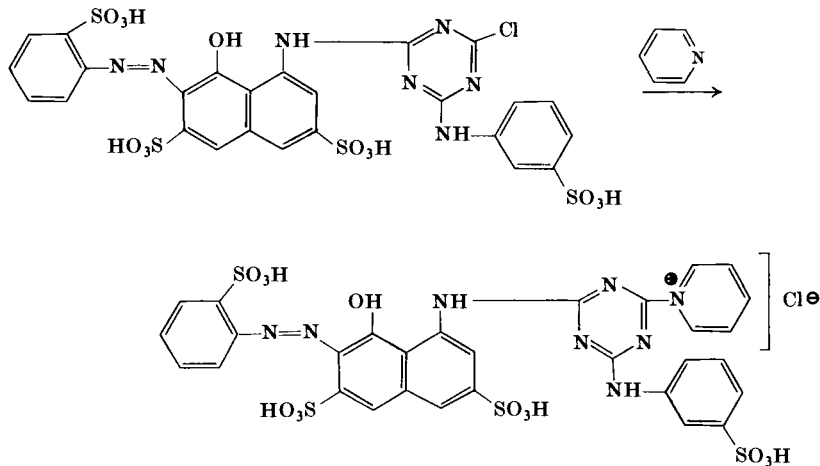
⁴⁷⁶ Asahi, *JP* 4,042/64 (18.1.1960).

⁴⁷⁷ FBy, *BeP* 570,021 (2.8.1957).

⁴⁷⁸ ICI, *BP* 846,765 (7.8.1957); *FP* 1,284,237; 1,287,648; 1,287,649; 1,287,651 (14.3.1960); 1,294,284 (13.4.1960).



i. Quaternary ammonium groups. In 1959 ICI discovered that monochlorotriazine dyestuffs in aqueous solution react smoothly with 1 mole of tertiary base (e.g., trimethylamine, pyridine, or 1,4-diazabicyclo-[2.2.2]octane, Dabco), forming definite triazinylammonium compounds with increased cellulose reactivity which can be isolated in substance (type Procion Brilliant Red M—X3BS).³⁶⁷



Ref. 467

⁴⁷⁹ HCC, *JP* 10,733/63 (22.12.1960).

⁴⁸⁰ MCI, *JP* 12,082/64 (1.11.1961); ICI, *FP* 1,419,946 (22.11.1963).

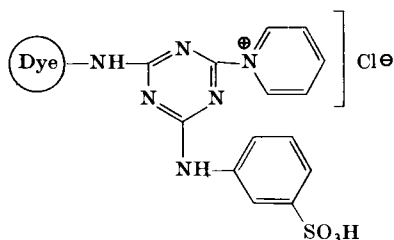
⁴⁸¹ ICI, *BP* 970,585 (31.7.1961).

⁴⁸² S, *BeP* 612,026 (29.12.1960).

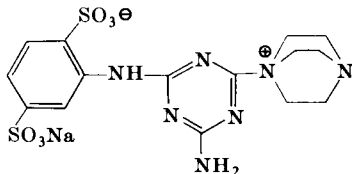
⁴⁸³ NSK, *JP* 7,931/64 (17.1.1962); 24,844/64 (15.12.1961).

It was surprising that these new triazine derivatives, like dichlorotriazine dyestuffs, could be dyed at 25° from a long liquor, giving the same dyeings as those obtained with monochlorotriazine types, i.e., also with their better wet-fastness properties. The technical value of this group of compounds is due to this, and also to the realization that to increase the reactivity of a monochlorotriazine dyestuff a stoichiometric quantity of tertiary base is not required, but that smaller (about 10 mole %) or even catalytic quantities of the amine continually released during the cellulose reaction are sufficient.

Instead of using catalytic quantities of the free tertiary amines, small amounts of quaternized dyestuffs, such as^{368, 466}

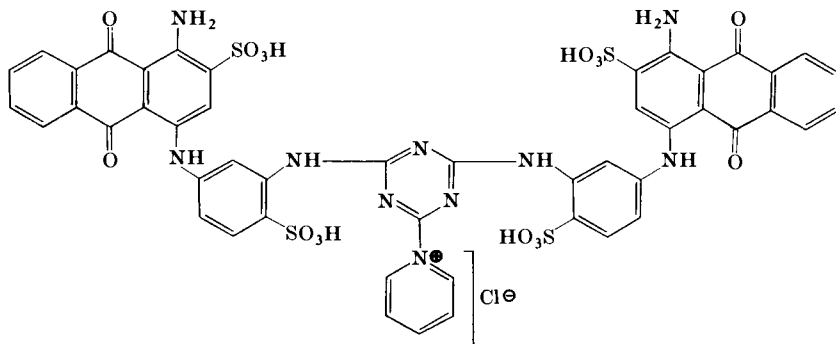


or quaternary nitrogen compounds without the character of dyestuffs, such as^{466a}

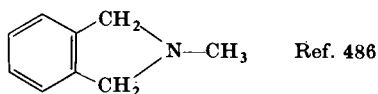
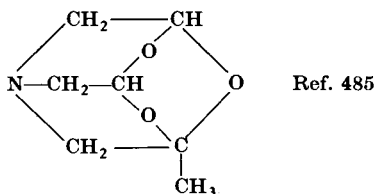
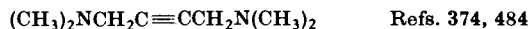


may also be added to the monochlorotriazine dyestuff to be activated.

In addition to azo and anthraquinone dyestuffs with a triazinyl-ammonium group,⁴⁶⁷ dyestuffs containing two bromaminic acid chromophores, such as⁴⁶⁸

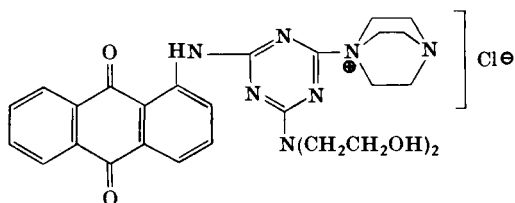


are claimed. Certain patent applications treat specific tertiary amines as quaternization components for monochlorotriazinylamino dyestuffs.



Monochlorotriazine dyestuffs with a urea bridge between triazine ring and dyestuff are also activated by tertiary amines.⁴⁸⁹

Dyestuffs free from sulfonic groups, such as



which owe their solubility in water only to the triazinylammonium and ethanolamine groups dye cellulosic fibers either in the usual way in the presence of acid-binding agents⁴⁹⁰ or without alkali, combined with an aftertreatment with anionic surfactants (e.g., dinaphthylmethane disulfonate).⁴⁹¹

⁴⁸⁴ S, *BeP* 633,581 (10.8.1962).

⁴⁸⁵ ICI, *BP* 999,233 (18.2.1963).

⁴⁸⁶ ICI, *BP* 1,015,508 (27.5.1963).

⁴⁸⁷ Acna, *SP* 447,433 (9.8.1965).

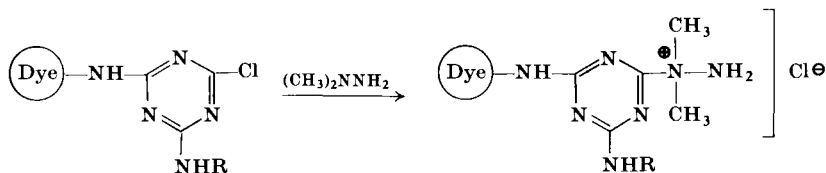
⁴⁸⁸ Acna, *BeP* 667,043 (17.7.1964).

⁴⁸⁹ Gy, *DP* 6,600,220 (8.1.1965).

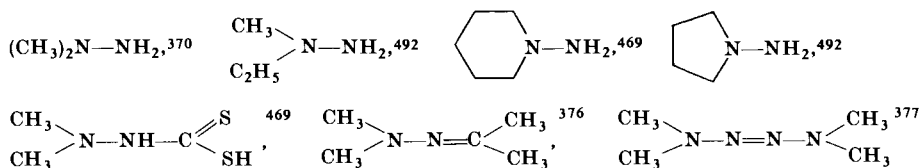
⁴⁹⁰ ICI, *BP* 950,327 (1.2.1961).

⁴⁹¹ HCC, *JP* 8,315/66 (30.5.1962).

ii. *Quaternary hydrazonium groups.* Just as easily as tertiary amines, *N,N*-dialkylhydrazines and their derivatives are introduced between chlorine atom and triazine ring, forming triazinylhydrazonium compounds.^{370, 469, 492}

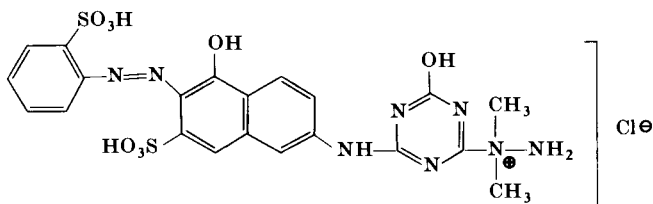


N,N-Disubstituted hydrazines are similar to tertiary amines in catalytic effect and activation of the reactive system. The following are examples of hydrazines or hydrazine derivatives:



In a series of patent applications (priority 15.5.62), ICI claimed all azo, anthraquinone, and phthalocyanine types with a triazinylhydrazonium reactive group which are important for reactive dyes.³⁷¹⁻³⁷³

The 2-chloro-4-hydroxy-*s*-triazinylamino-(6) group, which reacts too slowly for practical purposes, is raised to an adequate level of reactivity by quaternization with *N,N*-dimethylhydrazine.⁴⁹³

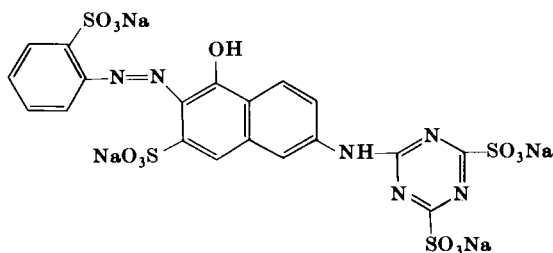


iii. *Sulfonic acid groups.* Dichlorotriazine and monochlorotriazine derivatives are easily substituted by sulfite anions.⁴⁷⁰ Thus, a neutral suspension of 2-[2',4'-dichloro-*s*-triazinyl-(6')-amino]-5-hydroxynaphthalene-7-sulfonic acid in aqueous sodium sulfite solution is converted

⁴⁹² S, *FP* 1,344,532 (7.11.1961); *BeP* 625,538 (1.12.1961).

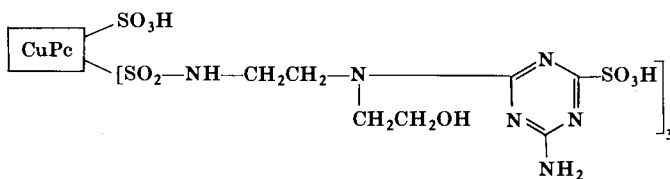
⁴⁹³ S, *BeP* 633,382 (7.6.1962).

by stirring at room temperature for 2 hours into the corresponding 2',4'-disulfo-*s*-triazine derivative, which after coupling with diazotized aniline-2-sulfonic acid gives the very freely soluble reactive dye⁴⁷⁰



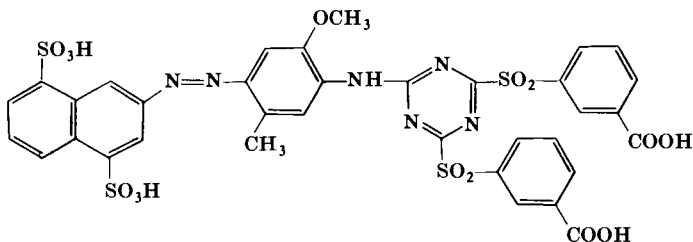
This dye produces brilliant orange shades on cellulosic fabrics by the cold pad-batch process with sodium bicarbonate.

Despite a certain instability and tendency to split off sulfurous acid, this mobile group is technically important for polyfunctional phthalocyanine dyes,⁴⁷¹ e.g., the turquoise



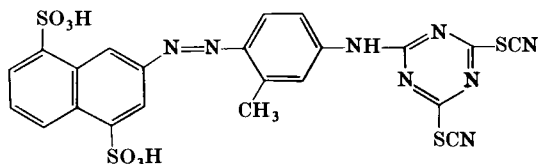
on which it confers the required water solubility for a high fixation yield and good penetration.

iv. Sulfonyl groups. Sulfinate anions substitute successively both chlorine atoms in dichloro-*s*-triazine components. The dyestuffs thus obtained, e.g., the golden yellow¹³³



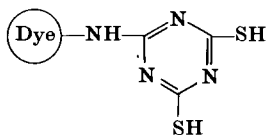
are just as reactive as the fundamental dichlorotriazine dyestuffs, but unlike the 2-alkylsulfonylpyrimidylamino derivatives have acquired no technical importance.^{303, 378}

v. Other groups containing sulfur. Chlorotriazines can also be reacted smoothly with other nucleophilic sulfur compounds. 2-Chloro-4,6-dithiocyano-*s*-triazine, easily obtained from cyanuric chloride and potassium thiocyanate, condenses with amino dyestuffs, splitting off the chlorine atom and forming 2,4-dithiocyano-*s*-triazinyl-(6)-amino dyestuffs.⁴⁷³



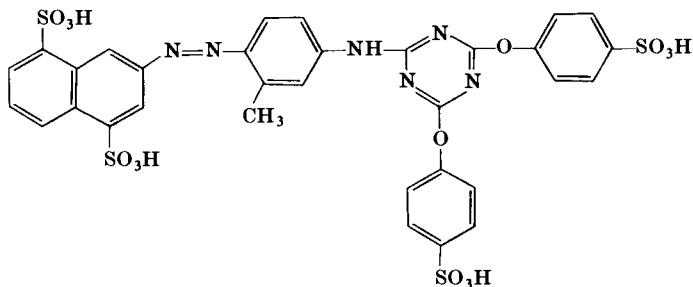
None of the systems (6)–(12) listed at the beginning of Section *d* is of any practical importance.

Mercaptotriazine derivatives^{472, 476}

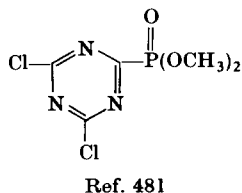
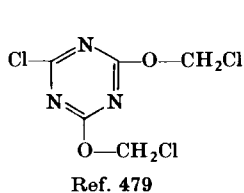


have less the character of reactive dyes than of sulfur dyes.

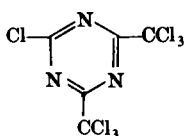
vi. Negatively substituted phenol and thiophenol groups. This extensively developed group^{388, 477, 479} has a medium reactivity and is best fixed by steaming



vii. Other groups bound through O, N, P, and C. While the systems containing mobile groups (15), (17), and (18) are synthesized from the triazine derivatives

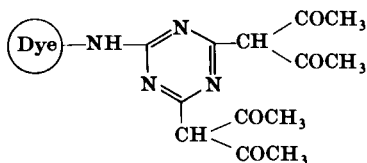


and



Ref. 482

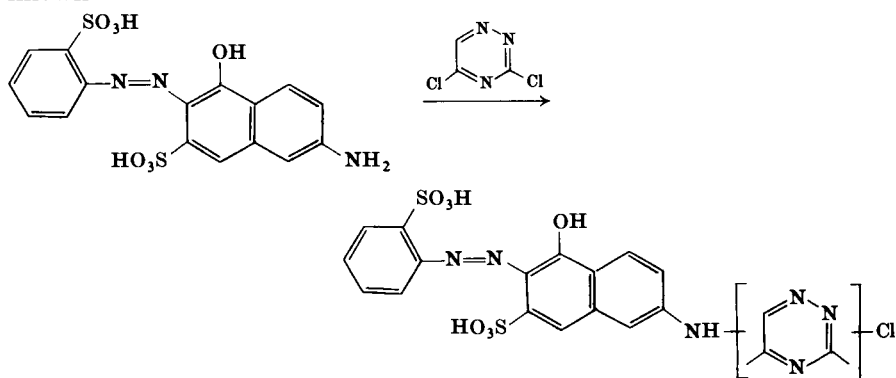
the types (16), (19), and (20) are obtained by halogen exchange in the fundamental dichlorotriazine dyestuffs with sodium azide,⁴⁸⁰ potassium cyanide,⁴⁸³ or with compounds containing reactive methylene groups, such as cyanoacetic ester, malonic ester, or acetylacetone:



The reactive groups mentioned in this section have no commercial importance.

7. 1,2,4-Triazine Derivatives

Halogen derivatives of the not easily available 1,2,4-triazine are also suitable as reactive components.⁴⁹⁴ Finely powdered 3,5-dichloro-1,2,4-triazine condenses with the appropriate aminoazo dyestuff in aqueous solution at 0–5° and pH 4.5–6, forming a reactive dyestuff, the constitution of which (substitution position on 1,2,4-triazine) is not exactly known.



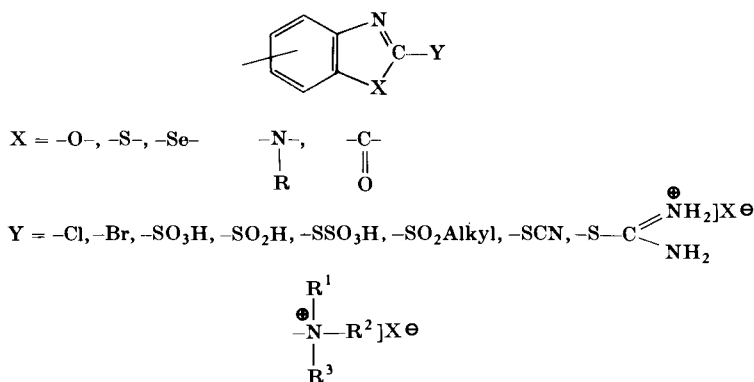
8. Benzazole Derivatives with Reactive Mobile Groups in the 2-Position

In the basic patent applications of Francolor²⁸⁵ and Bayer⁴⁹⁵ and also in a subsequent patent of BASF,²⁸⁷ all benzazoles [benzoxazole, benzo-

⁴⁹⁴ S, BeP 607,999 (8.9.1960).

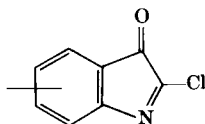
⁴⁹⁵ FBy, BeP 614,896 (10.3.1961).

thiazole, benzoselenazole, benzimidazole, indolone-(3)] with all important mobile groups in the 2-position were claimed as reactive components:



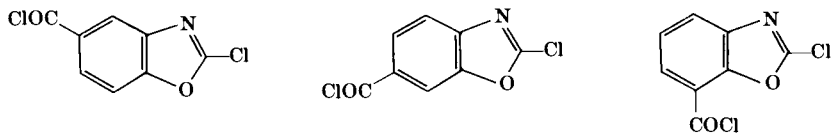
Practical importance has, however, been attained only by benzothiazole derivatives with chloro- or alkylsulfonyl groups in the 2-position (Reatex and Levafix P dyestuffs).

While dyestuffs based on benzimidazole^{285, 495} react too slowly for practical purposes, derivatives of isatin chloride²⁸⁵

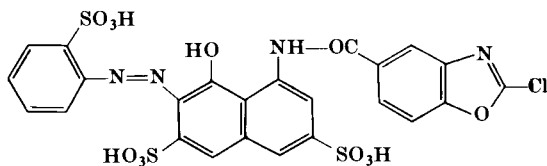


hydrolyze too quickly.

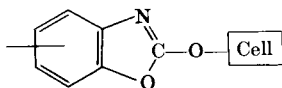
a. Benzoxazole Derivatives. 2-Chlorobenzoxazolecarbonyl chlorides, e.g.,



were tested thoroughly as reactive components by Bayer.^{146, 495} Dyestuffs such as the red

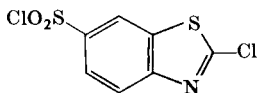


are fixed on cellulose with sodium bicarbonate at room temperature, but the fiber-dyestuff bond formed

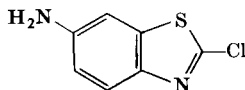


is split very easily under stronger alkaline conditions (e.g., in a single wash at the boil with soda), i.e., the wet-fastness properties of the dyeing are not sufficient.

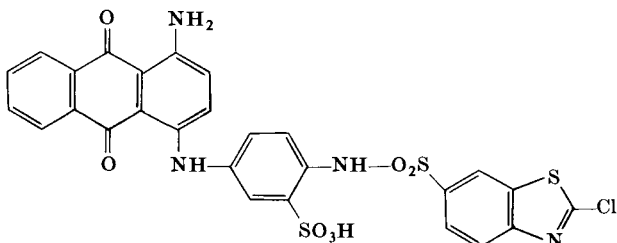
b. Benzothiazole Derivatives. i. 2-Chlorobenzothiazole derivatives. By nitration or sulfochlorination of 2-chlorobenzothiazole⁴⁹⁵ Bayer and FMC²⁸⁵ obtained the corresponding 6-derivatives, which can be used, in the case of the sulfonyl chloride directly and in that of the nitro compound after catalytic reduction to the amine, for the synthesis of dyestuffs with a medium reactivity (Reatex dyestuffs, Francolor⁴⁹⁶)^{285, 287, 495, 497}:



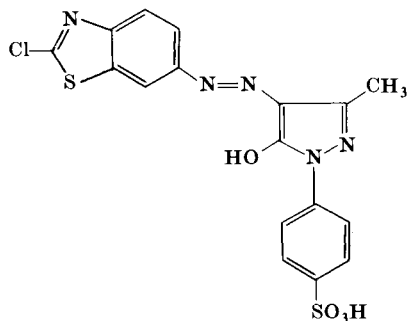
Ref. 495



Ref. 285



Blue

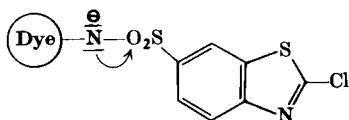


Yellow

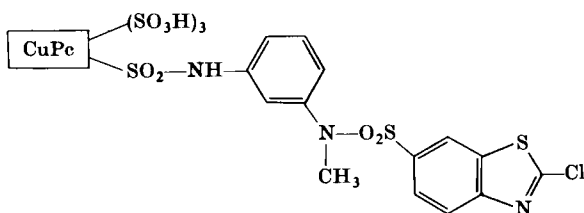
⁴⁹⁶ M. A. Avsac, *Teintex* **30**, 163-183 (1965).

⁴⁹⁷ Acna, *BeP* 642,489 (15.1.1963).

The sulfonamide bridge dissociated in the alkaline application medium inactivates the mobile group.

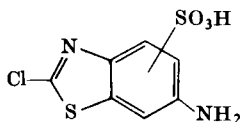


N-Alkylsulfonamide dyestuffs,⁴⁹⁸ such as the turquoise⁴⁹⁹



are therefore more reactive.

Francolor obtained a technically valuable reactive component by sulfonation of 6-amino-2-chlorobenzothiazole.⁵⁰⁰



The chlorine atom in the 2-position of the benzothiazole system, despite its activation through the electron-attracting bridge links $-\text{SO}_2-$ or $-\text{N}=\text{N}-$ in the 6-position, is so resistant to hydrolysis that these dyes can be subjected to an oxidation-copper treatment with H_2O_2 and copper salts without any loss of reactivity. Hydrogen atoms on the nucleus⁵⁰¹ and also sulfonic acid groups⁵⁰² can be replaced in this way by a complex-forming hydroxyl group.

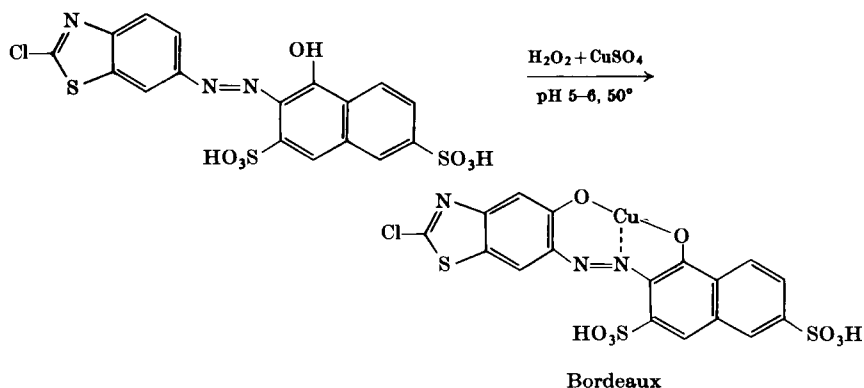
⁴⁹⁸ Fran, *FP* 1,417,225 (24.9.1964); 1,473,306 (3.2.1966).

⁴⁹⁹ Fran, *FP* 1,488,404 (3.6.1966).

⁵⁰⁰ Fran, *FP* 85,590 (addition to 1,290,839) (10.4.1964).

⁵⁰¹ BASF, *FP* 1,390,080 (24.4.1963).

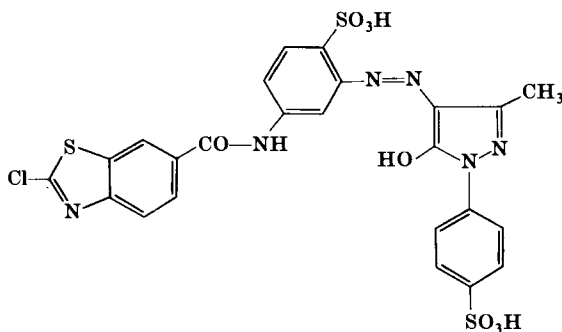
⁵⁰² Fran, *FP* 87,166 (addition to 1,290,839) (12.1.1965).



Bayer^{146, 495} and Ciba⁵⁰³ showed that 2-chlorobenzothiazolecarbonyl chlorides, such as

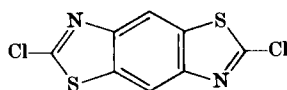


can also be used as reactive components. However, they offer no advantages over the sulfonyl chlorides or amines; they are more expensive and the dyestuffs formed from them, e.g., the yellow



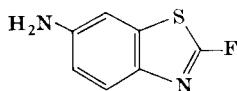
do not possess such high color strength as the corresponding yellows produced from diazotized 6-amino-2-chlorobenzothiazole.

An interesting type of 2-chlorobenzothiazole dye is based on the bifunctional reactive component⁴⁹⁵



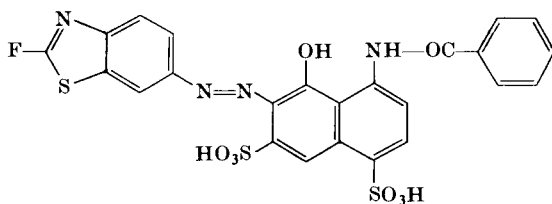
⁵⁰³ CIBA, *BeP* 619,274 (23.6.1961).

ii. *2-Fluorobenzothiazole derivatives.* 6-Amino-2-fluorobenzothiazole (produced from 6-nitro-2-chlorobenzothiazole by halogen exchange with alkali fluoride and reduction to the amine)



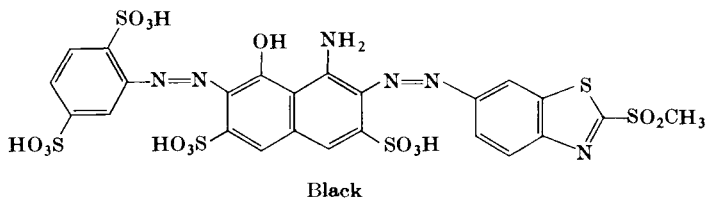
can be used as diazo component in the synthesis of reactive dyes; it can also be condensed with dyestuff sulfonyl chlorides or carbonyl chlorides.⁵⁰⁴

2-Fluorobenzothiazole dyestuffs, such as the bluish red



are very reactive; they dye cellulosic fibers at 40° from a long liquor. A disadvantage is a certain instability of shade.

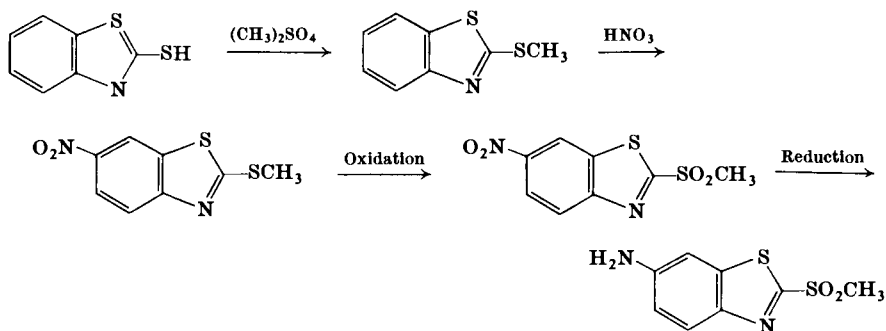
iii. *2-Sulfonylbenzothiazole derivatives.* Commercial importance has been attained by dyestuffs produced from 2-alkylsulfonyl-6-aminobenzothiazole as diazo component.⁵⁰⁵



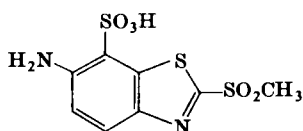
Reactive dyestuffs of this type are included in the Levafix P range of Farbenfabriken Bayer. Fixation is obtained by steaming prints containing sodium bicarbonate for one minute; they are dyed from a long liquor at 40°. Synthesis of the reactive diazo component proceeds through the following steps:

⁵⁰⁴ Acna, *BeP* 657,193 (17.12.1963).

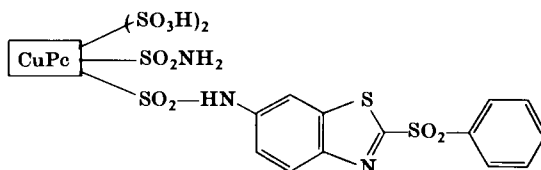
⁵⁰⁵ FBy, *DP* 6,607,159 (24.5.1965).



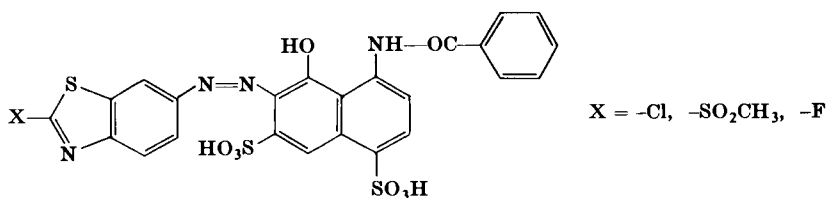
Similar to the corresponding 2-chloro derivative, 2-methylsulfonyl-6-aminobenzothiazole can be sulfonated, giving the likewise technically interesting aminosulfonic acid



6-Amino-2-alkyl(or aryl-)sulfonylbenzothiazoles condense with phthalocyanine sulfonyl chlorides, forming reactive dyestuffs, such as the turquoise⁵⁰⁶



The reactivity of the three dyestuffs



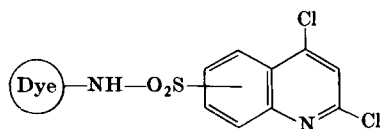
⁵⁰⁶ FBy, DP 6,615,763 (12.11.1965).

increases from the 2-chloro through 2-methylsulfonyl to the 2-fluoro derivative. As a parameter, the pseudo-monomolecular hydrolysis constant K_w may be used at pH 10 and 40°.⁵⁰⁷

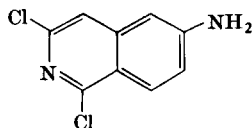
$X = -Cl$	$-SO_2CH_3$	$-F$
$K_w = 1.0 \times 10^{-5}$	7.0×10^{-4}	$1.2 \times 10^{-3} \text{ (min}^{-1}\text{)}$

9. Chloro Derivatives of Quinoline and Isoquinoline

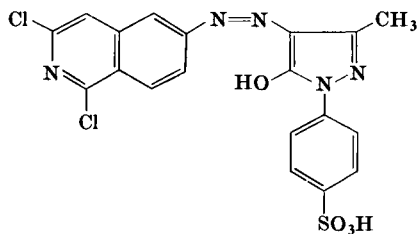
Sulfochlorination of the easily produced 2,4-dichloroquinoline gives a sulfonyl chloride which is suitable as a reactive component. Dyestuffs synthesized from this product⁵⁰⁸



possess only a moderate reactivity. Less readily available is the diazo-tizable dichloroisoquinolinamine⁵⁰⁹



As in the case of the dichloroquinoline derivatives, these dyestuffs, e.g.,



show only a medium reactivity.

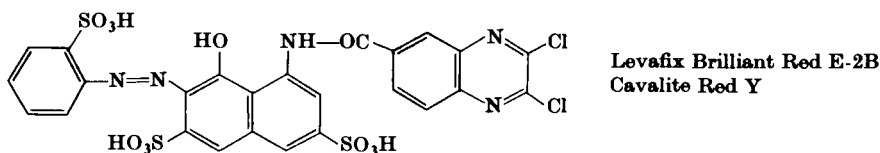
⁵⁰⁷ D. Hildebrand, H. Jäger, and E. Siegel, unpublished data (1967).

⁵⁰⁸ Fran, *FP* 1,324,434 (10.3.1962).

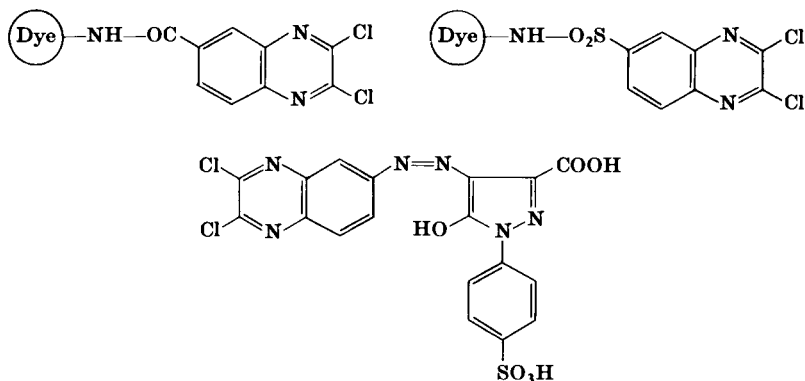
⁵⁰⁹ BASF, *FP* 1,386,005 (16.3.1963).

10. Quinoxaline Derivatives

This technically important reactive principle was developed in the years 1961–62 by Farbenfabriken Bayer,^{146, 510} Ciba,⁵¹¹ DuPont,⁵¹² and Francolor.⁵¹³ Commercial products on this basis are Levafix E dyestuffs (Bayer) and the Cavalite dyestuffs (DuPont).¹⁴⁶



a. Quinoxaline Derivatives Linked to the Chromophore through the Benzene Nucleus. i. Haloquinoxaline derivatives. 2,3-Dichloroquinoxaline derivatives, which are bound to the chromophore system through a negative and, therefore, additionally activating carbonylamino, sulfonylamino, or azo bridge, are extremely suitable as reactive dyes for cellulosic fibers.^{510–514}



Their reactivity—they are dyed from a long liquor in presence of soda ash at 40°—is nearly as high as that of the cold-dyeing dichloro-*s*-triazinylamino dyestuffs, over which they offer the advantage of more stable pad solutions and print pastes.¹⁴⁶ They also react with wool and

⁵¹⁰ FBy, *BeP* 613,586 (7.2.1961).

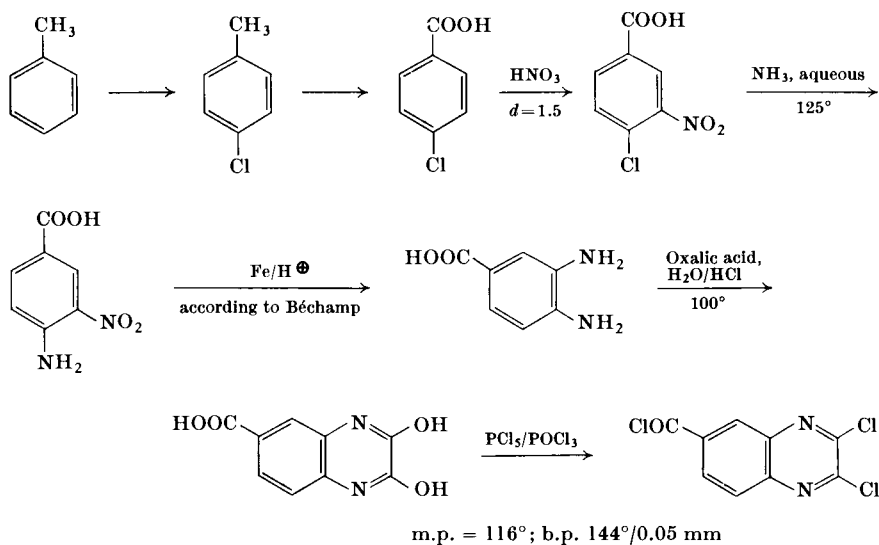
⁵¹¹ CIBA, *BeP* 617,695 (16.5.1961).

⁵¹² DuP, *FP* 1,359,644 (21.11.1961).

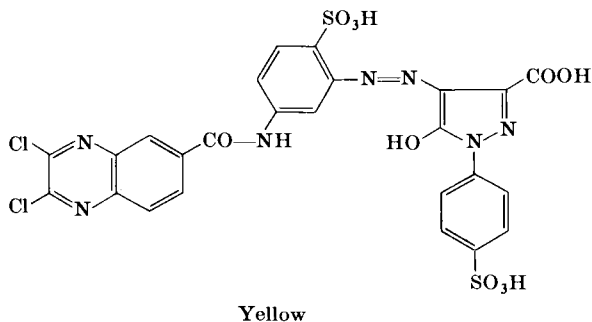
⁵¹³ Fran, *FP* 1,319,429 (19.1.1962).

⁵¹⁴ Fran, *FP* 1,307,329 (13.9.1961).

gelatin (diffusion-fast dyes for the azo-silver bleaching process).⁵¹⁵ Particularly important is 2,3-dichloroquinoxaline-6-carbonyl chloride, which is synthesized as follows¹⁴⁶:



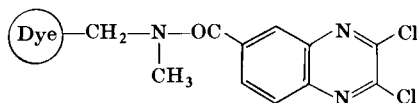
This reactive component has a considerable intrinsic affinity, so that reactive dyestuffs with a high fixation yield are obtained even with low-affinity chromophores, e.g., the pyrazolone yellow



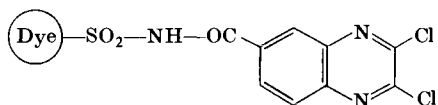
On the other hand, the specific affinity of the 2,3-dichloroquinoxaline system increases the tendency to association and reduces the solubility

⁵¹⁵ AGFA-Gevaert, *FP* 1,443,003 (14.8.1964).

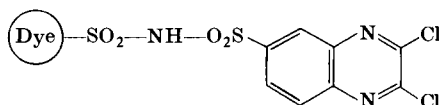
of the dyestuffs. The opposite effect is achieved by aliphatic bridge links,⁵¹⁶ e.g.,



or by diacylimino bridges, such as



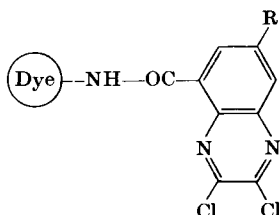
Ref. 517



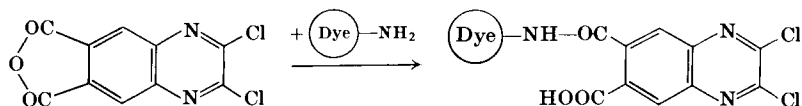
Ref. 518

Although as a result of this stability to hydrolysis 2,3-dichloroquinoxaline-6-carbonylamino dyestuffs possess good storage properties even without an addition of buffer mixtures, further stabilization can be achieved in certain cases with sulfates (Glauber's salt) in the pH range 5.5-8.⁵¹⁹

Less favorable sterically and therefore also somewhat inferior in dyeing performance are dyestuffs produced from 2,3-dichloroquinoxaline-5-carbonyl chloride ($R = H$)^{510, 513} or from its 7-chloro substitution product ($R = Cl$).⁵²⁰



A further variant, which has remained without any commercial importance, is 2,3-dichloroquinoxaline-dicarboxylic anhydride.⁵²¹



⁵¹⁶ FBy, *BeP* 662,569 (23.9.1961); 652,741 (12.9.1963).

⁵¹⁷ Fran, *FP* 1,388,101 (28.12.1963).

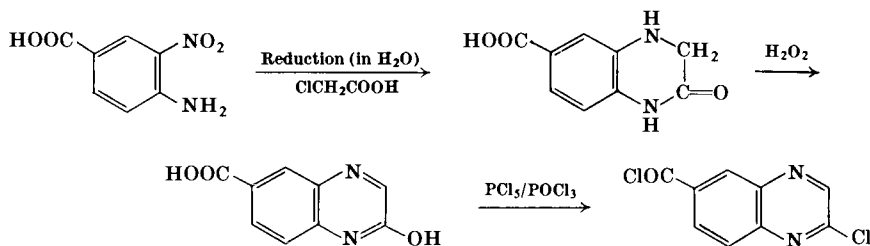
⁵¹⁸ FBy, *BeP* 668,146 (12.8.1964); 679,424 (14.4.1965).

⁵¹⁹ DuP, *USP* 3,313,797 (17.1.1963).

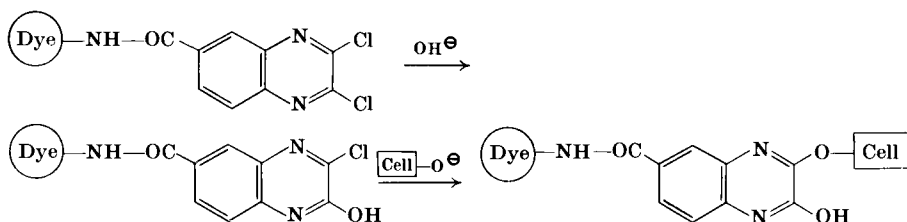
⁵²⁰ G, *BP* 1,139,297 (31.12.1964).

⁵²¹ DuP, *FP* 1,385,595 (5.12.1962).

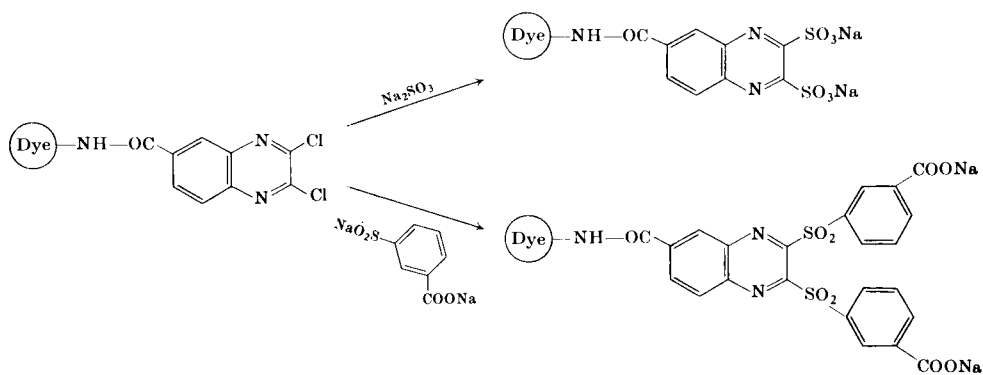
Despite the presence of only one mobile chlorine atom, 2-chloroquinoxaline-6-carbonyl chloride is a good reactive component, although it does not quite attain the properties of the 2,3-dichloro analog in application and, furthermore, is less readily accessible.^{510, 522}



2-Hydroxy-3-chloro derivatives obtained in the selective alkaline hydrolysis of 2,3-dichloroquinoxaline-6-carbonylamino dyestuffs also react with cellulose under energetic conditions (pad-steam process).⁵²³



ii. Quinoxaline derivatives with mobile groups other than halogen. The chlorine atoms in 2,3-dichloroquinoxaline dyestuffs can be substituted on the nucleus by other mobile groups

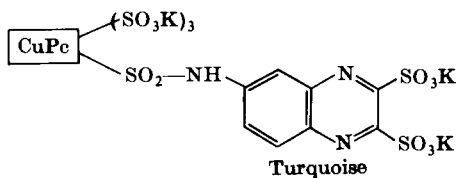


Ref. 133

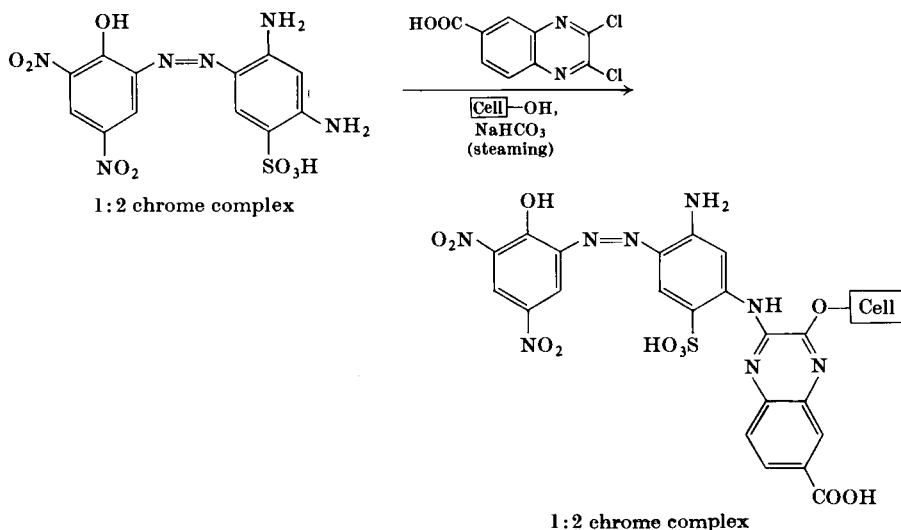
⁵²² DuP, USP 3,326,888 (2.5.1963).

⁵²³ DuP, FP 1,395,388 (21.5.1963).

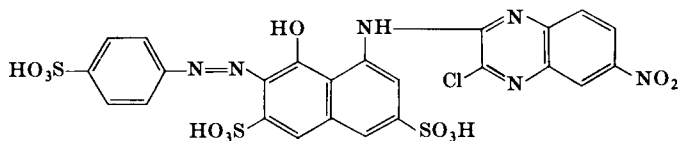
Cellulose-reactive products are also obtained, in certain cases with an improved solubility in water.⁵²⁴



b. Quinoxaline Derivatives Linked to the Chromophore through the Heterocycle. In addition to water-soluble 2,4-dichloro-*s*-triazine derivatives, the water-soluble 2,4-dichloroquinoxaline-6-carboxylic acid was also mentioned in an early patent application of ICI⁵²⁵ as a bifunctional linking component between amino dyestuffs and cellulose.



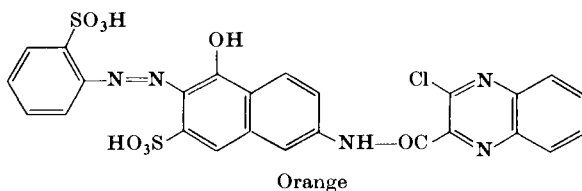
Not until later were activated (e.g., nitro-substituted) 2,3-dichloroquinoxalines reacted in substance with chromophores containing amino groups, forming (moderately reactive) dyestuffs, such as⁵¹⁴.



⁵²⁴ ICI, *FP* 1,367,010 (21.6.1962).

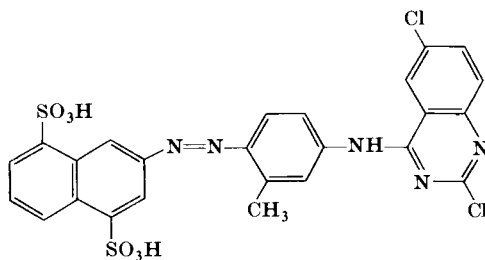
⁵²⁵ ICI, *USP* 2,928,711 (21.11.1956).

The mobility of the quinoxaline chlorine atom is increased by substituting for the inactivating imino bridge an electron-attracting carbonyl group on the heterocycle. Such products are obtained from 2-chloroquinoxaline-3-carbonyl chloride.⁵²⁶

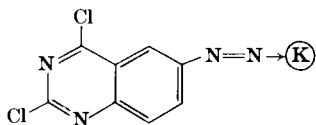


11. Quinazoline Derivatives

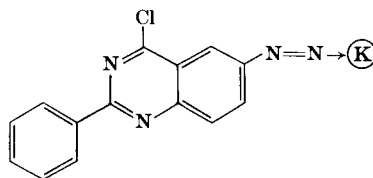
2,4-Dichloroquinazoline is unsuitable as a reactive component.⁵²⁷ Only when the benzene nucleus is substituted negatively, e.g., by halogen, nitro, sulfo, or carboxyl groups, are dyestuffs obtained which are capable of adequate fixation.⁵²⁸



An azo bridge on the chloroquinazoline system also causes activation (see also ref. 146).



Ref. 528



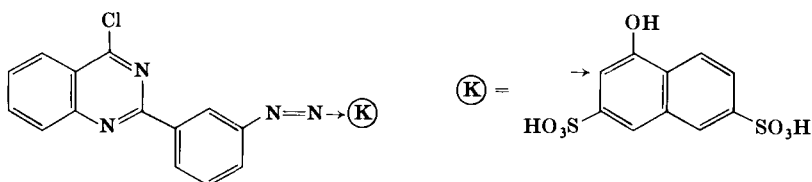
Ref. 529

⁵²⁶ ICI, BP 1,039,379 (23.9.1963); S, BeP 656,696 (13.12.1963).

⁵²⁷ H. Zollinger, *Angew. Chem.* **73**, 125 (1961).

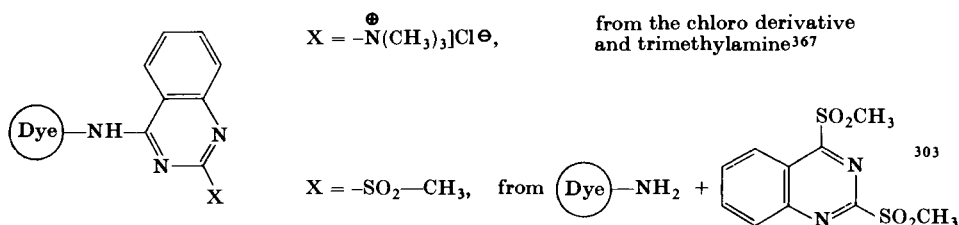
⁵²⁸ Fran, FP 1,308,044 (22.9.1961); BeP 621,643 (13.9.1961).

⁵²⁹ BASF, BeP 618,973 (16.6.1961).



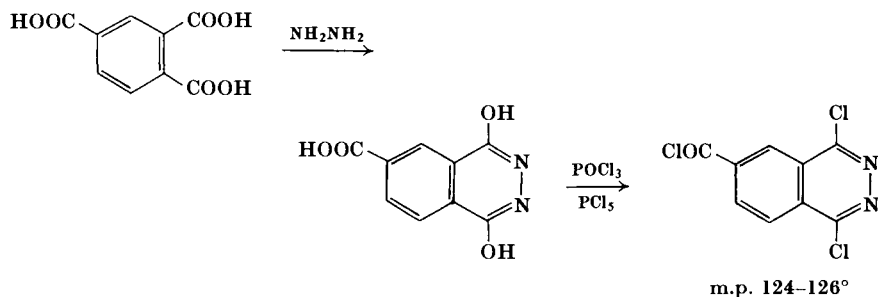
Ref. 529

The required activation can also be achieved by a stronger electron-attracting mobile group.



12. Phthalazine Derivatives

1,4-Dichlorophthalazine-6-carbonyl chloride is produced from trimellitic acid and hydrazine with subsequent halogenation.



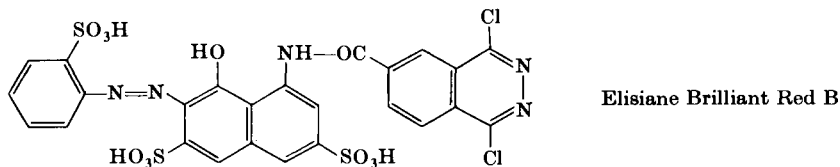
Dyestuffs with this reactive component are extremely suitable for textile printing and for continuous dyeing; they do not quite attain the standard of the isomeric 2,3-dichloroquinoxaline products when dyed from a long liquor.¹⁴⁶

Bayer,⁵³⁰ DuPont⁵¹² and Francolor⁵³¹ recognized the value of this

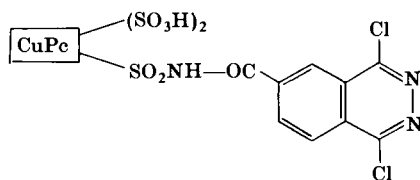
⁵³⁰ FBy, *BeP* 614,375 (27.2.1961).

⁵³¹ Fran, *FP* 1,336,679 (16.4.1962).

dyestuff group, which is marketed by the last-mentioned firm under the designation *Elisiane dyestuffs*.

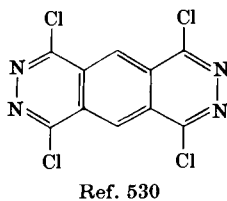
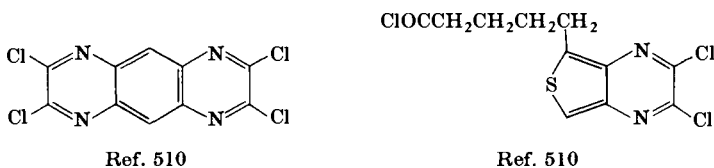


In this case also, linkage to the chromophore through a diacylamide bridge improves the solubility of the resulting dyestuffs.⁵³²



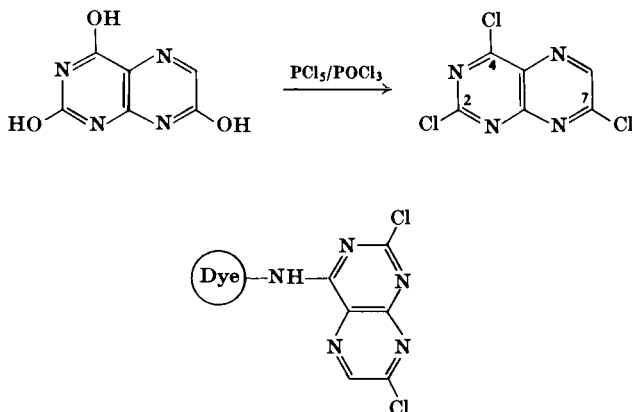
13. Condensed Systems with Two Nitrogen Heterocycles

In their dichloroquinoxaline⁵¹⁰ and dichlorophthalazine⁵³⁰ patents, *Farbenfabriken Bayer* also describe the following chloro heterocycles as reactive components:



⁵³² Fran, *FP* 1,394,020 (26.10.1963); 89,178 (addition to 1,394,020) (9.12.1965).

Fiolka discovered that 2,4,7-trichloropteridine is suitable as a fixation component.⁵³³

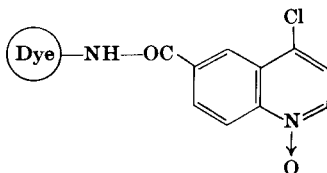


In dioxane, the reaction with amines always occurs first with the chlorine atom in the 4-position, then with that in the 2-position and, finally, with that in the 7-position.

Cassella mentions trichloropurine as a fiber-reactive bridge between the dye and a second reactive group, present in the same molecule.^{533a}

14. *N*-Oxides of Halogen Heterocycles

The reactive dyestuffs based on *N*-oxides of heteroaromatic five- or six-membered rings with anionic mobile groups,⁵³⁴ which were widely claimed by Bayer, attained no practical importance. While 4-chloroquinoline-*N*-oxide-6-carbonyl chloride is not readily available and does not lead to very reactive dyestuffs⁵³⁴

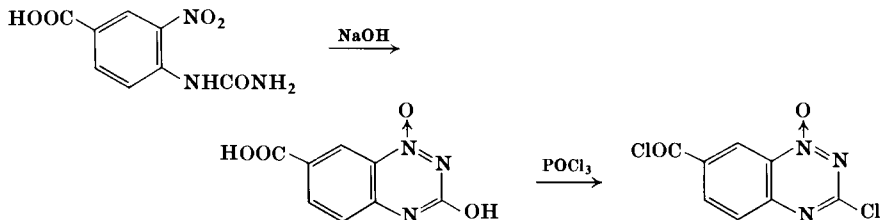


⁵³³ D. Fiolka, Dissertation, University of Stuttgart (10.6.1965).

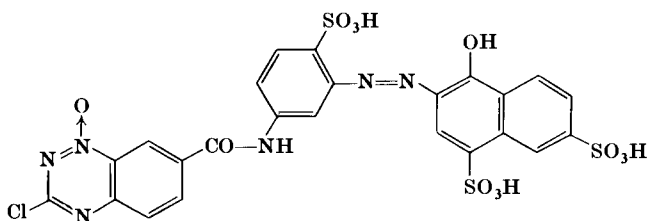
^{533a} CFM, *FP* 83,421 (31.3.1962).

⁵³⁴ FBy, *BeP* 637,526 (29.9.1962).

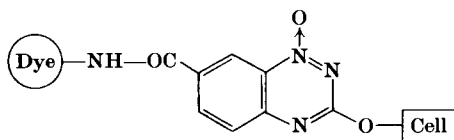
3-chloro-1,2,4-benzotriazine-1-*N*-oxide-7-carbonyl chloride, described by Sandoz,⁵³⁵ is easily produced.



The dyeings obtained with these dyestuffs, e.g., the red



do not possess satisfactory wet-fastness properties since the cellulose-ether bridge formed is very easily hydrolyzed.



D. ACID DERIVATIVES AS REACTIVE GROUPS

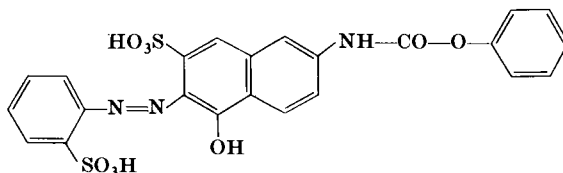
With the exception of the thiosulfato esters (color salts) which have attained a certain importance in the Inthion dyestuffs of Farbwerke Hoechst, acid derivatives, in contrast with the commercial products with heterocyclic and aliphatic carrier systems, have found no practical application up to the present. This may be explained by an excessive

⁵³⁵ S, *FP* 1,462,672 (31.12.1964); K. Brenneisen, O. Thumm, and J. Benz, *Helv. Chim. Acta* **49**, 651-660 (1966).

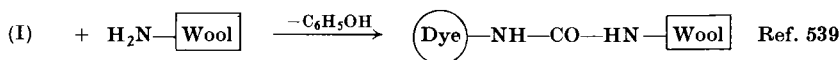
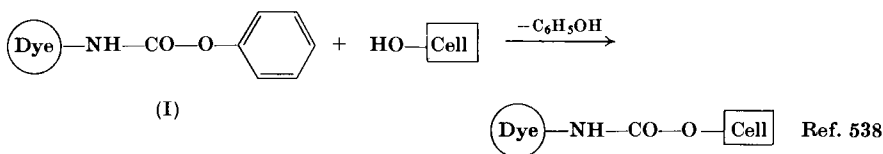
susceptibility to hydrolysis of the reactive acid derivatives and too little reactivity of the others, and also by the very low general affinity of these types.

1. Carbonic Acid Derivatives

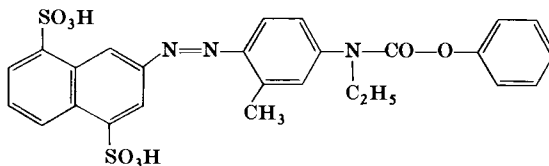
a. *Arylcarbamates*, $\text{(Dye)}-\text{NH}-\text{CO}-\text{OAr}$ l. By acylation of amino dyestuffs or of intermediate products containing amino groups with phenyl chloroformate, dyestuffs such as the brilliant orange



are readily available in practice.^{536, 537} They react with cellulosic and polyamide fibers, splitting off phenol when the fabrics are printed or padded and then steamed in presence of acid-binding agents.



DuPont describes corresponding cellulose-reactive dyes with a particularly low affinity containing *N*-alkylarylcarbamate groups.⁵⁴⁰



⁵³⁶ CFM, *DAS* 1,091,677 (20.4.1957); CIBA, *FP* 1,237,664 (30.10.1958).

⁵³⁷ S, *SP* 360,746; 365,168; 368,250 (6.9.1957).

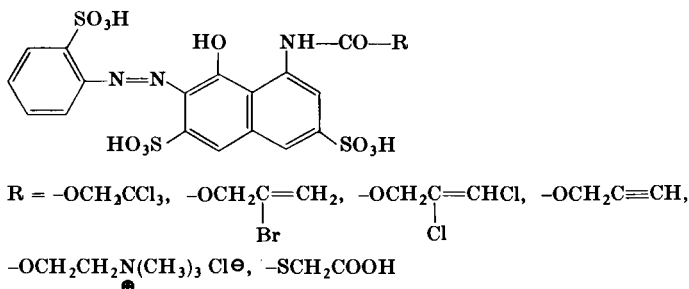
⁵³⁸ CIBA, *BeP* 584,125 (30.10.1958).

⁵³⁹ CIBA, *BeP* 584,126 (30.10.1958).

⁵⁴⁰ DuP, *FP* 1,268,654 (15.9.1959).

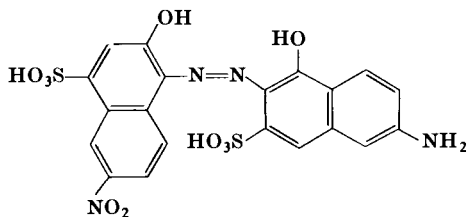
Carbamates of heterocyclic hydroxy compounds are also suitable as reactive groups.⁵⁴¹

b. *Alkylcarbamates*, $(\text{Dye})-\text{NH}-\text{CO}-\text{OAlkyl}$, show sufficient reactivity only in the case of negative substitution on the alkyl group.^{537, 542} For example, dyestuffs such as



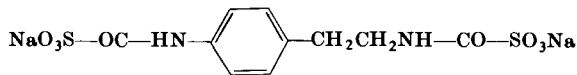
are suitable for fixation on cellulosic fibers by steaming or in dry heat in the presence of acid-binding agents.⁵⁴²

c. *Isocyanates*. Free isocyanate groups are unstable in water-soluble dyes containing the usual auxochromes. Their reactivity is also too high for application in water. Satisfactory results are achieved by applying separately water-soluble dyestuffs containing external amino groups, e.g., of the copper phthalocyanine range⁵⁴³ or 1:2 chrome complex blue⁵⁴⁴



and the water-stable diisocyanate-bisulfite addition products, such as^{543, 544}

$\text{NaO}_3\text{S}-\text{OC}-\text{HN}(\text{CH}_2)_6\text{NH}-\text{CO}-\text{SO}_3\text{Na}$ or



⁵⁴¹ S, *SP* 364,756 (1.10.1959).

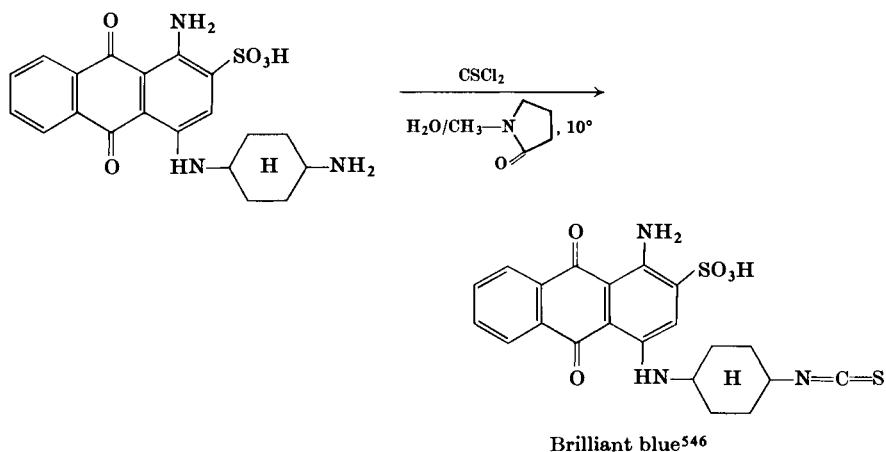
⁵⁴² FBy, *BeP* 600,433 (24.2.1960).

⁵⁴³ FBy, *BeP* 587,578 (14.2.1959).

⁵⁴⁴ CIBA, *BeP* 602,600 (20.10.1959).

The best method is to aftertreat the dyeings or prints of these dyestuffs on cellulosic fibers with the diisocyanate-bisulfite addition products in the presence of acid-binding agents and urea by steaming or prolonged storage at room temperature. In addition to a reaction with the amino groups of the dyestuffs and the hydroxyl groups of the fiber, only a dyestuff-to-dyestuff linkage may occur in certain cases.

d. Isothiocyanates. In contrast to the isocyanate group, the slower-reacting isothiocyanate group is stable in water-soluble dyestuffs. It can be introduced smoothly with thiophosgene in an aqueous organic medium (pyridine, dimethylformamide, *N*-methylpyrrolidone) at 0–10° into dyestuffs containing primary amino groups.^{545, 546}



Cellulosic fibers can be dyed with isothiocyanate dyestuffs in presence of soda ash by the steaming or curing process with good wet-fastness properties.⁵⁴⁷ Dyestuffs of this type, e.g., the above-mentioned brilliant blue, are also suitable for the dyeing of wool and polyamide fibers. The wet-fastness properties of the dyeings are improved by increasing the initial acid pH of the dyebath with ammonia or hexamethylenetriamine to 6.5–8.5.⁵⁴⁸

2. Carboxylic Acid Derivatives

a. Anhydrides. Hodogaya took up again the old Gunther's isatoic anhydride group (see ref. 390) and recommended isocyanates of isatoic

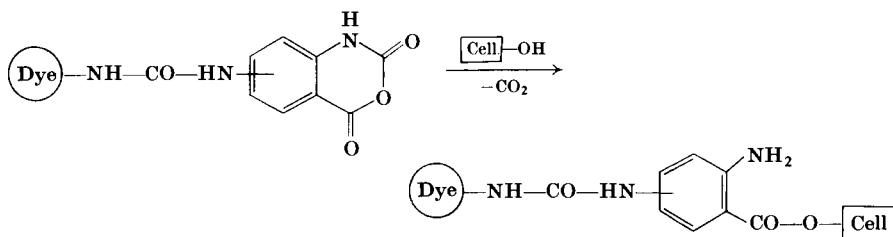
⁵⁴⁵ CIBA, *SP* 356,225 (6.5.1958); *BeP* 578,416 (6.5.1958).

⁵⁴⁶ FBy, *BeP* 598,651 (2.1.1960).

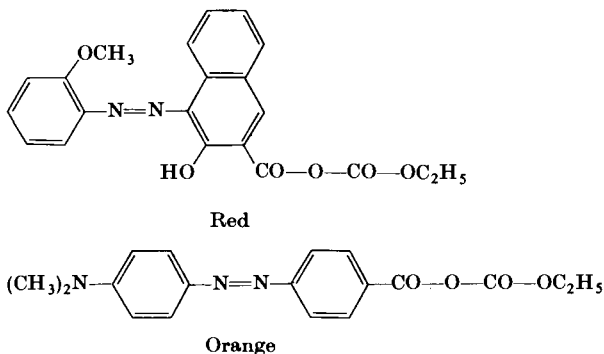
⁵⁴⁷ CIBA, *BeP* 578,415 (6.5.1958).

⁵⁴⁸ FBy, *BeP* 611,423; 611,424 (12.12.1960).

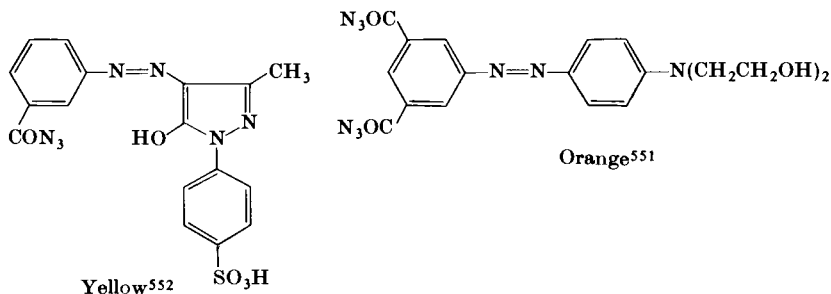
anhydride as reactive components. With aminoazo dyestuffs a urea bridge is formed, the resulting products dyeing cellulosic fibers with soda ash at a low temperature.⁵⁴⁹



Mixed anhydrides as obtained from dyestuff carboxylic acids and alkyl chloroformates are reactive dyes for polyamide fibers, particularly where the dyeing is aftertreated with soda ash.⁵⁵⁰



b. Azides. Diazotization of an aminobenzoic hydrazide leads directly to the diazonium compound of the carbazide, which on coupling gives dyestuffs such as



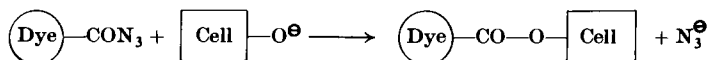
⁵⁴⁹ HCC, *JP* 14,936/62 (9.3.1960).

⁵⁵⁰ British Nylon Spinners, Ltd., *BP* 1,009,204 (23.11.1961).

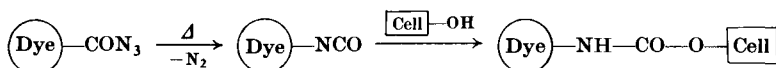
⁵⁵¹ FB, *BeP* 611,823 (24.12.1960).

⁵⁵² Manake, O., Konishi, H., Urakato, T., Hameo, T., and Hiyama, H., *Yuki Gosei Kagaku Kyokai Shi* **20**, 936-939 (1962).

Dyestuffs of this type react, on the one hand, with polyamides and with cellulose in an alkaline medium with nucleophilic exchange of the azide group, e.g.,

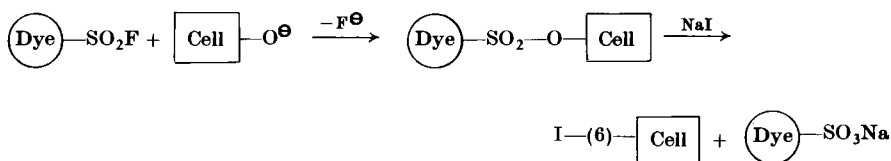


forming cellulose esters which are extremely susceptible to hydrolysis, while on the other hand they form more stable urethane bonds through intermediate isocyanates when fixed in heat.



3. Sulfonic Acid Derivatives

a. Sulfonyl Fluorides. It is well known that aromatic sulfonyl fluorides are far less susceptible to hydrolysis than sulfonyl chlorides. They can generally be recrystallized from boiling water. ICI, Cassella, Ciba,⁵⁵³ and Hoechst⁵⁵⁴ recognized almost simultaneously that water-soluble dyes containing sulfonyl fluoride groups in the molecule react with cellulosic fibers in the presence of alkalies. The colored cellulose derivatives formed in this way correspond to the well-known reaction products of cellulose with *p*-toluenesulfonyl chloride. As in the case of these products, sodium iodide in acetone exchanges the sulfoester group in the 6-position for iodine, which Zollinger considered to prove the existence of a covalent bond in such reactive dyeings.⁵⁵⁵

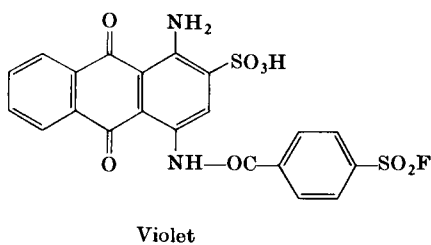
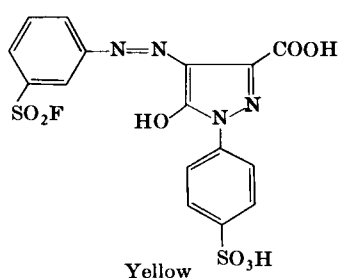


Sulfonyl fluoride dyestuffs show little affinity and are suitable only for padding and printing on cellulosic fabrics.⁵⁵³

⁵⁵³ ICI, *DAS* 1,052,946 (12.9.1956); CFM, *FP* 1,193,706 (6.12.1956); CIBA, *FP* 1,192,485 (18.1.1957); ICI, *USP* 3,131,021 (7.8.1961).

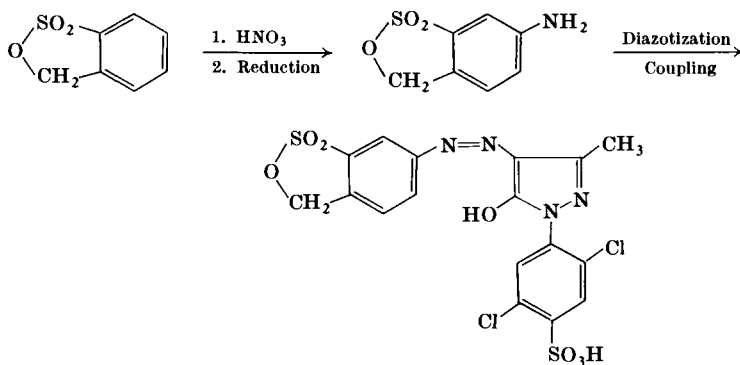
⁵⁵⁴ FH, *BeP* 578,517 (7.5.1958).

⁵⁵⁵ B. Krazzer and H. Zollinger, *Helv. Chim. Acta* **43**, 1513-1522 (1960).

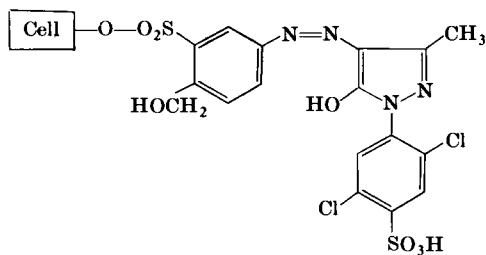


According to the statements of Hoechst,⁵⁵⁴ these products are also obtained from dyes containing sulfonic and carboxyl groups and fluorosulfonic acid, for example at 60°.

b. Sulfonic Acid Esters. Ciba claims cyclic sulfonic acid esters as fiber-reactive groups in dyes such as the yellow⁵⁵⁶

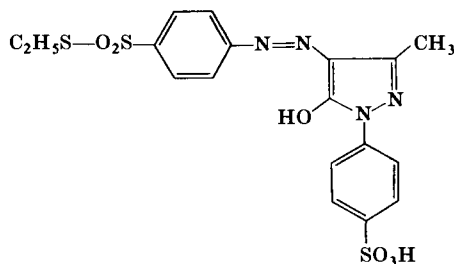


They react with cellulose, forming a sulfonic acid ester bond (see ref. 527).



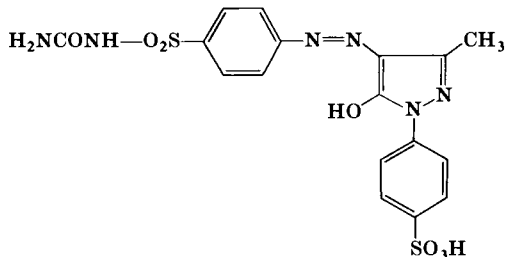
⁵⁵⁶ CIBA, *BeP* 570,888 (3.9.1957).

c. Thiosulfonic Acid Esters. The thiosulfonic acid ester group reacts mainly with the functional groups of wool keratin and of polyamides. Dyestuffs such as the yellow

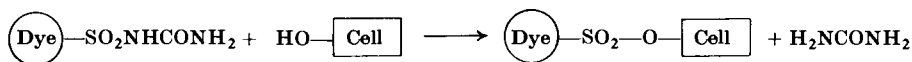


are therefore recommended only for wool and polyamide fibers.⁵⁵⁷ Francolor formed from dyestuff-sulfonyl chlorides and sodium sulfide, reactive dyes for cellulose, to which the constitution of thiosulfonic acid dyestuffs was assigned.⁵⁵⁸

d. N-Sulfonylureas. Farbwerke Hoechst recognized that the *N*-sulfonylurea group



under energetic conditions—curing at 140–160°—reacts with cellulose.⁵⁵⁹ Presumably, cellulose-sulfonic acid esters are also formed in this case with separation of urea.

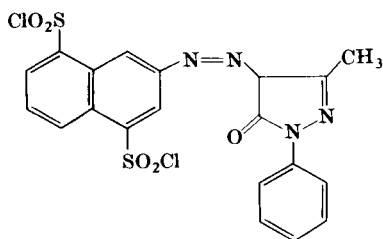


⁵⁵⁷ Lwowskij Politechnitscheskij Inst., UdSSR, *GP* 1,298,219 (28.4.1964); *FP* 1,394,571 (19.5.1964).

⁵⁵⁸ Fran, *FP* 1,413,126 (18.7.1964).

⁵⁵⁹ FH, *BeP* 631,934 (5.5.1962); *IP* 845,491 (23.10.1968); *BeP* 723,008 (28.10.1968).

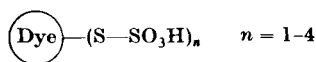
Francolor claims the corresponding sulfonylthioureas, obtained from dyestuff-sulfonyl chlorides, e.g.,



and thiourea in aqueous solution at pH 7 and 32°, as reactive dyestuff, mainly for pad-dyeing.⁵⁶⁰

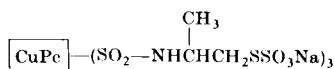
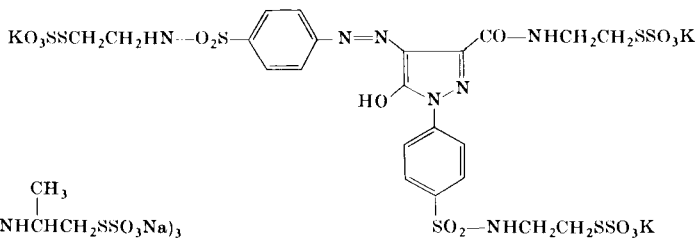
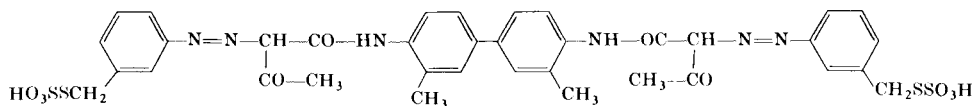
4. Thiosulfato S-Alkyl Esters

Dyestuffs of the type



Inthion dyestuffs, Hoechst

e.g.,



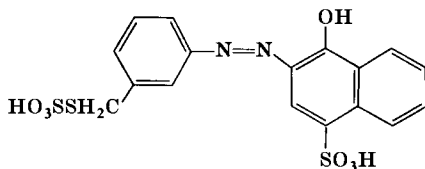
are not reactive but polycondensation dyes. They were developed extensively by Farbwerke Hoechst^{204, 561} and subsequently also by Martin-Marietta.⁵⁶² Sandoz⁵⁶³

⁵⁶⁰ Fran, *FP* 1,413,129 (22.7.1964).

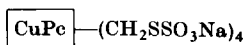
⁵⁶¹ FH, *BeP* 590,124; 590,125 (24.4.1959); 590,397 (30.4.1959); *GP* 1,216,835 (30.4.1959); *BeP* 593,886 (8.8.1959); *DAS* 1,145,576 (16.3.1960); *BeP* 608,829 (4.10.1960); *GP* 1,173,485 (2.8.1962); *FP* 84,893 (addition to 1,269,613) (6.12.1962); 86,567 (addition to 1,269,613) (12.10.1963).

⁵⁶² Martin-Marietta, *DP* 6,413,710 (16.7.1964); *BeP* 669,010 (2.9.1964); 669,348 (11.9.1964); *FP* 1,481,543 (28.5.1965).

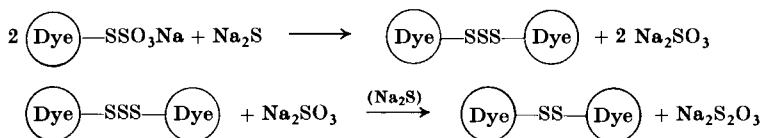
⁵⁶³ S, *BeP* 606,571 (25.11.1960).



and ICI⁵⁶⁴



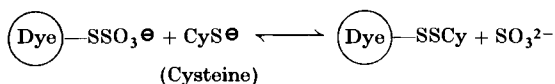
also made special patent applications in this field. Inthion dyestuffs condense quantitatively under the conditions of application—preferably in the presence of sodium sulfide—to the insoluble disulfides, with loss of the water-solubilizing thiosulfato ester group²⁰⁴:



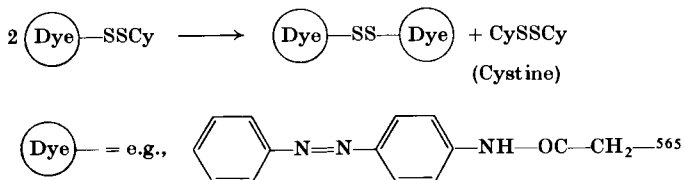
In certain cases, thiosulfato ester dyestuffs nevertheless react with the fiber. On the strongly activating β -sulfonylethyl carrier



SSO₃Na is a technically important anionic mobile group similar to its oxygen analog.¹¹⁸ They react with the cysteine of wool, forming mixed disulfides



In addition, considerable quantities of dyestuff-disulfide are always formed.^{204, 565, 566}



⁵⁶⁴ ICI, *FP* 1,328,180 (7/7/1961).

⁵⁶⁵ B. Milligan and J. M. Swan, *Textile Res. J.* **31**, 18–25 (1961).

⁵⁶⁶ F. Osterloh, *Angew. Chem.* **74**, 699 (1962).

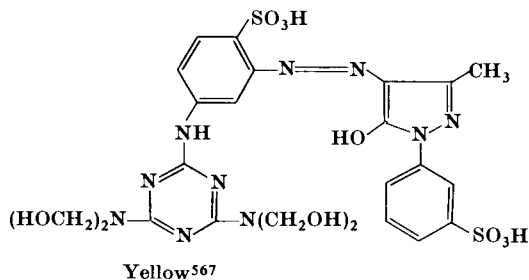
E. FORMALDEHYDE DERIVATIVES AS REACTIVE GROUPS

1. Formaldehyde Derivatives Incorporated into Dyestuffs

Since acetal bonds are formed in the linkage of dyestuffs to cellulose through formaldehyde derivatives, the reaction must take place in an acid medium. For this reason, these dyestuffs cannot be combined with the other reactive dyes applied in the presence of alkalis. Another disadvantage is that the reaction with cellulose proceeds satisfactorily only when fixation is obtained in dry heat, i.e., dyestuffs of this type can neither be dyed from a long liquor nor fixed satisfactorily by steaming. Finally, the acetal bonds formed are easily split up again by acids, so that all acid wet-fastness tests give poor results.

The linking of dyestuffs to cellulose through formaldehyde derivatives in an acid medium offers two advantages: (1) Dyeing and crease-proofing can be carried out in a single operation (Resacron dyestuffs, Ciba). (2) Cotton/polyester fabrics can be dyed in one bath together with disperse dyes which are often unstable in an alkaline medium, thus permitting a simultaneous fixation of dyes of both types in dry heat (curing or Thermosol process, Calcobond dyes, American Cyanamid). The disadvantages pointed out above have evidently prevailed up to the present since dyes of this type have only a very small share of the market.

Ciba^{567, 568} and BASF^{569, 570} described in 1956/1957 the production of methylolreactive dyes by reaction of formaldehyde at pH 8–10 in aqueous solution with organic dyestuffs containing reactive hydrogen atoms in carbamide or sulfonamide groups, (thio-)urea groups, (thio-)lactam or melamine residues, aromatic hydroxyl or sulfhydryl groups, and also in activated methylene groups.

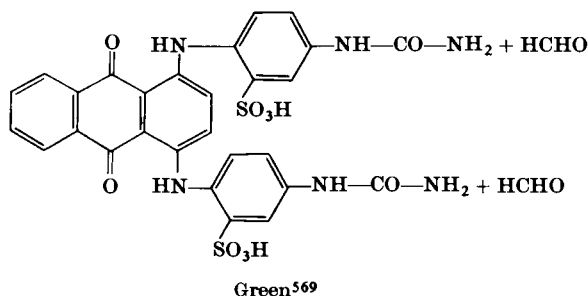


⁵⁶⁷ CIBA, *SP* 349,721 (19.11.1956).

⁵⁶⁸ CIBA, *BeP* 626,202 (27.2.1962).

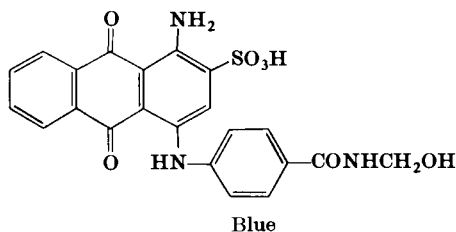
⁵⁶⁹ BASF, *DAS* 1,079,756 (18.5.1957).

⁵⁷⁰ BASF, *BP* 895,029 (28.7.1959).

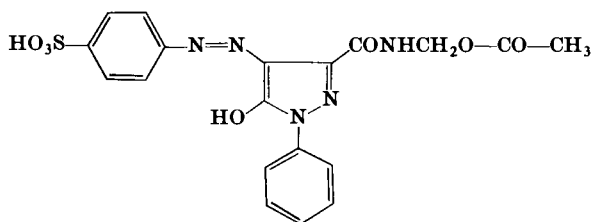


Their fixation on cellulosic fibers in the presence of ammonium chloride as acid source by heating for 5 minutes at 150° has also been claimed by Ciba.⁵⁶⁷

A patent application of BASF relates especially to the production of methylene ethers by acid etherification of these polymethylol dyestuffs with alcohols.⁵⁷¹ American Cyanamid also subsequently developed this field.⁵⁷²



Dyestuffs with esterified *N*-methylol reactive groups were obtained by Farbenfabriken Bayer from the appropriate carbamides with para-formaldehyde and acetic anhydride in glacial acetic acid.⁵⁷³ For example, yellow shades are obtained with



on cotton with high fastness to light and good wet-fastness properties.

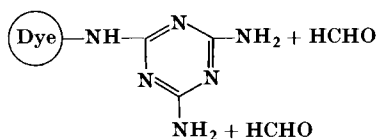
Aminotriazines as carriers of the methylol or alkoxymethylene groups

⁵⁷¹ BASF, *FP* 1,271,330 (19.9.1959).

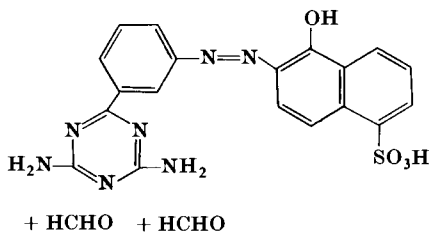
⁵⁷² CCC, *FP* 1,322,452 (11.4.1961).

⁵⁷³ FBy, *BeP* 614,660 (7.3.1961).

were described, in particular, by American Cyanamid⁵⁷⁴ and BASF.^{575,576} These dyes can be produced by acylation of dyestuffs containing amino groups with 2-chloro-4,6-diamino-*s*-triazine⁵⁷⁵ or by synthesis from 2-aminophenyl-4,6-diamino-*s*-triazine⁵⁷⁶ and subsequent reaction with formaldehyde.

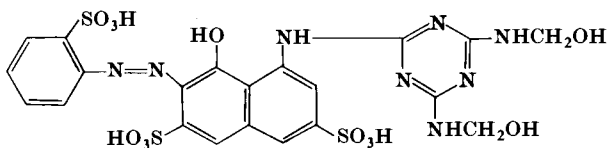


Ref. 575



Ref. 576

The Calcobond dyes of American Cyanamid, introduced in 1965, e.g.,



Calcobond Red 3B

contain methylolmelamine reactive groups.⁵⁷⁴ They find a limited application together with disperse dyes in the one-bath dyeing of cotton-polyester fabrics by the pad-cure process.

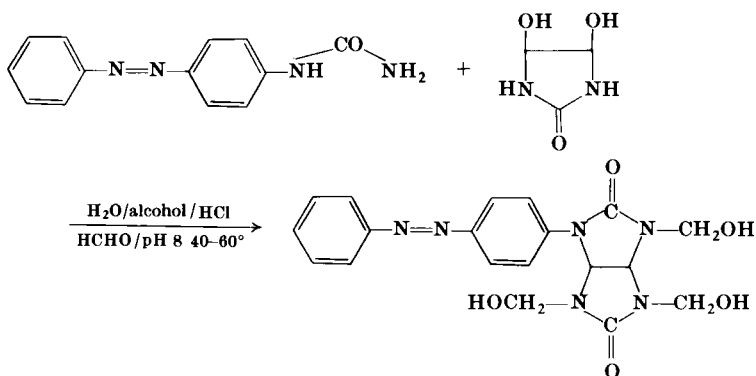
In addition to melamine, glyoxaldiureine is an important component in creaseproof finishing agents based on methylol groups. This molecule has also been incorporated into dyestuffs as carrier of the methylol groups. This can be done in several ways⁵⁷⁷:

⁵⁷⁴ CCC, *FP* 1,241,346 (28.10.1958); *USP* 3,072,454 (7.7.1960).

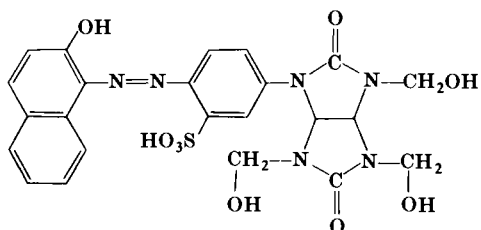
⁵⁷⁵ BASF, *BeP* 591,120 (23.5.1959).

⁵⁷⁶ BASF, *BeP* 591,121 (23.5.1959).

⁵⁷⁷ BASF, *DAS* 1,070,760 (19.11.1955).

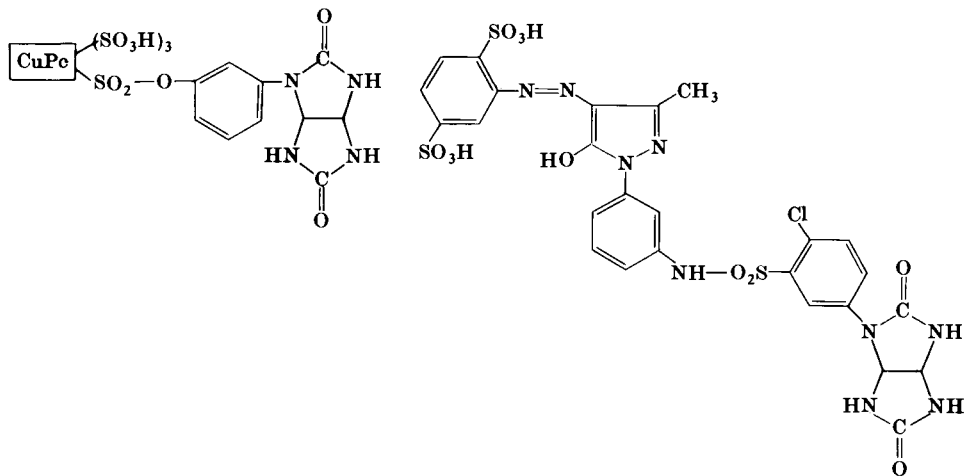


For example, the dyestuff



gives red shades on cellulose with good wet-fastness properties.⁵⁷⁸

Another method of synthesis starts from phenols containing glyoxal-ureine which are condensed with phthalocyaninesulfonyl chlorides, or from corresponding benzenesulfonyl chlorides which are condensed with aminoazo or aminoanthraquinone dyes.^{579, 580}

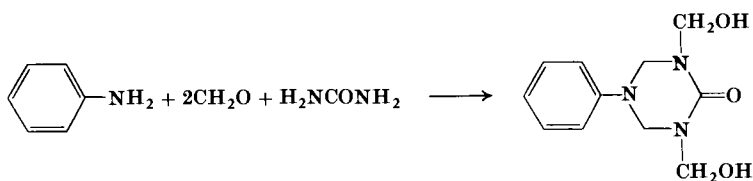


⁵⁷⁸ BASF, *FP* 1,260,335 (11.6.1959).

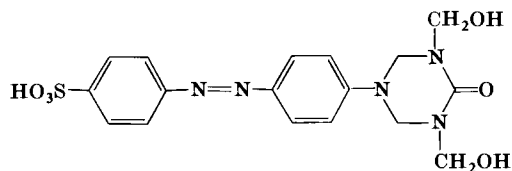
⁵⁷⁹ DH, *FP* 1,348,380 (3.8.1961).

⁵⁸⁰ DH, *FP* 1,348,381 (3.8.1961).

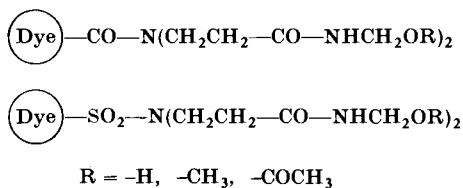
Methyloltriazinone dyestuffs are also described.⁵⁸¹



e.g.,



In the course of the extensive development of this field, American Cyanamid also produced by condensation of carbonyl or sulfonyl chlorides with iminodipropionitrile, saponification to bis-propionamide, and formaldehyde addition, dyestuffs and optical brightening agents of the type⁵⁸²



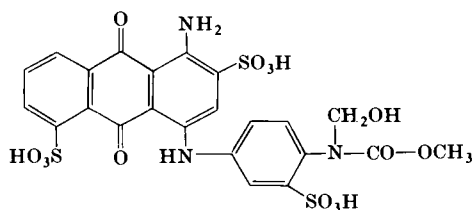
N-Methylolurethane groups were incorporated into dyestuffs in two different types of linkage. General Aniline acylated amino dyestuffs with chloroformates and then condensed with formaldehyde,⁵⁸³ while Farbenfabriken Bayer converted dyestuffs containing aliphatic hydroxyl groups with methoxymethyl isocyanate into the corresponding urethanes.⁵⁸⁴

⁵⁸¹ American Aniline Prod., Inc., *USP* 3,152,111 (18.12.1961).

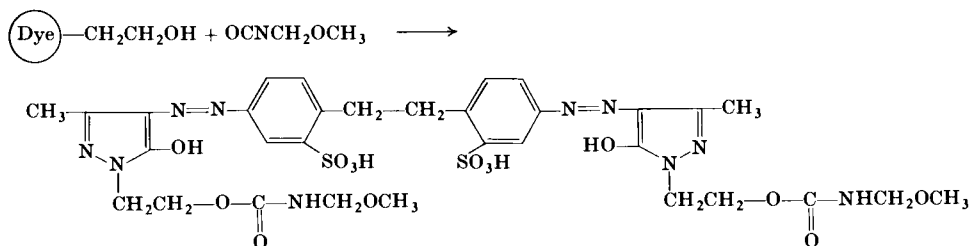
⁵⁸² CCC, *FP* 87,375 (3.1.1964); M. Löwenstein and Sons, *USP* 3,447,888 (19.4.1966); CCC, *USP* 3,413,074 (31.8.1967); *GP* 1,817,266 (27.12.1967).

⁵⁸³ G, *USP* 3,248,379 (21.11.1962).

⁵⁸⁴ FBy, *BeP* 690,912 (15.12.1965).

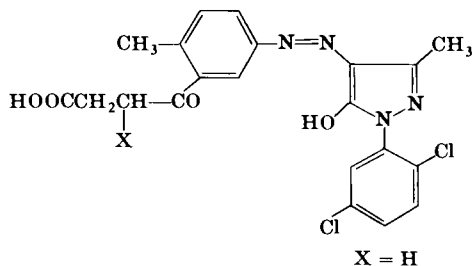


Ref. 583



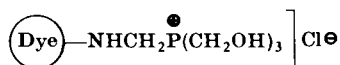
Ref. 584

Activated methylene groups in dyestuffs such as



can also be aminomethylated with formaldehyde and amines (e.g., dibutylamine, pyridine) to fiber-reactive derivatives [$X = -CH_2N(C_4H_9)_2$].⁵⁸⁵

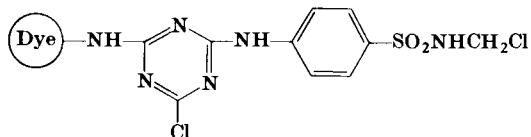
The tetrakis(hydroxymethyl)phosphonium salts, which are used as flame-protective agents, condense with amino dyestuffs, giving products which can be fixed on cellulosic or keratin fibers at room temperature by aftertreatment with ammonia.⁵⁸⁶



⁵⁸⁵ BASF, *FP* 1,262,441 (14.7.1959).

⁵⁸⁶ Albright and Wilson, Ltd., *BeP* 626,626 (29.12.1961).

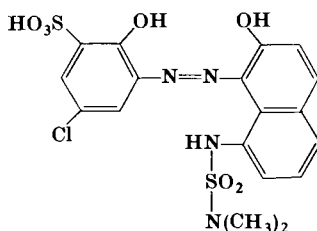
A Japanese patent application claims reactive dyestuffs with a chloro-*s*-triazine and an *N*-chloromethylsulfonamide group which can be applied in an alkaline medium.⁵⁸⁷



2. Fixation of Dyestuffs by Simultaneously Applied Aminoplast Pre-condensates

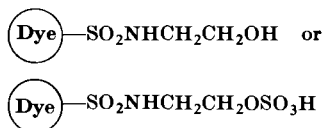
This principle gives dyeings with excellent wet-fastness properties which do not, however, always possess sufficient fastness to light. This disadvantage can be partly overcome by using particularly lightfast dyestuffs. Resacron dyestuffs of Ciba (1963), which are members of this group, have not attained much importance.

a. Dyestuffs with Groups which React with Formaldehyde Derivatives.
i. Dyestuffs containing acid amide groups. According to a patent of Ciba,⁵⁸⁸ blue-gray dyeings with good fastness to light and washing are obtained by padding cotton fabric with a solution consisting of the 1:2 chromium complex of the dimethylsulfamic amide dyestuff



highly methylated hexamethylolmelamine, and ammonium chloride, and subsequent heating for 6 minutes at 150°.

ii. Dyestuffs containing N-(β-hydroxyethyl)sulfonamide groups. Dyes of the type

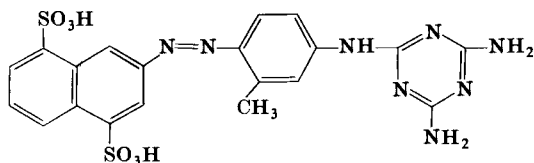


⁵⁸⁷ E. Kobayashi, *JP* 2,626/67 (26.12.1963).

⁵⁸⁸ CIBA, *BeP* 614,315 (24.2.1961).

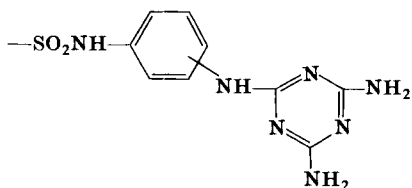
also give dyeings with very good wet-fastness properties at 150° with aminoplasts (e.g., tetramethylurea) and acid catalysts (NH₄Cl).⁵⁸⁹

iii. *Dyestuffs containing amino-s-triazine groups.* In the reaction, for example, of 1 mole of the dyestuff



with 10–100 moles of an aminoplast-former (urea, melamine, dicyanodiamide, etc.) and 20–600 moles of formaldehyde, a precondensate is formed which after etherification with a lower alcohol, such as methanol, is applied to cellulosic fibers from an aqueous solution or dispersion and is fixed in the presence of acid catalysts [(NH₄)₂SO₄, (NH₄)₂HPO₄, Zn(NO₃)₂, etc.], giving dyeings fast to washing and solvents and with a more or less marked creaseproof effect.⁵⁹⁰

In addition to Ciba, Bayer and ICI have also developed this field,⁵⁹¹ ICI particularly for metal-containing phthalocyanine dyestuffs with the partial structure



iv. *Dyestuffs of the phthalocyanine range containing sulfonic hydrazide groups.* Phthalocyanine dyes with sulfonic hydrazide groups react with methylol compounds. They can be fixed on the fiber, for example, with *N,N'*-dimethylol-glyoxal-monoureine and ammonium nitrate by heating for 8 minutes at 150°.⁵⁹²

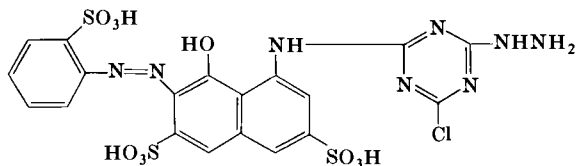
⁵⁸⁹ CIBA, *BeP* 619,191 (21.6.1961).

⁵⁹⁰ CIBA, *BeP* 576,192 (28.2.1958); 590,514 (6.5.1959); 592,257 (26.6.1959); 592,772 (10.7.1959).

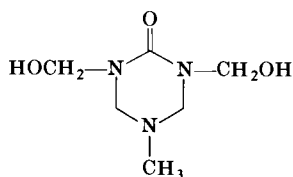
⁵⁹¹ ICI, *FP* 1,257,598 (27.5.1959).

⁵⁹² BASF, *DAS* 1,099,986 (3.10.1959).

v. *Dyestuffs containing hydrazino-s-triazine groups.* Hydrazino-s-triazine dyestuffs can be incorporated into aminoplast systems in a similar manner to that described above.⁵⁹³ For example, 20 parts of



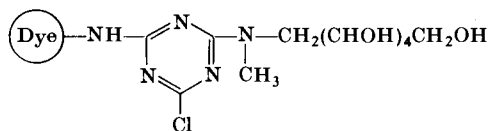
with 50 parts of 1,3-dimethylol-5-methylhexahydrotriazinone-(2)



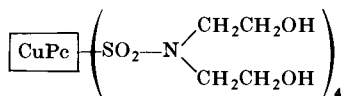
and 8 parts of $\text{NH}_4\text{H}_2\text{PO}_4$ give at 145° a red dyeing on cotton fabric with very good wet-fastness properties.

vi. *Acid dyestuffs containing amino groups.* A combination of acid dyes containing amino groups and a cyclic methylol system is claimed by Mitsubishi.⁵⁹⁴

vii. *Dyestuffs containing polyhydroxyalkyl groups.* Polyhydroxyalkyl-substituted dyes were developed almost simultaneously by ICI and Bayer. Suitable hydroxyalkyl groups are contained, for example, in diethanolamine residues, glucamine, or *N*-methylglucamine residues. These can be linked to the chromophore through chloro-s-triazine or chloropyrimidine groups, e.g.,⁵⁹⁵



through carbonyl or sulfonyl groups, e.g.,⁵⁹⁶



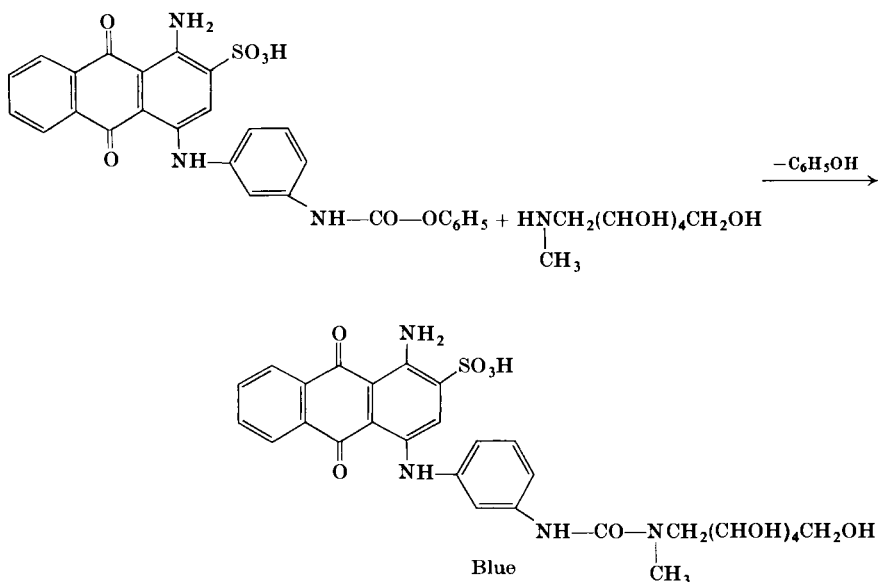
⁵⁹³ BASF, *BeP* 600,074; 600,075; 600,076 (13.2.1960).

⁵⁹⁴ MCI, *JP* 27,393/65 (22.7.1958).

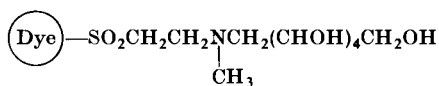
⁵⁹⁵ ICI, *BeP* 592,553 (2.7.1959); *BP* 906,140 (20.11.1959).

⁵⁹⁶ FBy, *DAS* 1,143,482 (16.10.1959); *BeP* 606,906 (5.8.1960); MCI, *JP* 5,969/64 (8.4.1961).

or through urea bridges.⁵⁹⁷



Suitable dyestuffs are also obtained by exchange of the mobile chlorine in β -chloroethyl sulfone dyes with the above-mentioned amines.⁵⁹⁸



Curing with aminoplast-formers (methylolmelamine or methylolurea derivatives) and acid catalysts gives dyeings with excellent wet-fastness properties and fastness to crocking, but with a fastness to light which is not always sufficient, particularly in bright red shades.

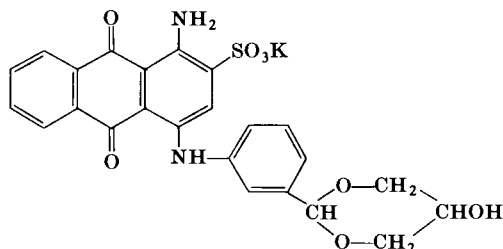
In this connection, mention must also be made of those dyestuffs which are linked through oxygen or nitrogen atoms to high-polymer compounds, such as cellulose ethers, water-soluble polysaccharides, pectins, or alginates, and which can also be fixed on the fiber together with urea- or melamine-formaldehyde derivatives.⁵⁹⁹

⁵⁹⁷ FBy, *BeP* 620,205; 620,206; 620,319 (19.7.1961).

⁵⁹⁸ ICI, *FP* 1,277,461 (20.11.1959).

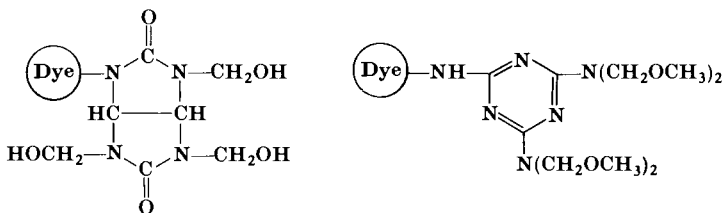
⁵⁹⁹ CIBA, *BeP* 610,709 (24.11.1960).

viii. *Dyestuffs containing aldehyde or acetal groups.* According to a process patented by BASF,⁶⁰⁰ cotton fabric is impregnated with water-soluble dyestuffs, such as the blue



and cured for several minutes at 140–170° together with, for example, *N,N'*-dimethylol-glyoxal-monoureine and zinc chloride, giving dyeings with a higher color strength than those obtained with corresponding dyestuffs without aldehyde (or acetal) groups.

The simultaneous condensation of dyestuffs containing groups able to react with aldehydes and of di- or polyaldehydes (glyoxal, terephthalaldehyde, mesitylenetri-aldehyde) in the presence of acid catalysts is to a certain extent a reversal of this principle.⁶⁰¹ Suitable dyestuffs contain, for example, the groups



ix. *Dyestuffs containing isothiuronium groups.* Isothiuronium-substituted dyestuffs together with resin-forming components and acid catalysts also give dyeings with good fastness to washing.⁶⁰²

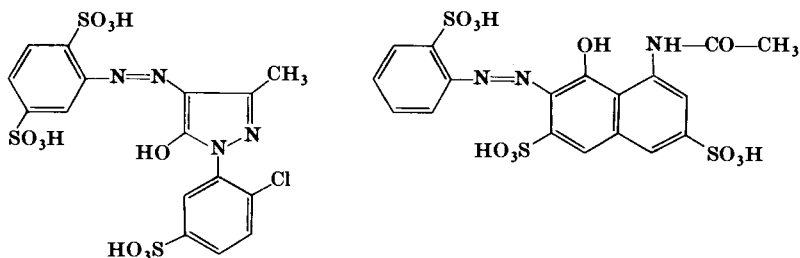
b. *Dyestuffs without Groups which React Specifically with Formaldehyde Derivatives.* It is interesting that normal acid dyestuffs without specific methylol-reactive groups can also be fixed by heat with water-soluble or water-dispersed aminoplast-formers and acid catalysts with good fastness to washing and chlorine on cellulosic fabric. Suitable dyestuffs are,

⁶⁰⁰ BASF, *GP* 1,140,897 (9.6.1960).

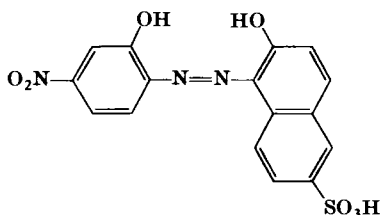
⁶⁰¹ BASF, *BeP* 618,888 (14.6.1961).

⁶⁰² ICI, *BP* 912,348 (12.5.1960); *FP* 1,294,458 (6.7.1960).

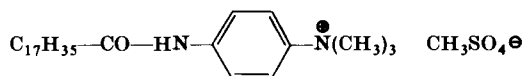
for example, the yellow and the red⁶⁰³



copper phthalocyanine tetrasulfonic acid⁶⁰⁴ or 1:2 chromium/cobalt complex dyes with at least one sulfonic group,⁶⁰⁵ e.g., the violet 1:2 chromium complex of

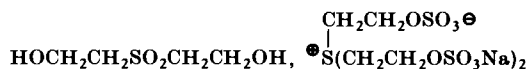


Pretreatment of the cellulosic fabric with cationic agents which improve the wet-fastness properties, such as



increases the fastness properties of such dyeings obtained from acid dyestuffs and formaldehyde precondensates.⁶⁰⁶

An improvement of the wet and dry wrinkle recovery angles of the resin finish obtained during dyeing is achieved by simultaneous application of alkaline-reactive crosslinking agents, e.g.,



and alkaline aftertreatment.⁶⁰⁷

⁶⁰³ Fran, *FP* 1,271,144 (26.7.1960); BASF, *FP* 1,345,370 (10.1.1962); S. M. Kirov, Leningrad Textile and Light Ind. Inst., *RP* 218,116 (15.4.1966).

⁶⁰⁴ CIBA, *BeP* 613,657 (9.2.1961).

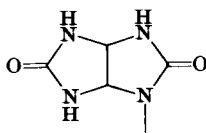
⁶⁰⁵ CIBA, *BeP* 614,314 (24.2.1961).

⁶⁰⁶ CIBA, *BeP* 632,096 (13.7.1962).

⁶⁰⁷ ICI, *BP* 993,663 (2.11.1962).

According to patents of Courtaulds,⁶⁰⁸ acid dyestuffs can be fixed on cellulosic fibers by heating together with formaldehyde, an ammonium salt, and magnesium chloride, i.e., an aminoplast precondensate is not indispensable.

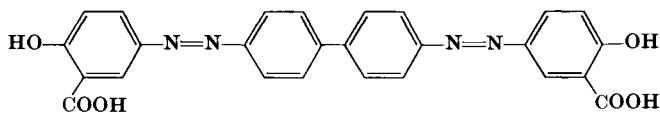
Finally, textiles made from a wide variety of fibers can also be dyed by incorporating dyestuffs with copolymerizable groups (e.g., $-\text{NH}-\text{CO}-\text{CH}=\text{CH}_2$),⁶⁰⁹ formaldehyde-reactive groups, (e.g.,⁶¹⁰



or reactive groups capable of nucleophilic substitution (e.g., 2,4-dichloro-*s*-triazinylamino groups)⁶¹¹ into polymers (vinyl polymers or polyurethanes) and by cross-linking the colored polymerization products obtained in this way on the substrate with methylol compounds.

F. OTHER REACTIVE GROUPS

Mention must be made of two types of "reactive dyes," the mechanism of which is not fully understood: on the one hand, cationic chromium(III) complexes of dyestuffs containing carboxyl groups, such as the yellow⁶¹²



and, on the other hand, systems produced from polymerizable monomers containing fiber-reactive groups and water-insoluble dyestuffs containing diazonium groups, e.g., the turquoise

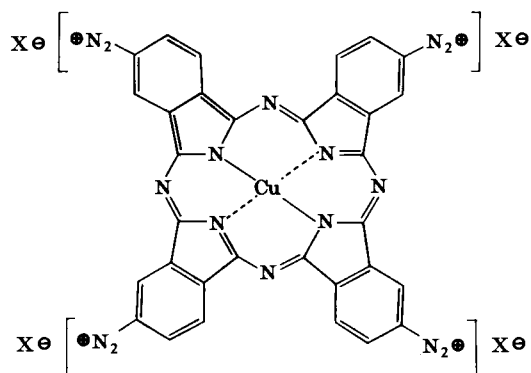
⁶⁰⁸ Courtaulds North America, *BP* 1,055,898; 1,055,899 (21.12.1962).

⁶⁰⁹ BASF, *BeP* 606,057 (12.7.1960); *GP* 1,143,480 (27.5.1961).

⁶¹⁰ BASF, *GP* 1,131,180 (28.2.1961); 1,140,171 (26.7.1961).

⁶¹¹ Seisan Kaihatsu Kagaku Kenkyujo, *JP* 18,629/65 (25.7.1963).

⁶¹² Ministerul, Industriei Petrolului si Chimiei, *FP* 1,272,808 (3.11.1960).



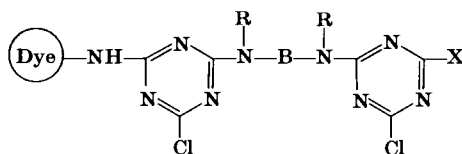
which act as polymerization catalysts for vinyl compounds.⁶¹³

G. DYESTUFFS CONTAINING SEVERAL REACTIVE GROUPS

In the various reactive systems, numerous examples have already been given in which several (the same or different) reactive groups are combined in a dyestuff molecule. Because of their thorough development and special technical importance in the Procion Supra brands of ICI, polyfunctional reactive dyestuffs with chlorotriazine residues will again be discussed comprehensively. Their advantage is the high fixation yield and therefore the small proportion of unfixed dye to be removed during washing. A disadvantage is the "ballast" at the chromophore which reduces the molar color strength.

1. *Dyestuffs Containing several Chloro-s-triazinylamino Groups*

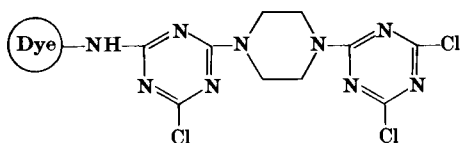
a. Chloro-s-triazinylamino Residues Linked through Uncolored Bridge Members as Reactive Groups. In 1961, ICI developed dyestuffs of the type



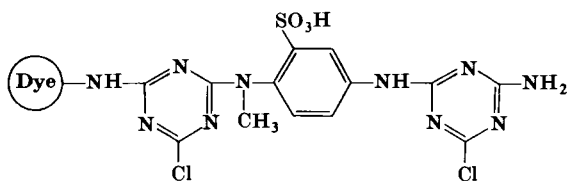
B = bridge link; X = -Cl or amino group; R = H, alkyl

⁶¹³ Dainichiseika Industry Co., JP 1,081/68 (10.3.1961); S. Horiguchi, *J. Soc. Org. Syn. Chem. Japan* **23**, No. 10, 893-899 (1965).

e.g.,

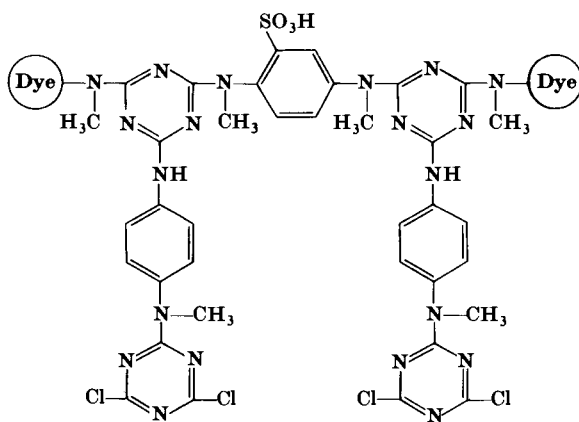


Ref. 614



Ref. 615

or



Ref. 616

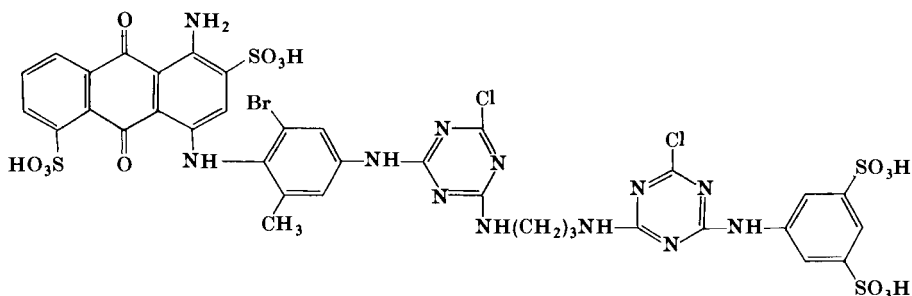
Later, they claimed anthraquinone dyestuffs, such as⁶¹⁷

⁶¹⁴ ICI, *BP* 1,015,932 (24.5.1961).

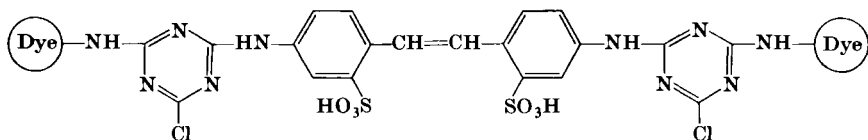
⁶¹⁵ ICI, *FP* 1,329,106 (24.5.1961).

⁶¹⁶ ICI, *BP* 1,017,271 (29.5.1961).

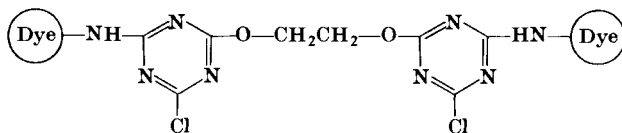
⁶¹⁷ ICI, *GP* 1,902,109 (16.1.1968).



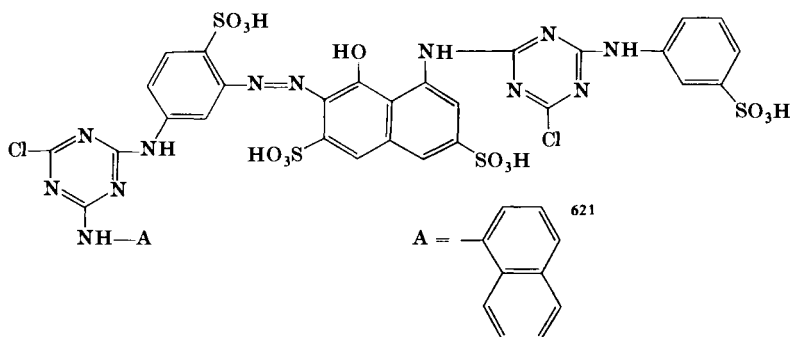
Other firms also took out patents in this sector, e.g., Nippon Kayaku for dyestuffs with two chlorotriazine residues linked through 4,4'-diaminostilbene-2,2'-disulfonic acid⁶¹⁸



or Acna for the reactive bridge link.⁶¹⁹



b. Dyestuffs with Several Chlorotriazinylamino Groups on the Chromophore. Procion Supra dyestuffs, which because of their two reactive groups give high fixation yields in textile printing, are synthesized on this principle. The brilliant red combination⁶²⁰



⁶¹⁸ Nippon Kayaku Co., JP 21,029/67 (9.12.1963); 15,276/66 (18.12.1963).

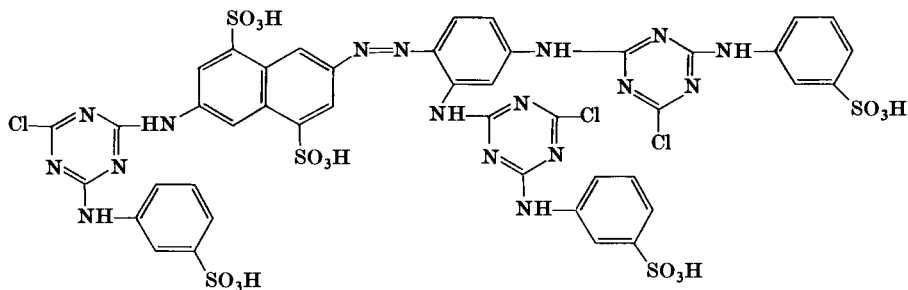
⁶¹⁹ Acna, USP 3,454,551 (5.5.1963).

⁶²⁰ ICI, FP 1,472,770 (29.3.1965).

⁶²¹ ICI, BeP 717,892 (10.7.1967); EGP 68,581 (18.6.1968).

is a typical example.

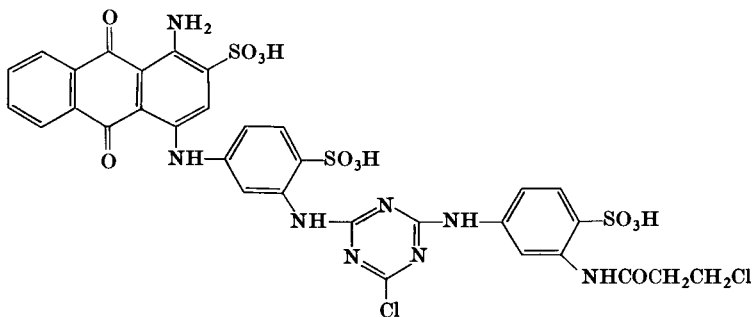
Of further types⁶²² a trifunctional yellow may be mentioned.



At a very early date, Hodogaya also claimed dyes of this type.⁶²³

2. Dyestuffs with a Monochloro-s-triazine and Another Reactive Group

a. Monochloro-s-triazine Groups as Bridge between Dyestuff and Other Reactive Groups. In 1959, Cassella was the first firm to recognize the value of dyestuffs which combine two different reactive groups in a molecule⁶²⁴ and claimed the linking of an amino dyestuff with an amine containing reactive group through the residue of a halogenated azine (e.g., cyanuric chloride, tri- and tetrachloropyrimidine, trichloropurine).^{533a, 624}

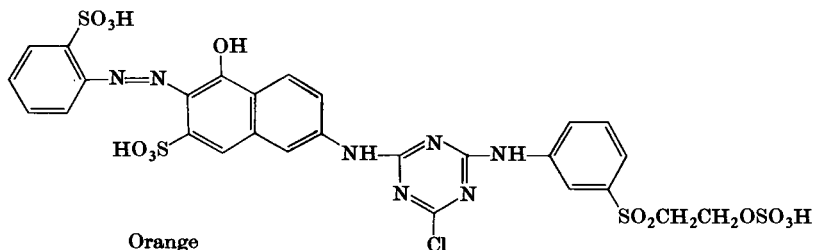


⁶²² ICI, *FP* 1,472,769 (29.3.1965); *EGP* 56,574 (3.9.1965); 63,826 (1.8.1966).

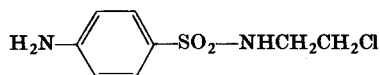
⁶²³ HCC, *JP* 5,181/64 (29.1.1962).

⁶²⁴ CFM, *FP* 1,262,875 (11.7.1959).

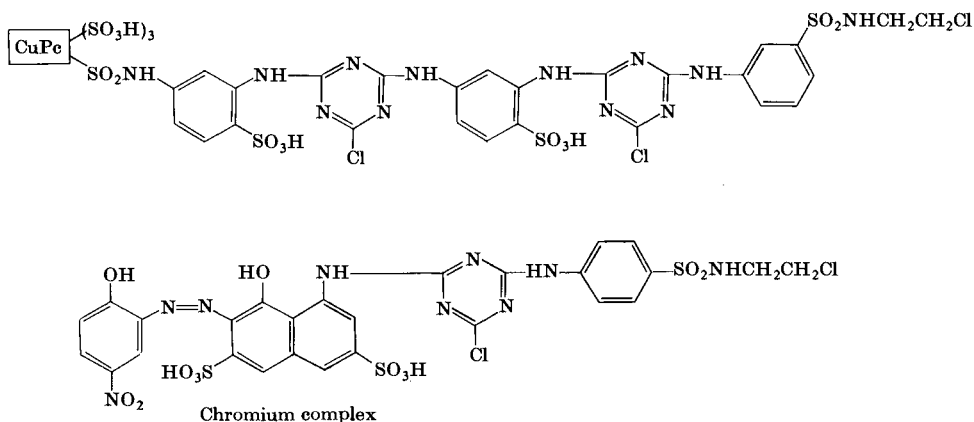
Patents of Hoechst and of ICI concern, in particular, amines with the vinyl sulfone group (or their derivatives).^{625, 626}



This type of polyfunctional reactive dyes was subsequently developed thoroughly by ICI, who describe in eight patent applications^{190, 191, 627} the combination of the halo-s-triazine (or halopyrimidine) group with *N*-(β-chloroethyl)sulfanilamides, such as



bound to various chromophores.

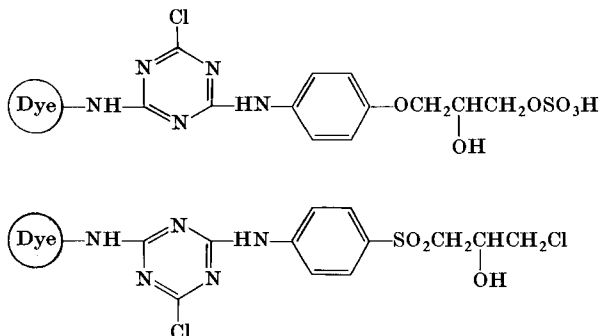


⁶²⁵ FH, *BeP* 617,323 (6.5.1961).

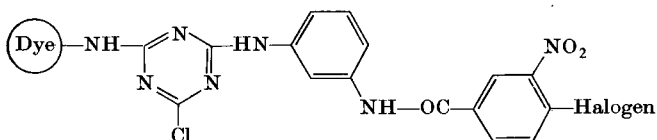
⁶²⁶ ICI, *FP* 1,534,280 (15.8.1966).

⁶²⁷ ICI, *FP* 1,468,386 (16.2.1965); 1,472,512 (23.3.1965).

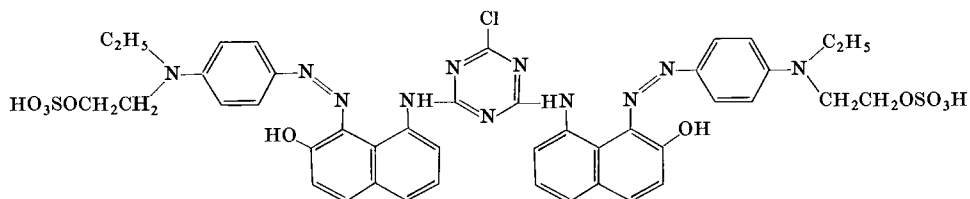
Further patents of ICI²³¹ concern amines with halohydrin or epoxide reactive groups, e.g.,



In addition to the monochloro-*s*-triazine bridge, aromatic compounds with mobile anionic groups are also suitable as a second reactive system.⁶²⁸



*b. Dyestuffs which Contain Independently of Each Other a Monochloro-*s*-triazine and Another Reactive Group.* In addition to difunctional polyamide dyestuffs of ICI,^{190, 191} special mention must be made of a patent application of BASF in 1957, in which dyestuffs free from sulfonic acid groups, such as the violet



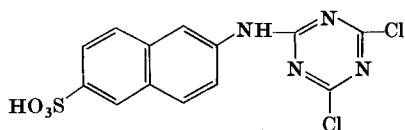
are described.⁶²⁹

⁶²⁸ K. Matsui and E. Kobayashi, *JP* 807/68 (5.3.1964); K. Matsui, *JP* 8,942/68 (13.3.1964).

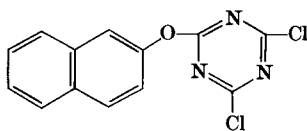
⁶²⁹ BASF, *DAS* 1,089,359 (11.9.1957).

III. Dyestuffs together with Separately Used Reactive Components

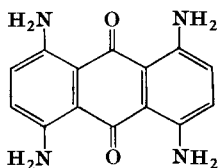
The principle of linking dyestuffs containing nucleophilically reactive groups (e.g., $-\text{NH}_2$, $>\text{NH}$, $-\text{OH}$, $-\text{SH}$) with the likewise nucleophilic hydroxyl groups (or anions) of cellulose by covalent bonds through polyfunctional reactive components was first developed by ICI for dyestuffs containing amino groups and for cross-linking agents, such as⁶³⁰



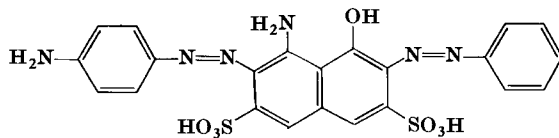
or⁶³¹



In this connection, water-insoluble dyestuffs, such as the blue

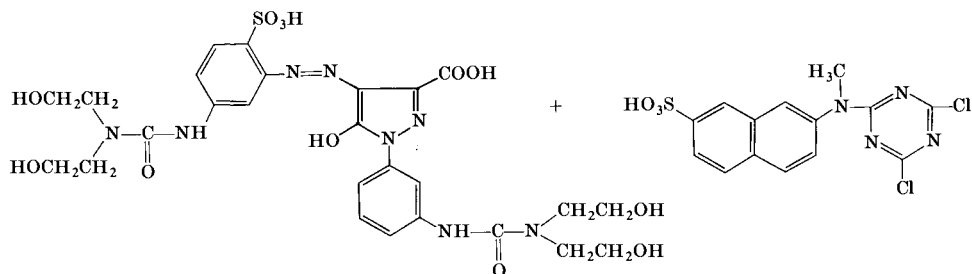


are particularly suitable for dyeing and printing on synthetic polyamide fibers and wool,⁶³⁰ while for cellulosic fibers water-soluble dyestuffs, such as Naphthalene Dark Green A



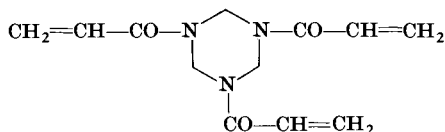
⁶³⁰ ICI, *BeP* 562,593 (21.11.1956); *DAS* 1,059,398; 1,068,661 (21.11.1956).

are given preference.^{525, 631} Dyestuffs containing nucleophilic hydroxy-alkyl groups were also subsequently bound to cellulose in this way.⁶³²



In these first "two-component systems" there was one basic disadvantage common to all: because of the too low affinity of the polyfunctional fixation components they were unsuitable for dyeing from a long liquor and could be used only for the pad-dyeing and printing of cellulosic materials. Moreover, a large amount of dichloro-*s*-triazine cross-linking agent in relation to the dyestuff must be used, so that sufficiently deep shades can be obtained despite the losses due to hydrolysis. It is also a disadvantage that by substitution of the first chlorine atom the remaining chlorine is inactivated, i.e., that the two chlorine atoms required for the linking reaction show very different reactivities.

During the following period, practically all the known reactive groups in difunctional and polyfunctional arrangement were tested as bridge links for the dyestuff-fiber bond.⁶³³ These systems have already been partly described under the respective carrier systems. To give a clearer picture the most important types may be mentioned again with examples, 1,3,5-triacryloylhexahydro-*s*-triazine (triacryloformal),



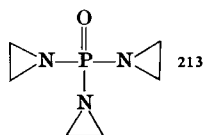
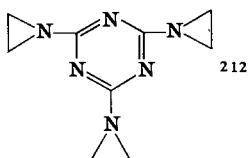
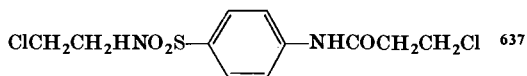
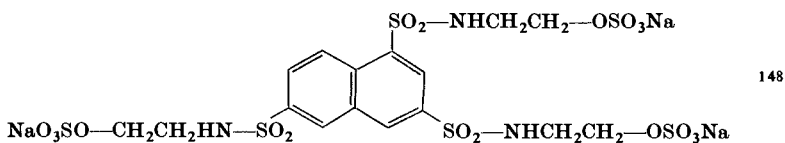
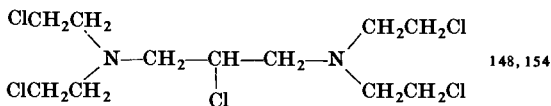
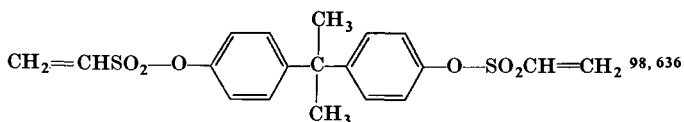
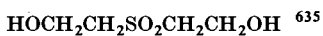
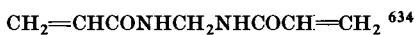
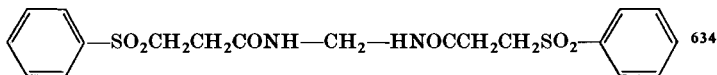
which has attained technical importance in the Basazol dyestuffs of BASF, and its derivatives being treated separately at the end.

⁶³¹ ICI, *DAS* 1,058,016 (23.10.1957).

⁶³² FBy, *BeP* 639,476 (2.11.1962).

⁶³³ G. Lützel, *Angew. Chem.* **77**, 308-313 (1965).

Examples of polyfunctional linking agents are listed:

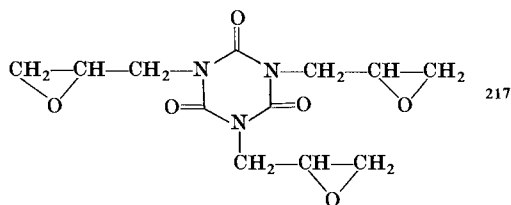
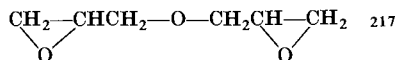
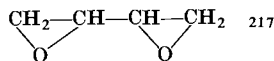
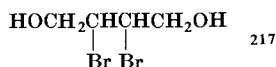


⁶³⁴ BASF, *DAS* 1,155 088 (2.11.1960); *BeP* 630,085 (28.3.1962); *BP* 932,080 (16.1.1962); *BeP* 631,235 (18.4.1963).

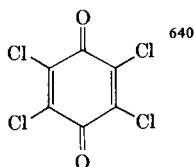
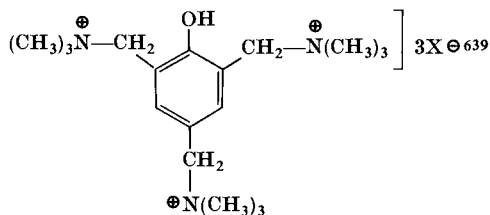
⁶³⁵ W. Saur, Dissertation ETH Zürich, 1966 (Prof. Zollinger); H. U. Rudolf, Dissertation ETH Zürich, 1966 (Prof. Zollinger); BASF, *BeP* 622,341 (13.9.1961).

⁶³⁶ BASF, *BeP* 614,346 (23.2.1961).

⁶³⁷ BASF, *FP* 1,359,997 (21.4.1962).



Polyglycidyl ether of sorbite⁶³⁸



BASF devoted particular attention to the problem of binding dye-stuffs to cellulose through bridge links, and in 1960 recognized the special value of triacryloformal (Fixing Agent P) as a linking agent.⁶⁴¹ This product is easily obtained industrially from acrylonitrile, para-formaldehyde, and sulfuric acid by a process discovered by Ballauf and Wegler in Farbenfabriken Bayer.⁶⁴²

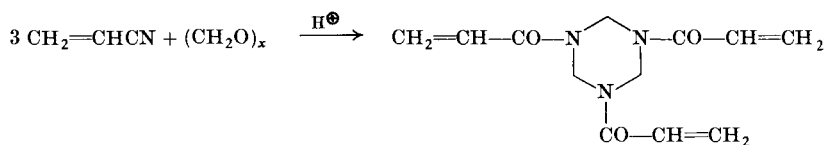
⁶³⁸ DuP, *USP* 3,044,843 (13.5.1959).

⁶³⁹ Deutsche Akademie der Wissenschaften, *FP* 1,402,211 (15.6.1964).

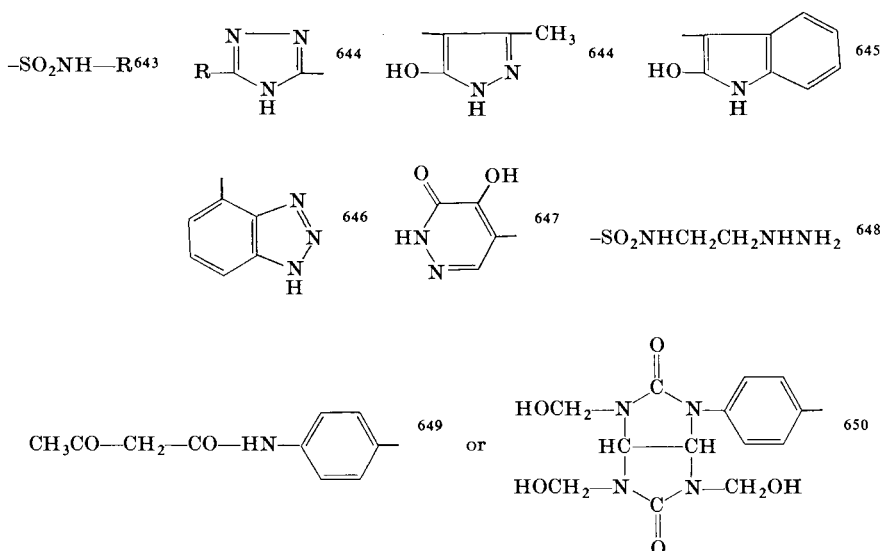
⁶⁴⁰ S. M. Kirov, Leningrad Textile and Light Industry, *RP* 218,807 (31.3.1967).

⁶⁴¹ BASF, *BeP* 609,825 (2.11.1960).

⁶⁴² FBy, *GP* 859,170 (22.3.1942).



With simple, water-soluble dyestuffs containing nucleophilically reactive groups such as



triacryloformal gives fixation yields of about 90%, calculated on the dyestuff used, when steaming is carried out in the presence of alkalis.⁶¹⁷ The advantage of this reactive component over dichloro-*s*-triazine cross-linking agents is that the acryloyl groups remain constant in their reactivity even after partial reaction, and also that partly hydrolyzed bridge links are still able to react with further triacryloformal.⁶³³

⁶⁴³ BASF, *BeP* 630,493 (3.4.1962); *FP* 1,359,470 (28.4.1962); *BeP* 662,774 (21.4.1964); *FP* 1,437,930 (24.6.1964); *BeP* 671,584 (29.10.1964); 621,896 (30.8.1961).

⁶⁴⁴ BASF, *BeP* 627,761 (31.1.1962); 631,586 (26.4.1962).

⁶⁴⁵ BASF, *FP* 1,361,694 (30.6.1962).

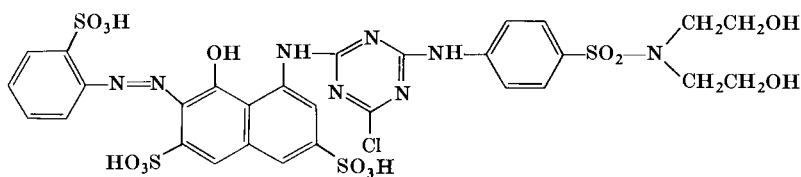
⁶⁴⁶ BASF, *FP* 1,368,650 (11.9.1962).

⁶⁴⁷ BASF, *GP* 1,231,368 (7.3.1964).

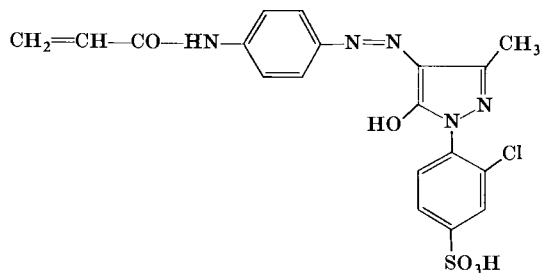
⁶⁴⁸ BASF, *BeP* 613,989 (16.2.1961).

⁶⁴⁹ BASF, *FP* 1,458,006 (17.12.1964).

⁶⁵⁰ BASF, *DAS* 1,153,839 (11.6.1959).

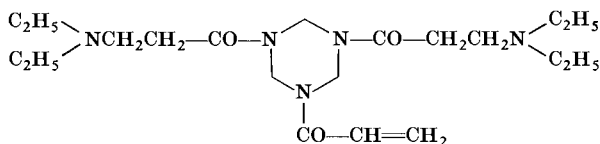


The copolymerization of triacryloformal with dyestuffs such as

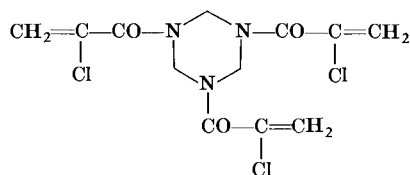


on the fabric in the presence of catalysts is also claimed.⁶⁵⁴

In addition to triacryloformal, BASF examined a large number of similar trifunctional hexahydro-*s*-triazine derivatives,⁶³³ of which the more water-soluble addition products of secondary amines, in particular, have attained importance.^{160, 644, 655}



They react by substitution of the β -activated tertiary amino groups likewise with cellulose and dyestuffs of the above-mentioned type. Other cross-linking agents of this type are, for example,

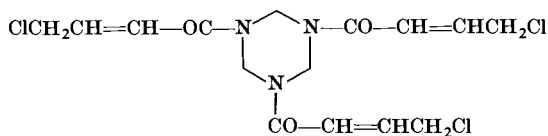


Ref. 656

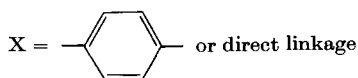
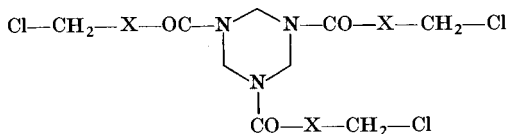
⁶⁵⁴ BASF, *GP* 1,139,093 (22.7.1961).

⁶⁵⁵ BASF, *GP* 1,259,897 (28.10.1965); *BeP* 624,513 (8.11.1961).

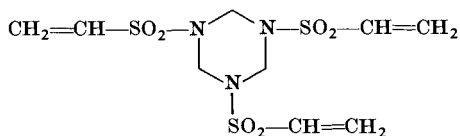
⁶⁵⁶ BASF, *BeP* 631,237 (19.4.1962).



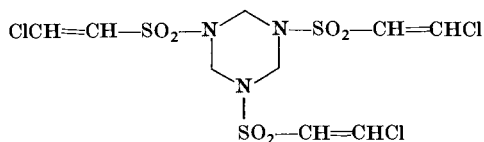
Ref. 253



Ref. 657



Ref. 97



Ref. 97a

IV. Mobile Groups

The atoms or groups ("mobile groups") split off in the nucleophilic reaction of the cellulose anions with the reactive groups have already been described under the individual carrier systems. The following summary may be given:

From a technical standpoint, by far the most important mobile groups are

—Cl (e.g., mono- and dichloro-*s*-triazinylamino dyestuffs; trichloropyrimidylamino dyestuffs; 2,3-dichloroquinoxaline-6-carbonylamino dyestuffs; 4,5-dichloropyridazone dyestuffs; 1,4-dichlorophthalazine-6-carbonylamino dyestuffs; 2-chlorobenzothiazole dyestuffs)

⁶⁵⁷ BASF, *BeP* 631,512 (26.4.1962).


$-\text{OSO}_3\text{H}$, $(-\text{SSO}_3\text{H})$ (e.g., β -sulfatoethyl sulfone dyestuffs, β -thio-sulfatoethyl sulfone dyestuffs).

In addition, more strongly electronegative mobile groups have recently gained increasing importance^{379, 658}:

- $-\text{N}^+(\text{CH}_3)_3]\text{Cl}^-$ (on the *s*-triazine system) (and other quaternary ammonium groups)
- $-\text{SO}_2\text{CH}_3$, $-\text{SO}_2\text{C}_2\text{H}_5$ (in the 2-position on the pyrimidine or benzothiazole system)
- $-\text{F}$ (on the pyrimidine system)

They permit the synthesis of highly reactive, rapidly fixed systems, or systems dyed at 30–40° from a long liquor, whose activation disappears to a large extent together with the mobile group, so that the dyestuff-fiber bond is much less susceptible to nucleophilic attack than the starting system, i.e., the dyeings possess excellent wet-fastness properties.

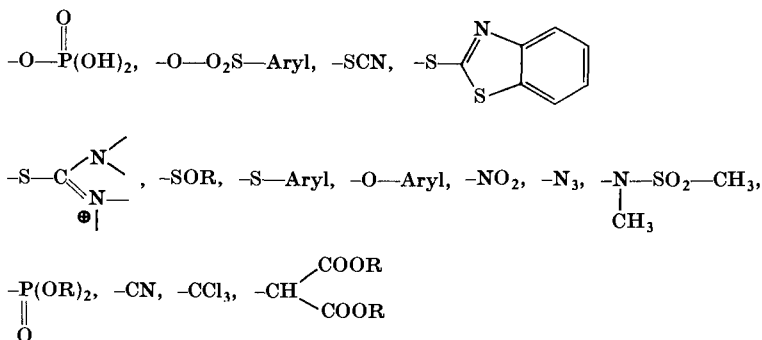
Here may also be mentioned (used technically):

$-\text{SO}_2$ - (on the β -propionylamino residue)

$-\text{Br}$ (in the α -bromoacryloyl residue) especially for wool

$-\text{SO}_3\text{H}$ (on the *s*-triazine system)

None of the remaining mobile groups, listed below, has attained any practical importance⁶⁵⁸:



⁶⁵⁸ E. Siegel, *Chimia (Aarau)* Suppl., pp. 100–114 (1968).

CHAPTER II

REACTIVE DYES: CHROMOPHORE SYSTEMS

Karl-Heinz Schünderhütte

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I. Synthesis of Reactive Dyes

With the discovery of reactive dyestuffs it became possible to dye numerous textile fibers with dyes containing practically any desired chromophore system. From the large number of suggested compounds, easily the greatest economic importance has been achieved, up to the present, by azo, anthraquinone, and phthalocyanine derivatives. Dyestuffs of these groups form the hard core of all commercial reactive dyestuff ranges. The widest range of shades is covered by the azo compounds, which comprise practically every shade from greenish yellow to black. Brilliant blue and green shades with high fastness to light are the main field of anthraquinone derivatives, while sulfonic acids of copper and nickel phthalocyanine are used to produce turquoise shades, and in combination with yellow dyestuffs to synthesize bright green dyes.

The type of combination between reactive component and dyestuff depends largely on the nature of the reactive component, to which the

dyestuff is generally adapted. In the most important reactive dyes combination is achieved by the following methods:

(1) By condensation of dyestuffs or dyestuff intermediates containing amino groups with polyfunctional reactive heterocycles or with carbonyl or sulfonyl halides containing further groups capable of addition or substitution. Examples are the condensation of aminoazo compounds with cyanuric chloride,¹ halopyrimidines,^{1a} acryloyl chloride,² or dichloroquinoxaline carbonyl chloride.³

(2) By the synthesis of dyestuffs from components which contain reactive groups. These include, for example, azo dyestuffs, which are obtained by coupling of diazonium compounds from β -sulfoethyl-sulfone-substituted aromatic amines⁴ or from diazotized 6-amino-2-chlorobenzothiazole.⁵

(3) By *C*-substitutions of the preformed dyestuff with the introduction of a reactive group, e.g., by condensation with "reactive" *N*-methylol-carbamides.⁶

(4) Through sulfamide, sulfimide, or heterocyclic NH groups. This linkage can be achieved either by changing certain substituents of the dyestuffs, e.g., by condensation of sulfonyl chlorides with aminoethanol-sulfate⁷ or, as in the case of the "multi-component reactive dyes," in the dyeing process on the fiber, e.g., as in dyeing with dyestuffs simultaneously containing sulfamide groups with triacryloformal.⁸

Since these different linkages between reactive component and dyestuffs require special dyestuff syntheses, these are described under the respective dyestuff types.

In the formulas used in the following section, $\text{---}\textcircled{\text{R}}$ represents a reactive component or the essential part of a reactive group.

The references cited need not necessarily be the first publications, and they do not indicate the legal patent position.

¹ ICI, *BP* 785,120; 785,222 (29.11.1954).

^{1a} ICI, *DAS* 1,075,245 (30.1.1957); BASF, *FR* 1,194,043 (5.4.1957); S, *DAS* 1,258,526 (29.11.1957).

² BASF, *DAS* 1,056,580 (14.12.1957).

³ FBy, *DAS* 1,186,160 (7.2.1961).

⁴ J. Heyna, in "Recent Progress in the Chemistry of Natural and Synthetic Colouring Matters and Related Fields" (T. S. Gore *et al.*, eds.), p. 473. Academic Press, New York, 1962.

⁵ Fran, *FP* 1,290,839 (26.12.1960).

⁶ S, *USP* 3,158,597 (24.6.1960).

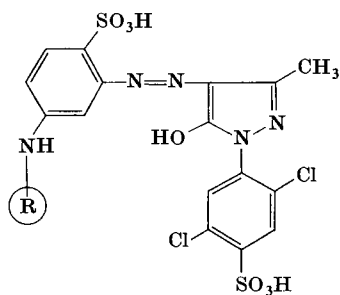
⁷ FBy, *FP* 1,293,555 (29.3.1960).

⁸ H. R. Hensel and G. Lützel, *Angew. Chem.* **77**, 303 (1965).

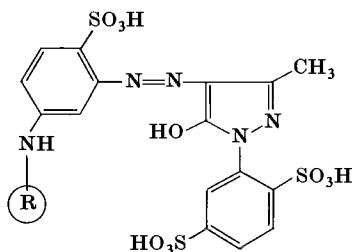
II. Azo Dyes

A. COUPLING PRODUCTS OF PYRAZOLONES AND OTHER CYCLIC OR OPEN-CHAIN ENOLS AND ENAMINES

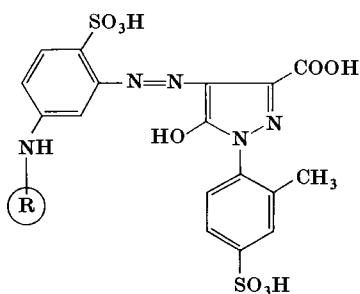
In the production of greenish yellow to golden yellow reactive dyes, coupling products of 1-aryl-5-pyrazolones or 1-aryl-5-aminopyrazoles are mainly used. Substituents in the 2' or 2',6'-positions of the aryl moiety give brilliant greenish yellow shades which are obtained, in particular, where the diazonium component also carries a substituent *ortho* to the diazonium group. Important dyes of this type with Cl, sulfonic acid, or methyl groups in the 2'-position of the aryl moiety are, for example,⁹ (I)–(IV).



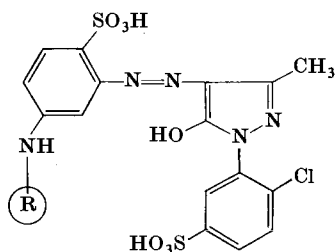
(I)



(II)



(III)

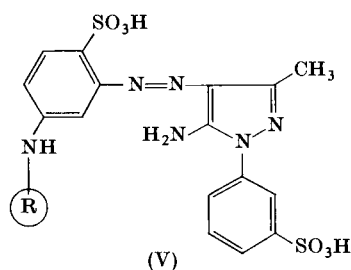


(IV)

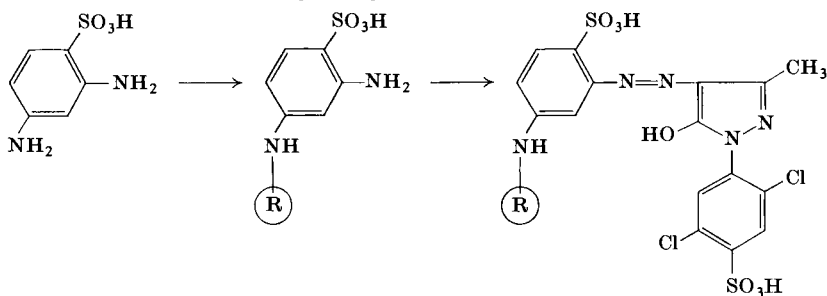
Similar shades are possessed by analogous coupling products of 1-aryl-5-aminopyrazoles even without *o'*-substituents, such as¹⁰ (V).

⁹ CIBA, *DAS* 1,112,225 (14.9.1956); S, *DAS* 1,215,842 (21.4.1961); FBy, *DAS* 1,191,059 (7.2.1961); S, *BP* 916,094 (28.5.1958).

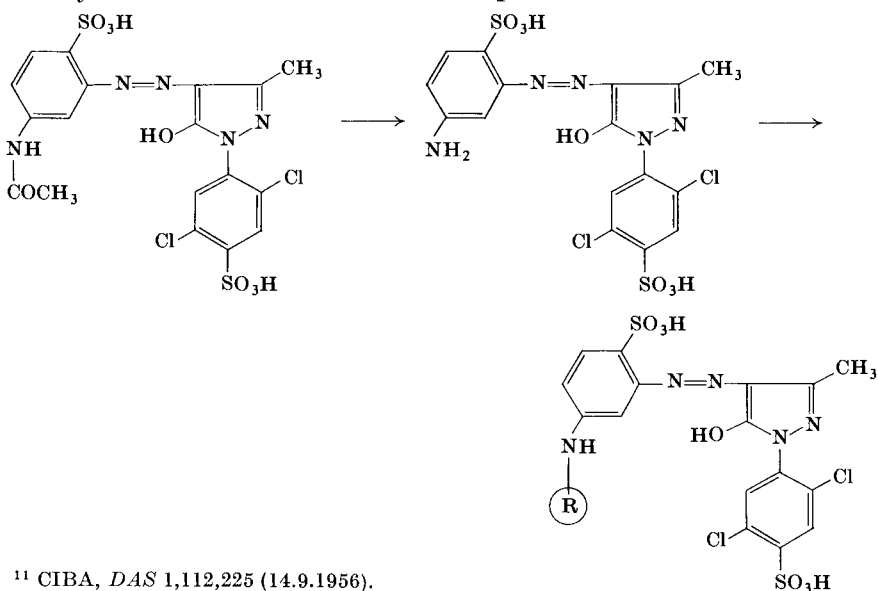
¹⁰ FBy, *BeP* 708,454 (23.12.1966); CIBA, *FP* 1,293,764 (9.6.1960).



These dyestuffs are produced either by a primary condensation of the reactive component with 1,3-diaminobenzene-4-sulfonic acid, subsequent diazotization and coupling,¹¹ e.g.,



or by synthesis of the azo compound from 1-acetylamino-3-amino-benzene-4-sulfonic acid and hydrolysis to the aminoazo compound which is finally condensed with the reactive component.¹²

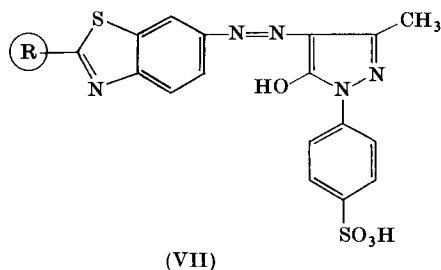
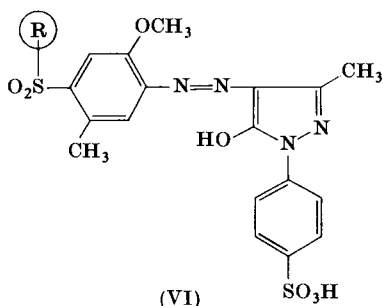


¹¹ CIBA, *DAS* 1,112,225 (14.9.1956).

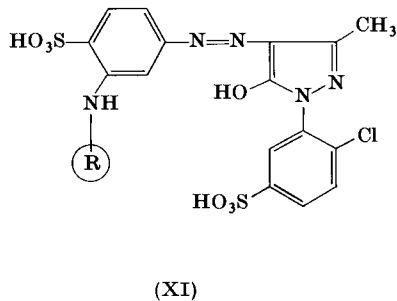
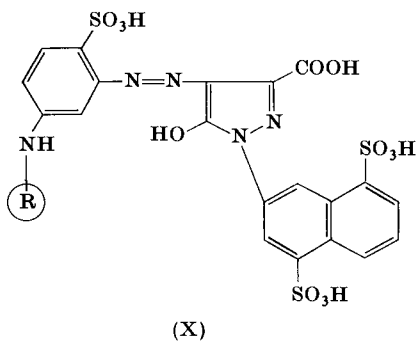
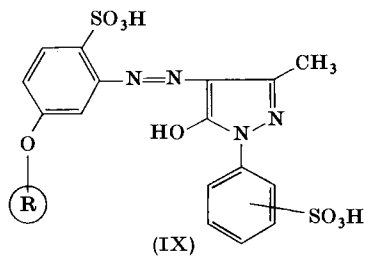
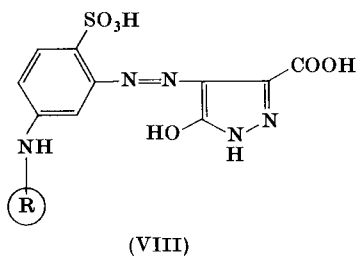
¹² DuP, *USP* 3,184,284 (11.4.1963).

The first method is to be preferred in the case of heterocycles, which permit a definite selective condensation with the sterically unhindered and more basic amino group of 1,3-diaminobenzene-4-sulfonic acid.

The synthesis of yellow dyes from diazonium compounds containing reactive groups is also based on this principle, as in the following examples¹³:



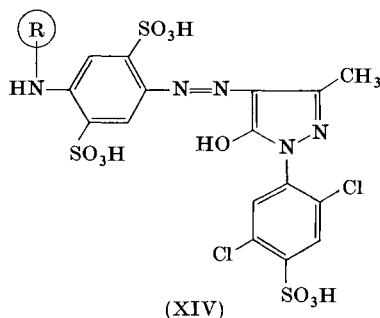
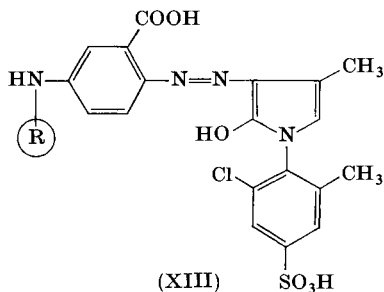
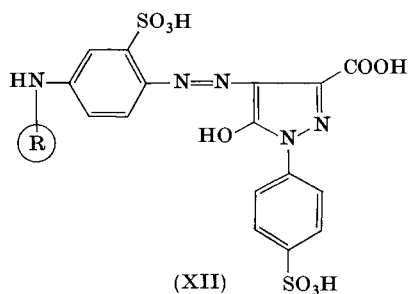
Numerous variations of this type are described, both in the diazonium compound and also in the pyrazole derivative. The following dyestuffs are mentioned as examples¹⁴:



¹³ FH, DAS 1,150,163 (13.2.1960).

¹⁴ CIBA, FP 1,207,925 (30.7.1957); DP 6,606,451 (12.5.1965); BASF, BeP 629,647 (17.3.1962).

Yellow dyestuffs with redder shades are obtained by using derivatives of 1,4-diaminobenzene as the diazonium compound.¹⁵



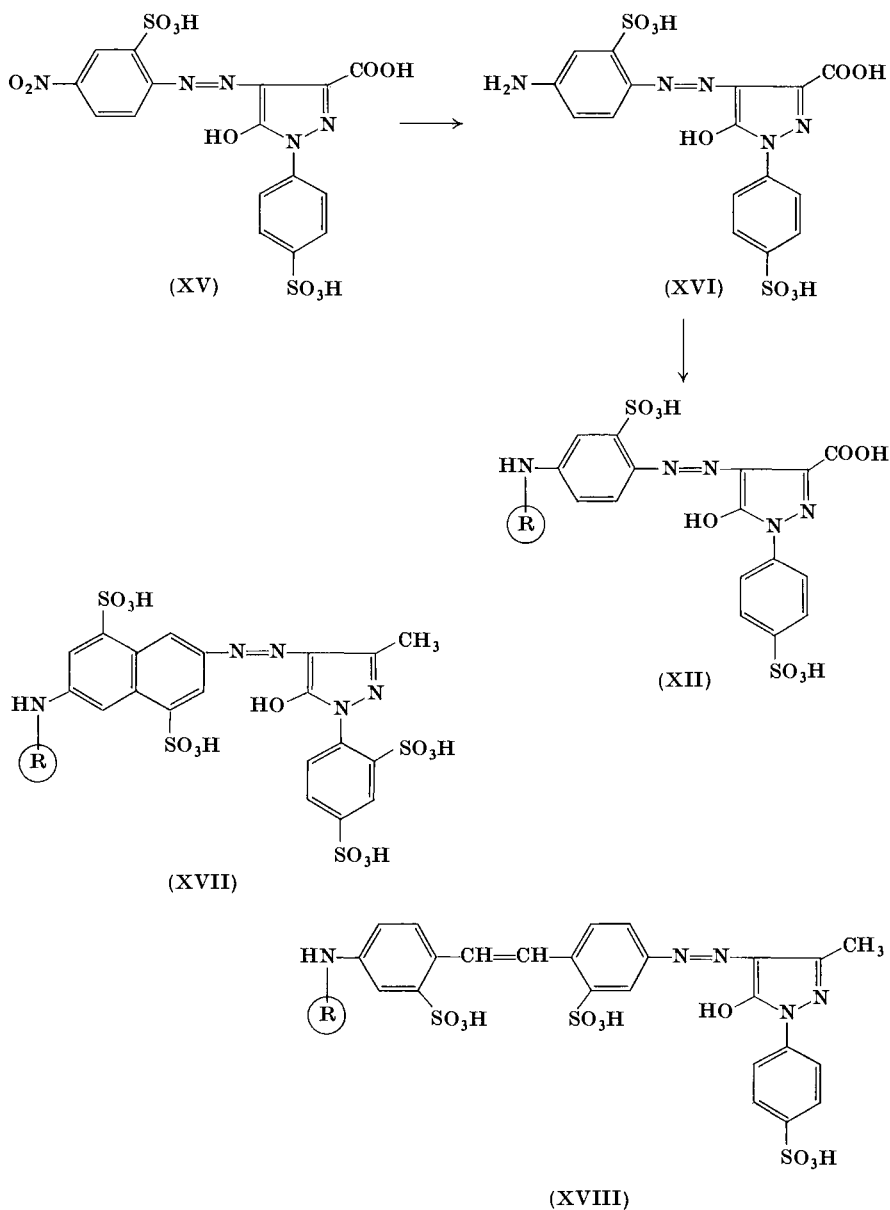
These dyestuffs are synthesized in a similar manner to those of the 1,3-diaminobenzene range.

A method of synthesis of major technical importance starts from the coupling product of 4-nitro-aniline-2-sulfonic acid, which is reduced to the aminoazo dyestuff and condensed, finally, with the reactive component.¹⁶ Moreover, this procedure is particularly interesting for dyestuffs of the naphthalene and stilbene series, where selective acylations are generally more difficult to achieve and the nitro compounds are commercially available.¹⁷

¹⁵ BASF, *BeP* 583,050 (30.9.1958); CIBA, *BeP* 666,009 (29.6.1964); *FP* 89,023/1,447,468 (13.10.1964).

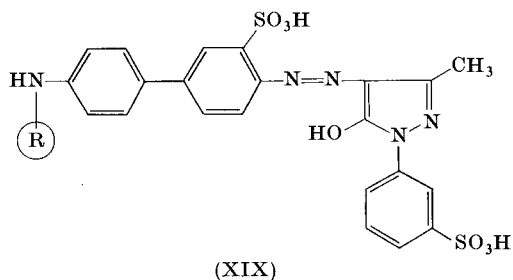
¹⁶ FBy, *DAS* 1,191,059 (7.2.1961); ICI, *DAS* 1,066,302 (25.11.1955).

¹⁷ S, *BeP* 598,831 (20.1.1960); ICI, *FP* 1,198,036 (25.2.1957).

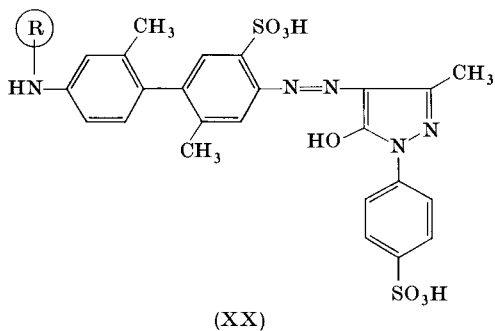


Coupling products of the monoacylated 4,4'-diaminodiphenyl-3-sulfonic acids likewise give golden yellow reactive dyes.¹⁸

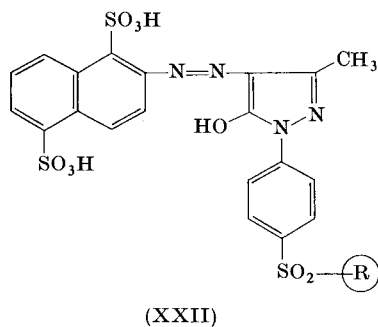
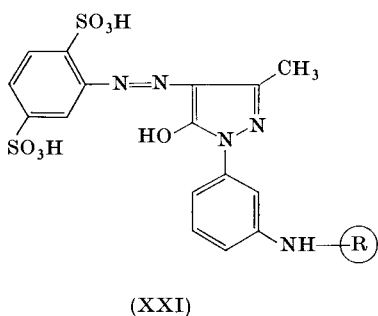
¹⁸ S, *BeP* 683,619 (16.7.1965); *FP* 1,233,348 (20.8.1958).



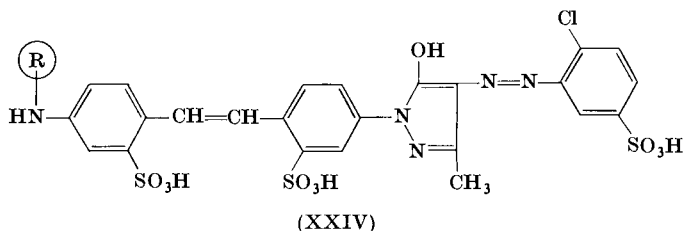
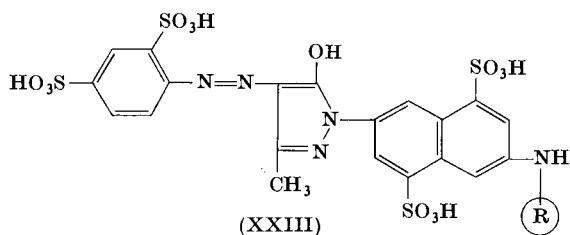
or



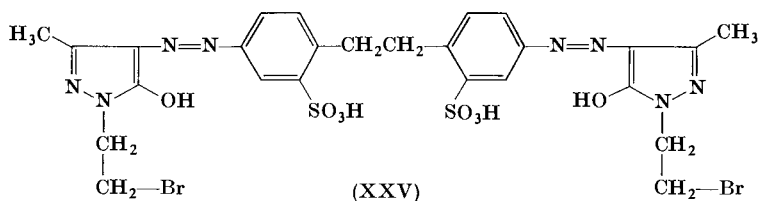
A further group of pyrazolone dyestuffs is obtained in which it is not the diazonium component, as described in the above-mentioned cases, but the pyrazolone component which carries the reactive group. Because of the larger number of possible diazonium compounds, very many different reactive dyes can also be synthesized in this case,¹⁹ e.g.,



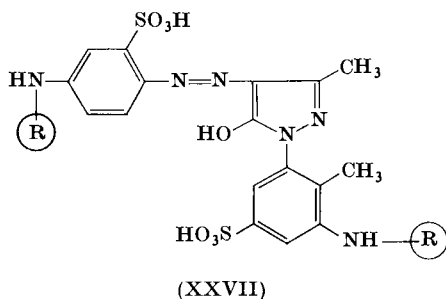
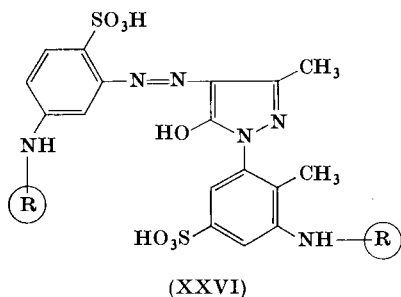
¹⁹ ICI, DAS 1,066,302 (25.11.1955); FH, BeP 663,540 (6.5.1964); FBy, DAS 1,243,801 (18.4.1963); S, BeP 613,757 (17.2.1961).



Interesting dyestuffs of this type are available in the coupling products of 1- β -bromoethyl-3-methyl-5-pyrazolone,



in which the pyrazolone ring itself contributes to the reactivity.²⁰ Reactive dyes containing two or more reactive groups in the molecule have recently become technically interesting, also with use of halogen-containing heterocycles. The dyes can also be obtained by combination of both methods of synthesis previously described, i.e., reactive groups in diazonium and coupling components.²¹

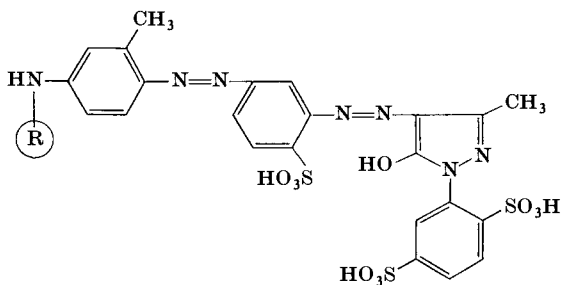


²⁰ FBy, *DAS* 1,126,544 (31.1.1959).

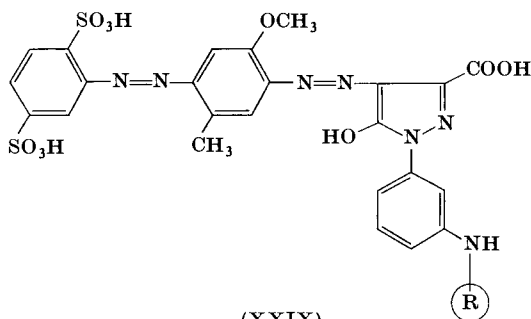
²¹ ICI, *DAS* 1,469,778 (7.4.1964).

The reactive groups contained in the dyestuff molecule may be the same or different. Dyes of this type attain particularly high fixation yields in the reaction with the fiber.

On the whole, the importance of disazo dyestuffs in the azopyrazole field is much less than that of monoazo dyestuffs; *p*- and *m*-disazo compounds are nevertheless described.²²

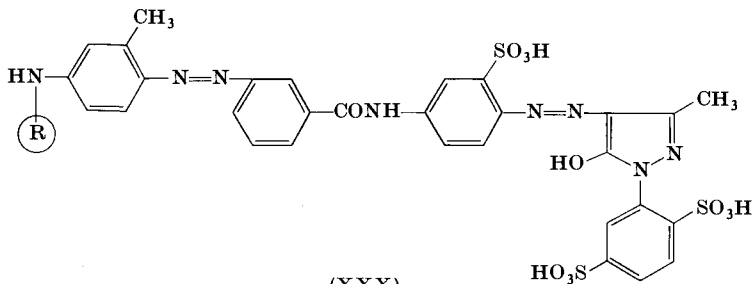


(XXVIII)



(XXIX)

Separation of the two azo groups, e.g., by a carbamide group as shown in the following example, has a beneficial influence on the properties of the dyestuffs.²³

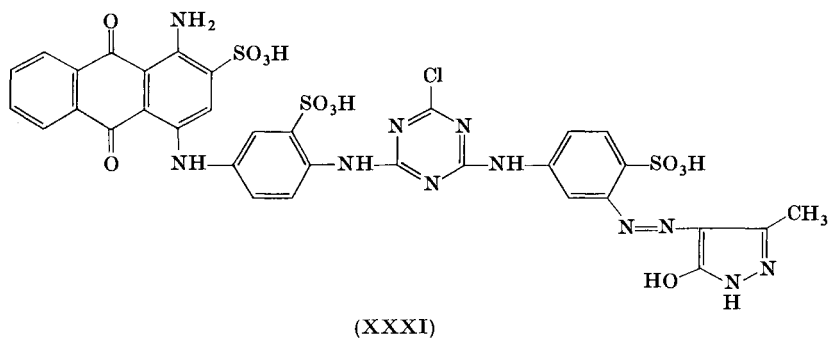


(XXX)

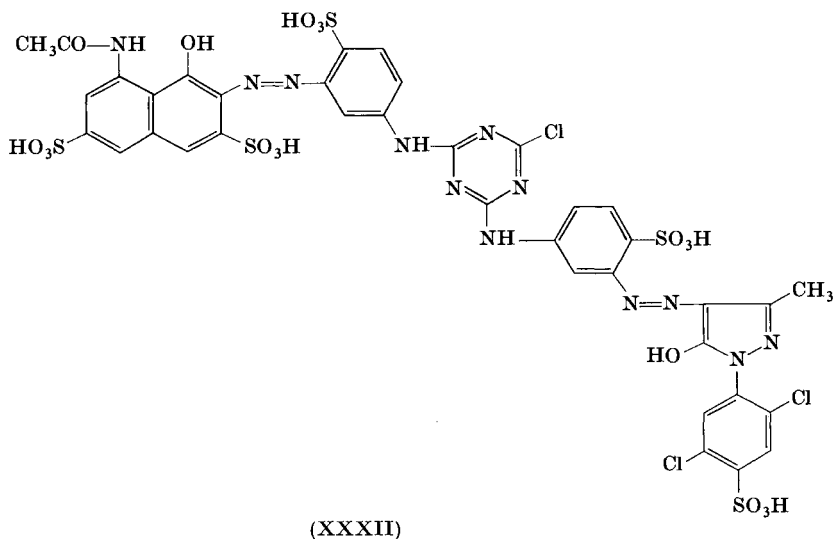
²² Gy, BeP 644,495 (1.3.1963); ICI, FP 1,252,269 (16.2.1959).

²³ Gy, BeP 615,776 (30.3.1961).

Coupling products of pyrazolones are also used as yellow components in intramolecular mixtures in the production of mixed shades, for example, with blue anthraquinone dyes to obtain green shades.²⁴



or in the production of yellowish red shades.²⁵

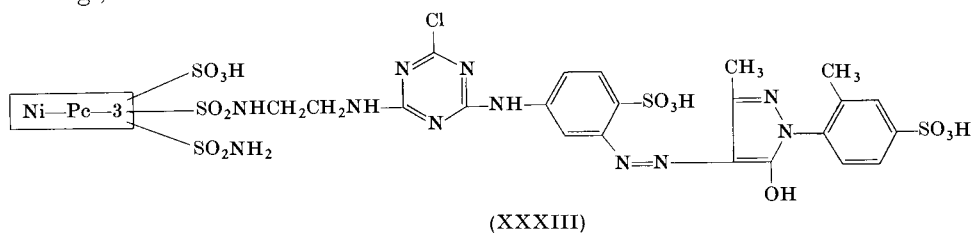


Very brilliant green dyes are obtained by combination of Cu or Ni phthalocyanine derivatives with pyrazolone coupling products. Tur-

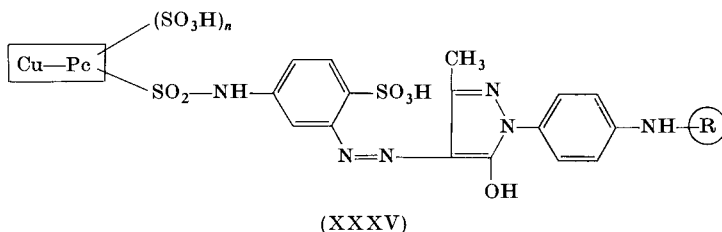
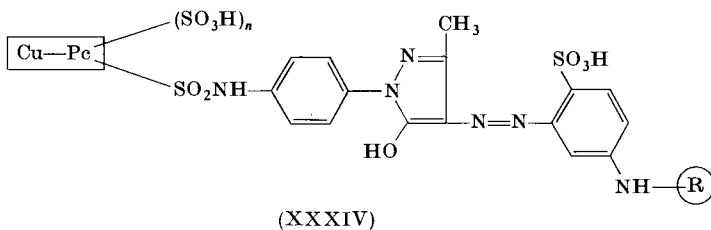
²⁴ CIBA, *DAS* 1,075,242 (27.1.1956).

²⁵ CIBA, *BeP* 571,238 (17.9.1957).

quoise and yellow components can be linked through bridge members,²⁶ e.g., as in

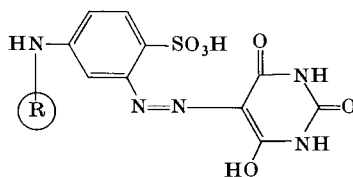
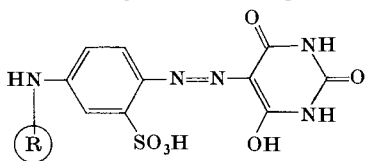


or directly, in which case the coupling or diazonium component can be linked with the phthalocyanine residue.



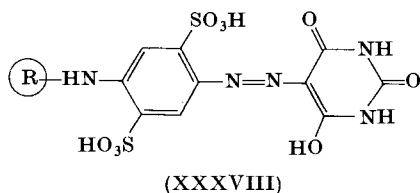
Compared with the pyrazolone reactive dyes, the coupling products of other cyclic or open-chain enols or enamines are of minor importance.

Noteworthy are coupling products of barbituric acid,²⁷

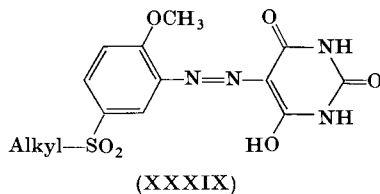


²⁶ CIBA, *DAS* 1,156,908 (13.1.1959); *BeP* 614,458 (28.2.1961); CFM, *DAS* 1,095,429 (7.8.1958); FBy, *BeP* 696,650 (5.4.1966); CIBA, *BeP* 586,569 (15.1.1959); *SP* 387,195 (20.11.1959).

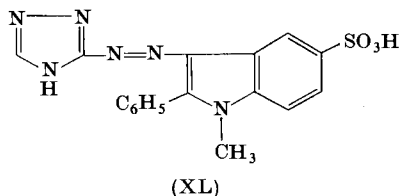
²⁷ CIBA, *SP* 358,884 (15.12.1961); *DAS* 1,066,301 (3.8.1956); *BeP* 666,009 (29.6.1964).



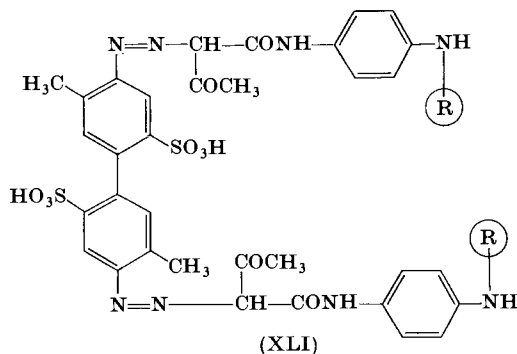
which give relatively bright, greenish yellow shades, although their color strength is generally lower than in the pyrazolone range. Barbituric acid derivatives were patented in connection with the "multi-component reactive dyes,"²⁸ e.g.,



In this connection, coupling products of 2-phenylindole derivatives are also interesting.²⁹



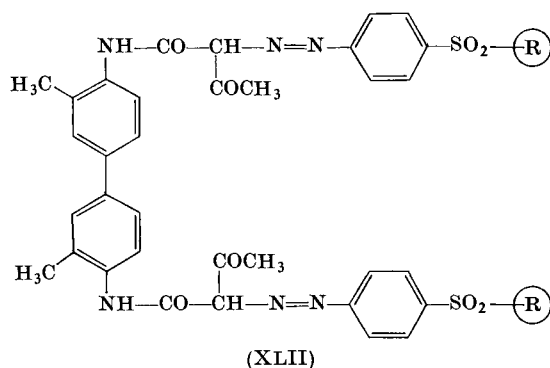
To illustrate the use of acetoacetic arylides the following formulae are given³⁰:



²⁸ BASF, *BeP* 662,774 (21.4.1964).

²⁹ BASF, *FP* 1,366,250 (22.6.1952).

³⁰ ICI, *BeP* 617,961 (24.5.1961); FH, *GE* 965,902 (18.7.1949).



In this case also, the color strength of the coupling products is generally insufficient.

Methods of Production

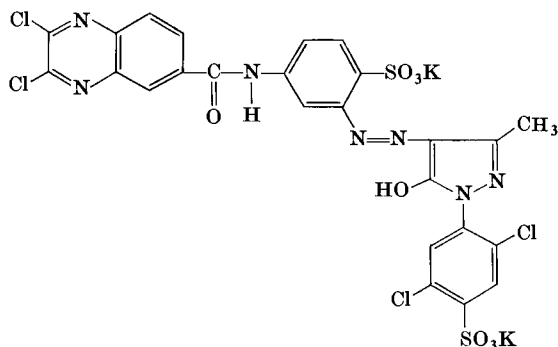
(1) Dyestuff of formula (I)¹²

With 2,3-dichloroquinoxaline-6-carbonyl chloride as reactive component.

To 500 parts of water are added 188 parts of 2,4-diaminobenzene-sulfonic acid and 100 parts of 30% sodium hydroxide. This slurry is stirred to effect solution, cooled to 25°, and diluted with 1400 parts of water. To this solution is added all at once 112 parts of acetic anhydride and stirring is continued for 1 hour, after which the pH is adjusted to 8 ± 0.5 and 69 parts of a 31% sodium nitrite solution is added. This solution is then added over $\frac{1}{2}$ hour to a solution of 500 parts of water, 500 parts of ice, and 120 parts of 30% hydrochloric acid. The resulting slurry is stirred for $\frac{1}{2}$ hour before the excess nitrite is destroyed with sulfamic acid, as shown by a negative test on starch-iodide paper. This diazo slurry is added with stirring at 5–15° over 1 hour to a solution of 500 parts of water, 323 parts of 1-(2',5'-dichloro-4'-sulfophenyl)-3-methyl-5-pyrazolone, 72 parts of 30% sodium hydroxide, 100 parts of sodium acetate, and 500 parts of ice. To this yellow-brown solution is added 120 parts of hydrochloric acid, the temperature is then raised to 90° over 1 hour, held at this temperature for 2 hours, cooled to 40°, and the precipitated solid dyebase is collected by filtration and washed with a dilute hydrochloric acid solution.

This wet dyebase cake is dissolved in a solution of 5000 parts of water and 165 parts of sodium hydroxide. To this rapidly stirred solution at 30°–35° are added 230 parts of 2,3-dichloro-6-quinoxalinecarbonyl

chloride dissolved in 700 parts of xylene. This mixture is stirred for 3 hours at 35°–40°, while maintaining the pH at 5.5–8.0 by addition of a sodium hydroxide solution. The reaction mass is then clarified by filtration, 150 parts of potassium chloride in 2000 parts of water is added over 1 hour, and the precipitated insoluble (in cold water, slightly soluble in boiling water) potassium salt of the formula



is filtered. This wet presscake is prepared for commercial use by drying below 60°, adding 4.2% K_2SO_4 , based on weight of dye, and grinding.

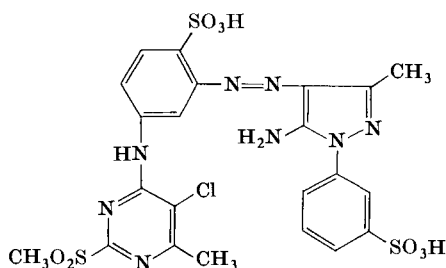
(2) Dyestuff of formula (V)¹⁰

With 2-methylsulfonyl-4,5-dichloro-6-methylpyrimidine as reactive component.

1,3-Diaminobenzene-4-sulfonic acid, 18.8 parts by weight (0.1 mole), is dissolved in 200 parts by volume of water at 60° and pH 6—adjusted with caustic soda—and 24.1 parts by weight of 2-methylsulfonyl-4,5-dichloro-6-methylpyrimidine is added. The reaction mixture is stirred at 60–65° for 2 to 3 hours, the liberated hydrochloric acid being neutralized by adding drop by drop a 20% sodium carbonate solution. A clear, almost colorless solution is obtained, from which the condensation product is precipitated by addition of 50 parts by weight of sodium chloride and can then be isolated as a slightly yellowish paste. The yield is practically quantitative.

The still moist reaction product is dissolved in 2000 parts by volume of water and the solution is acidified with 35 parts by volume of hydrochloric acid and diazotized with 24 parts by volume of a 30% sodium nitrite solution. After completion of diazotization, 25.3 parts by weight of 1-(3'-sulfophenyl)-3-methyl-5-aminopyrazole is added to the suspension of the diazonium compound and coupling is completed by addition of 160 parts by volume of a 20% sodium acetate solution. The coupling

product dissolves to give a yellow solution. It is precipitated by addition of 250 parts by weight of sodium chloride, isolated, and vacuum-dried at 60°. The resulting dyestuff corresponds to the formula:



This is a yellow powder which dissolves in water to form a yellow solution. It gives fast-to-light, bright yellow shades on cotton when applied by the printing or dyeing methods generally used for reactive prints or reactive dyeings.

(3) Dyestuff of formula (VI)¹³

With a β -sulfatoethylsulfonyl residue as reactive group.

3-Amino-4-methoxy-1-methylbenzene-6- β -hydroxyethyl sulfone, 24.5 parts by weight, m.p. 91 to 92°, is heated with 16.2 g of 60% sulfuric acid and converted to the acid sulfoester, then stirred with 150 parts by weight of ice and 17.8 parts by weight of hydrochloric acid (36.5%) and diazotized with 24 parts by weight of 5 *N* sodium nitrite solution at 0°–5°.

To the clear diazo solution 28.1 parts by weight of 1-(4'-sulfophenyl)-3-methyl-5-pyrazolone (90.2%) is added, followed by sodium bicarbonate until coupling is completed. The dyestuff is isolated by salting out with potassium chloride; it is filtered and dried in a vacuum drier at 50–60°; 82.4 parts by weight of a yellow powder is obtained, which dissolves in water to give a yellow solution. It is suitable as a printing dyestuff and, particularly, for dyeing. Bright yellow shades with a high color strength and good to very good fastness to wet processing, crocking, and light are obtained from salt-containing dye liquors with the aid of alkalies on natural and regenerated cellulosic fibers.

(4) Dyestuff of formula (XII)¹⁶

With cyanuric chloride as reactive component.

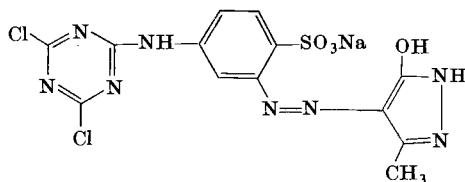
A neutral solution in 1400 parts of water of 51.1 parts of the disodium salt of the aminoazo compound obtained by reducing with sodium sulfide the monoazo compound produced by coupling diazotized 4-nitroaniline-2-sulfonic acid with 1-(4'-sulfophenyl)-3-carboxy-5-pyrazolone is added

gradually in a period of 40 minutes to a suspension formed by pouring a solution of 19.2 parts of cyanuric chloride in 100 parts of acetone into a stirred mixture of 300 parts of crushed ice. The temperature of the mixture is kept below 3°, and after completion of the addition of the solution of aminoazo compound the mixture is stirred for 15 minutes and the product is isolated.

The product is obtained as an orange powder which dissolves in water to give a yellow solution and when applied to textile materials gives reddish yellow shades having excellent fastness to repeated washing and light.

(5) Dyestuff of formula (XXXI)²⁴

1-Amino-4-(4'-aminophenylamino)anthraquinone-2-sulfonic acid, 8.18 parts, is dissolved in 200 parts of water with an addition of 0.9 part of sodium hydroxide and 1.1 parts of sodium carbonate at 40°. To the resulting solution 9.8 parts of dyestuff of the formula

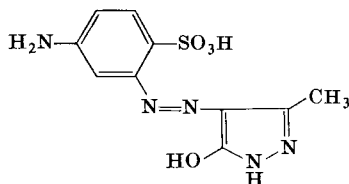


is added as an approx. 25% aqueous paste. The reaction mixture is stirred for 30 minutes at 35–40° and for 30 minutes at 45–50°. It is then heated to 70°.

The resulting dyestuff is filtered off at that temperature and washed with 150 parts of a 2% sodium chloride solution. The dried product is obtained as a dark powder which dissolves in water to give a green solution and produces bright green shades on wool from a neutral or slightly acid (acetic acid) bath.

The azo dyestuff of the specified formula to be used in this case as an intermediate can be produced, for example, as follows:

Cyanuric chloride, 18.5 parts, is suspended in 400 parts of ice water and mixed with 29.7 parts of a slurry of the acid-precipitated dyestuff of the formula

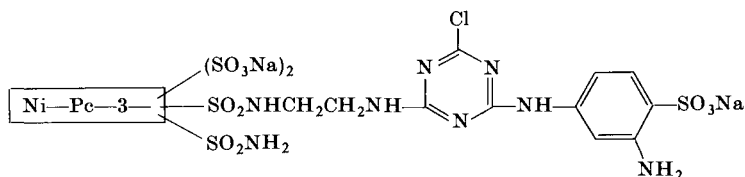


(produced by coupling of diazotized 1-acetylamino-3-aminobenzene-4-sulfonic acid with 3-methyl-5-pyrazolone and subsequent saponification of the acetylamino group) in 400 parts of water. Sodium carbonate, 10.6 parts, dissolved in 100 parts of water, is added drop by drop to this yellow suspension in a period of 3 hours at 2–5°. The color of the suspension changes to green-yellow. The condensation product is filtered and, as stated, condensed with 1-amino-4-(4'-aminophenylamino)anthraquinone-2-sulfonic acid.

(6) Dyestuff of formula (XXXIII)²⁶

With cyanuric chloride as reactive component.

Sixty-five parts of the compound of the formula



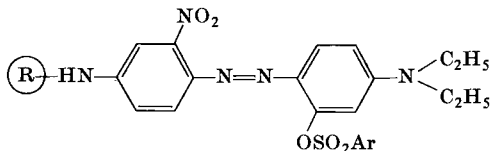
is dissolved in 500 parts of water, cooled to 0° by addition of crushed ice, and then 50 parts of concentrated hydrochloric acid is added with thorough stirring. The compound precipitated as a fine suspension is diazotized by adding drop by drop 25 parts by volume of 2 *N* sodium nitrite solution at 0°–5°. The diazo suspension is then poured with thorough stirring into a solution consisting of 14 parts of 1-(2'-methylphenyl)-3-methyl-5-pyrazolone-4-sulfonic acid, 250 parts of ice water, and 50 parts of anhydrous sodium carbonate. The temperature is increased in 2 hours to 20°, when the dyestuff dissolves. The solution is adjusted to pH 7 by addition of hydrochloric acid and heated subsequently to 50°. The dyestuff is precipitated by addition of sodium chloride, filtered off, and vacuum-dried at 60°. The dyestuff obtained produces brilliant green shades on cellulosic fibers, with good fastness to washing and very good fastness to light.

B. COUPLING PRODUCTS OF AROMATIC AMINES

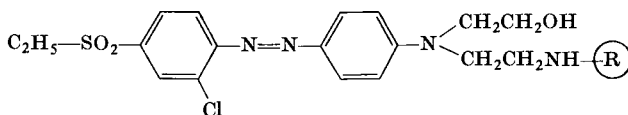
In the range of reddish yellow to orange reactive dyestuffs, coupling products of aniline and naphthylamine derivatives are extremely important, particularly where dyeings which are faster to chlorine are required. Simple derivatives of aminoazobenzene or diaminoazobenzene do not usually possess sufficient color strength to be used, after condensation with reactive components, as cotton dyestuffs. Compounds of

this range have, however, been patented as reactive disperse dyestuffs.

The nonacylated amino group may, in this case, be important for color strength.³¹

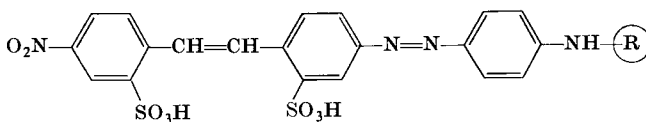


(XLIII)



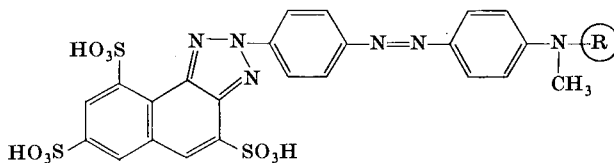
(XLIV)

Where larger aromatic systems are used as diazonium compounds, the products obtained possess a higher color strength and are of practical importance as cotton dyestuffs.³²



(XLV)

The combination with triazole residues gives relatively bright, greenish yellow dyes, such as³³ (XLVI).



(XLVI)

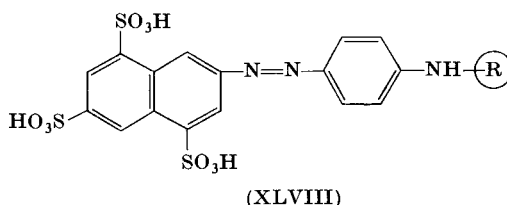
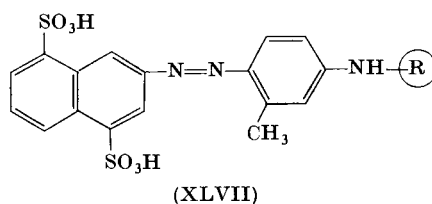
Among the most important dyestuffs of this range are compounds of the naphthalene-azo-benzene type, which were some of the first reactive

³¹ BASF, *FP* 1,213,545 (31.8.1957); ICI, *USP* 2,964,520 (9.4.1959).

³² ICI, *FP* 1,198,036 (25.2.1957); 1,346,756 (7.2.1962).

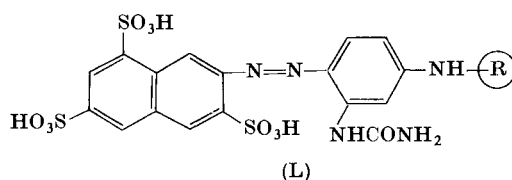
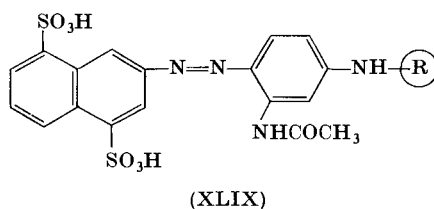
³³ FBy, *BeP* 588,834 (20.3.1959); DuP, *USP* 3,040,022 (7.11.1958).

yellow dyes to be introduced and which have maintained their importance up to the present time.³⁴



These dyestuffs are synthesized by coupling of diazotized aminonaphthalenesulfonic acids with substituted anilines or their *N*-methanesulfonic acids, hydrolysis of the methanesulfonic acid group, and subsequent condensation of the aminoazo dyestuff thus obtained with molar quantities of the reactive component.

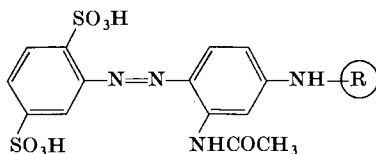
Numerous variants of this basic type—both in the diazonium and also in the coupling component—have been patented. In addition to the problem of adaptation to certain reactive components and to certain methods of application, the main considerations are color strength and certain fastness properties. For example, products with a very high color strength are obtained by coupling of 1,3-diaminobenzene derivatives,³⁵



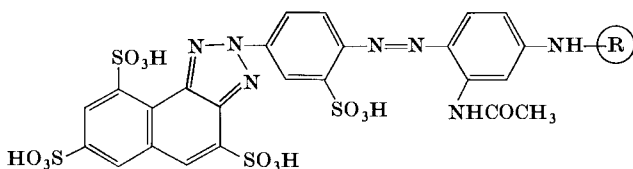
³⁴ CIBA, *SP* 350,388 (3.7.1956); ICI, *FP* 1,143,176 (29.11.1954); CIBA, *BeP* 629,952 (26.3.1962).

³⁵ CIBA, *DAS* 1,110,783 (6.9.1956); ICI, *BP* 970,475 (24.3.1961); 995,502 (15.2.1962).

in which case benzene derivatives as diazonium compounds also produce dyestuffs with sufficient color strength.³⁶

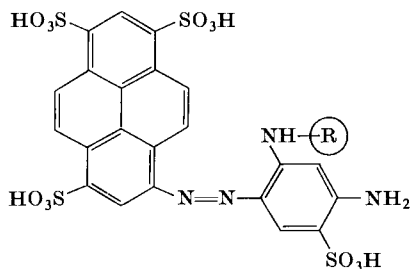


(LI)

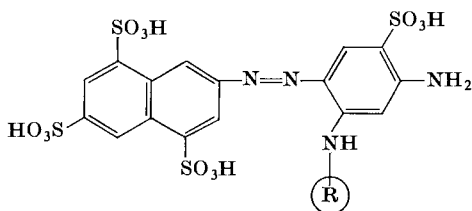


(LII)

The free amino group in dyestuffs (LIII) and (LIV) contributes, in particular, to a high color strength.³⁷



(LIII)



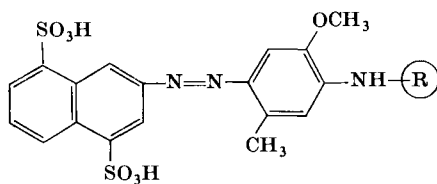
(LIV)

In this connection, coupling products of cresidine may also be mentioned, although they generally give somewhat less brilliant shades.³⁸

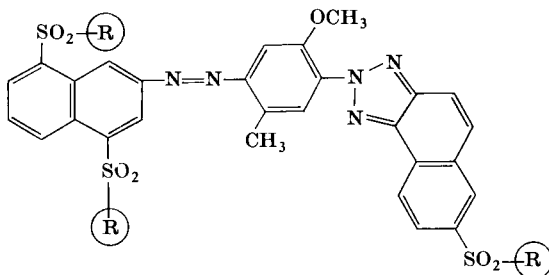
³⁶ CIBA, *DAS* 1,110,783 (6.9.1956); ICI, *DAS* 1,153,842 (7.11.1958).

³⁷ CIBA, *FP* 1,484,357 (22.6.1965); FBy, *BeP* 707,722 (9.12.1966).

³⁸ ICI, *BP* 797,946 (29.11.1954); FBy, *BeP* 588,834 (20.3.1959).

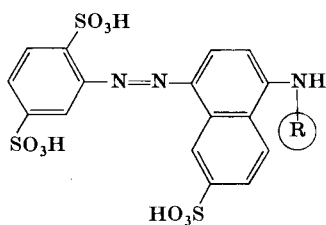


(LV)

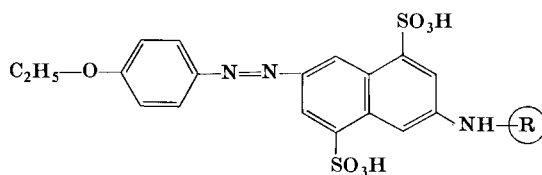


(LVI)

The reverse sequence, in which the reactive group is attached to the naphthalene intermediate, has so far not achieved practical importance.³⁹



(LVII)

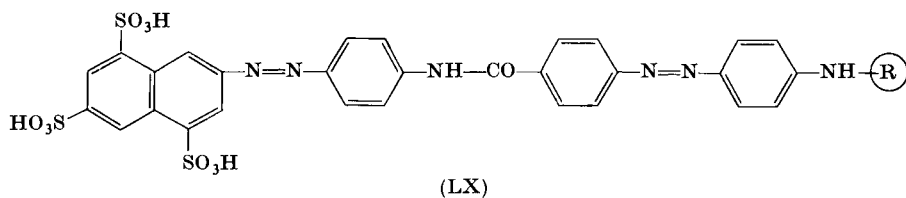
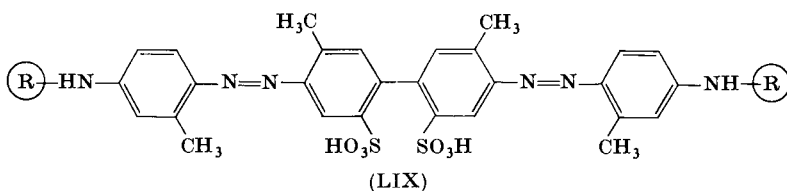


(LVIII)

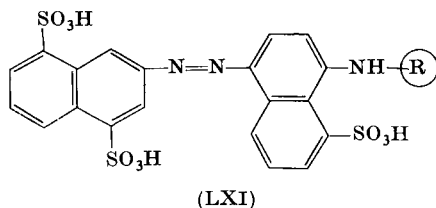
Mention must also be made here of disazo dyestuffs, which contain two separate diarylazo groups, their shades therefore being similar to those of monoazo dyestuffs.⁴⁰

³⁹ FBy, *DAS* 1,191,059 (7.2.1961); *BeP* 619,105 (22.6.1961).

⁴⁰ S, *SP* 403,131 (29.12.1960); *BeP* 620,833 (10.8.1961).

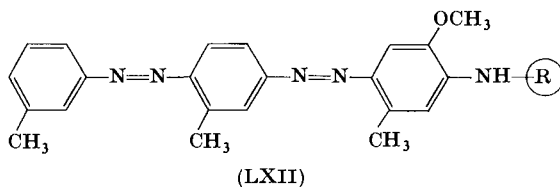


Important dyes are also obtained from the range naphthalene-azo-naphthalene, where more significance is attached to 1-aminonaphthalene-8-sulfonic acid in the production of yellow dyestuffs with good fastness to light and chlorine.⁴¹



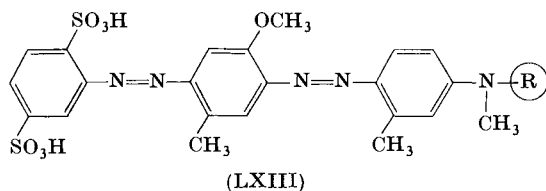
Since acylation of the amino group of these dyestuffs is severely restricted by the sulfonic acid group in the peri position, highly reactive components can be used in this case only in the first stage, e.g., cyanuric chloride or carbonyl chlorides.

p-Amino disazo reactive dyes comprise the range of shades from golden yellow to orange and to red-brown, the benzene derivatives being more on the yellow side.⁴²

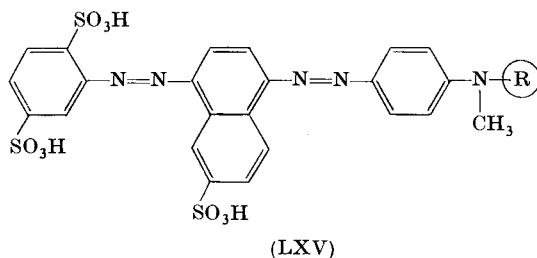
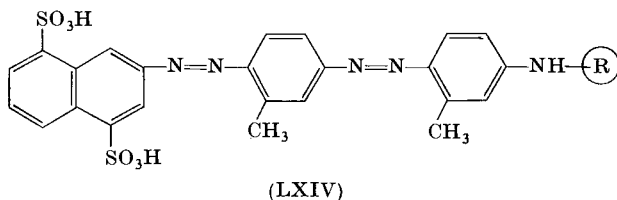


⁴¹ CIBA, *BeP* 624,821 (17.11.1961); FBy, *DAS* 1,191,059 (7.2.1961).

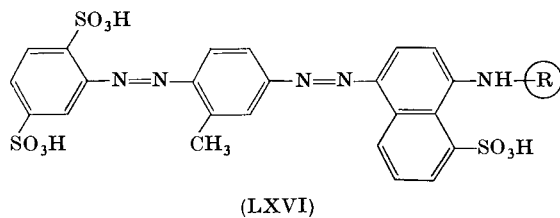
⁴² Acna, *BeP* 666,229 (2.7.1964); CIBA, *BeP* 637,176 (10.9.1962).



The use of naphthalene derivatives—as end or starting components or medially—gives orange shades,⁴³



1-aminonaphthalene-8-sulfonic acid also possessing particular importance in this combination.⁴⁴

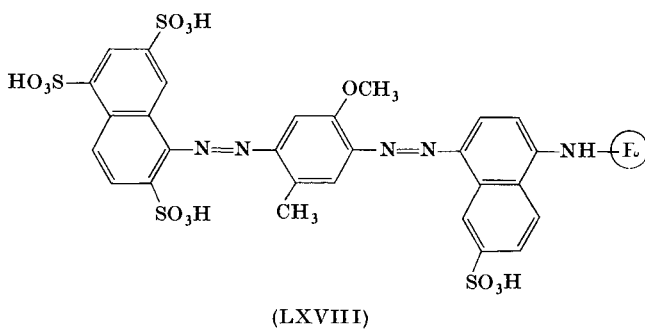
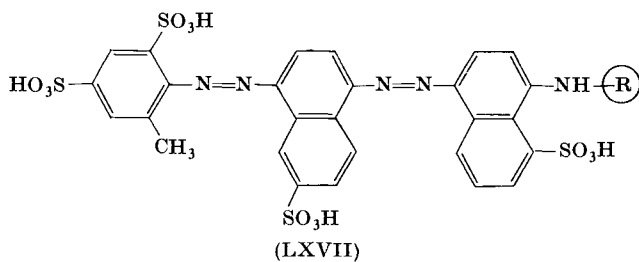


The preponderant use of naphthalene derivatives finally gives brown dyes.⁴⁵

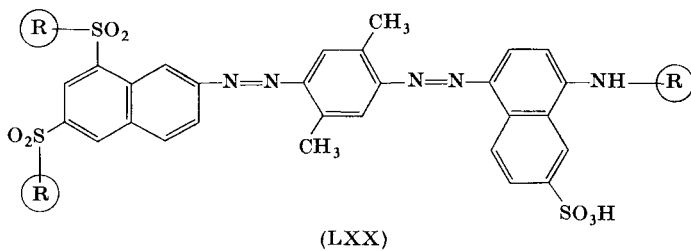
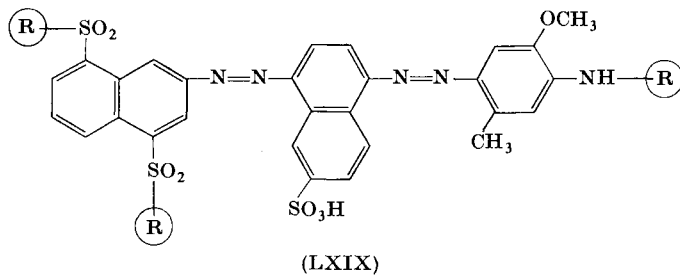
⁴³ S, *BeP* 666,524 (7.7.1964); CIBA, *DAS* 1,067,151 (3.7.1956); *BeP* 637,176 (10.9.1962).

⁴⁴ CIBA, *DAS* 1,246,907 (6.11.1961).

⁴⁵ CIBA, *BeP* 624,403 (6.11.1961); *FP* 1,483,235 (14.7.1965); *BeP* 607,178; 607,259 (18.8.1960).



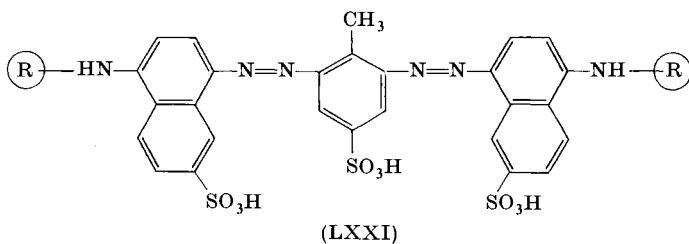
The following are examples of the numerous variants,⁴⁶



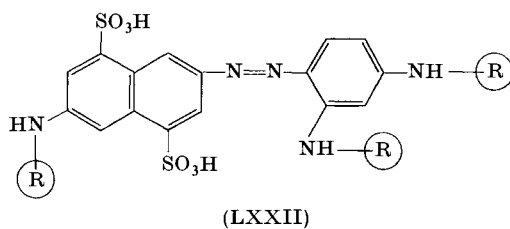
in which several different reactive groups may also be used.

⁴⁶ CIBA, *Bep* 620,899 (31.7.1961).

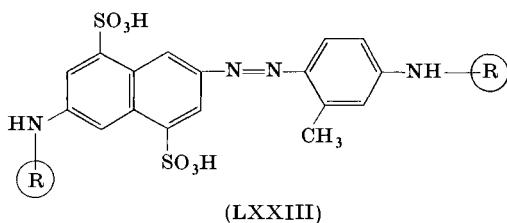
Further reactive dyes containing several reactive groups with *m*-linkage are also described⁴⁷



or, using 2,6-diaminonaphthalene-4,8-disulfonic acid and 1,3-diaminobenzene⁴⁸



or *m*-toluidine,⁴⁹



where three or two reactive groups are present. The last example is a golden yellow reactive dye.

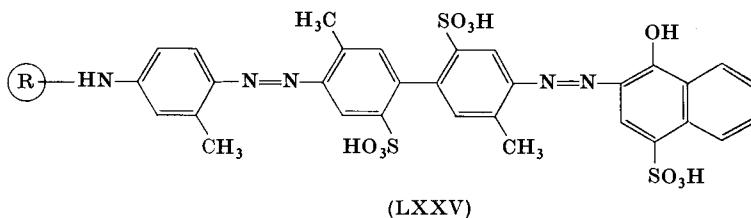
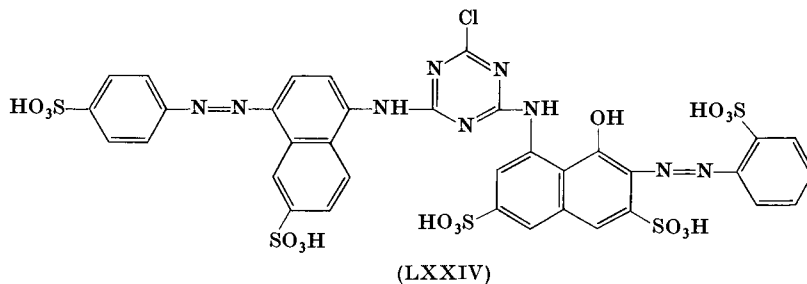
In numerous cases, aminoazo compounds of the type described above are used as yellow components in intramolecular color mixtures.

⁴⁷ CIBA, *DAS* 1,110,788 (24.3.1958).

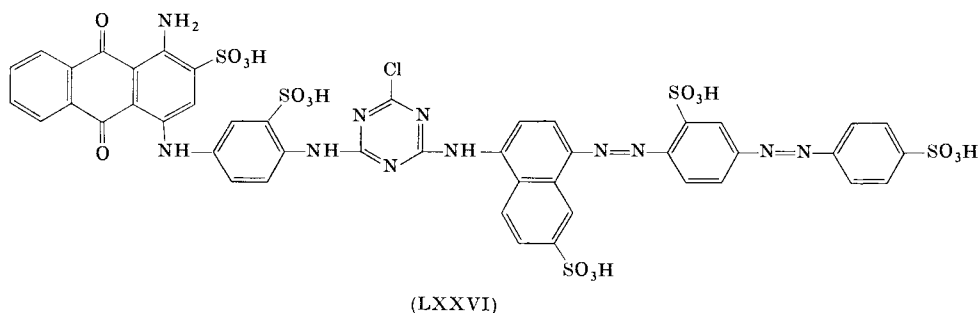
⁴⁸ ICI, *EGP* 56,574 (3.9.1965).

⁴⁹ ICI, *FP* 1,472,769 (29.3.1965).

For mixtures with red components the following examples may be given⁵⁰:



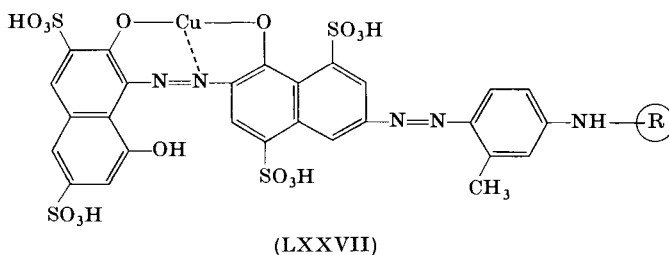
Yellowish red dyes are obtained in this way. Mixtures with blue anthraquinone dyes generally give heavy olive green shades.^{51, 47}



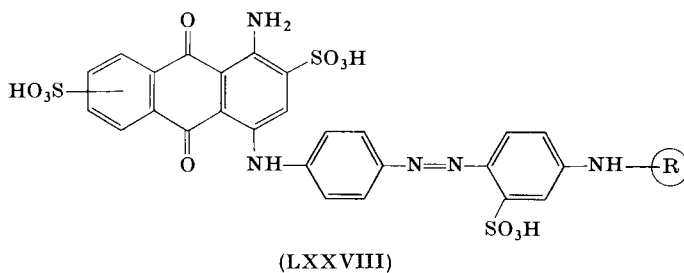
⁵⁰ CIBA, *BeP* 581,536 (11.8.1958); S, *BeP* 590,879 (22.5.1959); *BP* 969,855 (14.1.1960).

⁵¹ CIBA, *BeP* 588,350 (17.7.1959).

Similar shades are also obtained by addition to blue azo-copper complexes⁵²

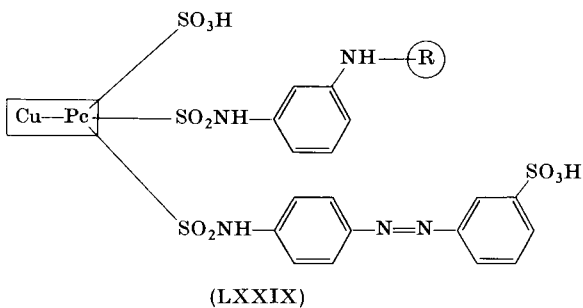


or to anthraquinone dyestuffs without a bridge link.⁵³



Brighter green dyes can be obtained by linking of aminoazo compounds with copper phthalocyanine or its sulfonic acids.

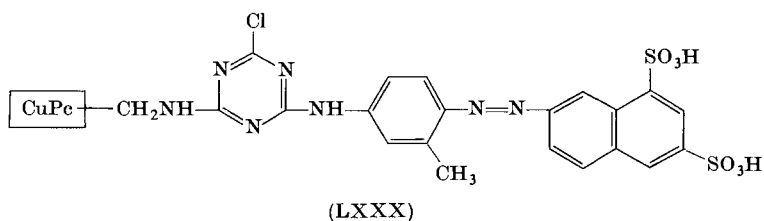
Dyestuffs (LXXIX) and (LXXX) are examples of the various types of linkage.⁵⁴



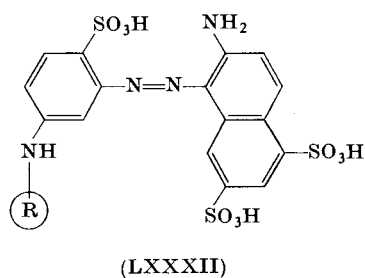
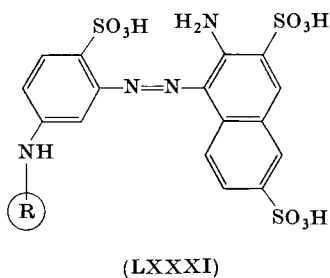
⁵² FBy, *BeP* 656,341 (27.11.1963).

⁵³ ICI, *BP* 910,849 (5.7.1960); *DAS* 1,057,707 (29.11.1954).

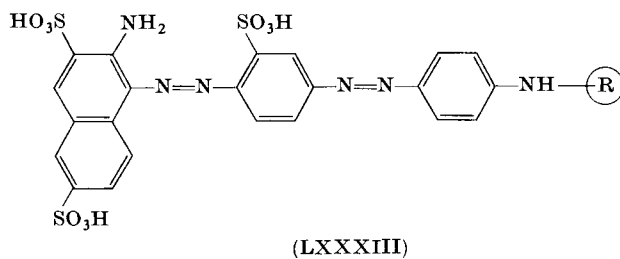
⁵⁴ CIBA, *BeP* 593,030 (16.7.1959); S, *USP* 3,133,050 (9.3.1962); CCC, *USP* 3,116,293 (15.5.1958).



o-Aminoazo compounds of the naphthalene series have also achieved practical importance in the production of orange shades. 2-Aminonaphthalene mono- and disulfonic acids are used as coupling components.⁵⁵



When aminoazo compounds are used as diazonium components, red shades are obtained.⁵⁶



⁵⁵ FBy, *DAS* 1,191,059 (7.2.1961); CIBA, *FP* 1,301,494 (9.7.1962); ICI, *BeP* 592,748 (23.10.1969).

⁵⁶ DuP, *FP* 1,265,526 (12.7.1960).

Methods of Production

(1) Dyestuff of formula (XLVII)³⁴

With cyanuric chloride as reactive component.

Cyanuric chloride, 18.5 parts, is dissolved with application of heat in 50 parts of acetone and poured in a fine stream into 300 parts of water and 200 parts of ice. The residue is filtered and stirred with 300 parts of ice and 200 parts of water. To this suspension is added in 1000 parts by volume of water the neutral solution of the monoazo dyestuff obtained by diazotization of 2-aminonaphthalene-4,8-disulfonic acid and coupling with *m*-toluidine.

The temperature during condensation must not exceed 0°. The liberated acid is bound with 1 *N* sodium hydroxide solution in such a manner that the pH is maintained between 5.5 and 6.5. As soon as the 1 *N* sodium hydroxide solution used up amounts to 100 parts by volume, precipitation is carried out by addition of 10 to 15 parts of sodium chloride per 100 parts by volume of the reaction mixture and the precipitate is filtered off and vacuum-dried at 45°. The dry yellow powder thus obtained dissolves in water and gives fast yellow shades on cotton from cold to lukewarm, salt-containing, alkaline baths.

(2) Dyestuff of formula (LII)³⁶

With cyanuric chloride as reactive component.

Diazotized 4-nitroaniline-3-sulfonic acid is coupled with 1-naphthyl-amino-3,6,8-trisulfonic acid, the resulting azo compound is treated with an aqueous solution of cuprammonium sulfate, and the nitro group is reduced with a mixture of iron and acetic acid; the amino compound thus obtained is diazotized and then coupled with *m*-aminoacetanilide in the presence of acetic acid.

Cyanuric chloride, 3.3 parts, is dissolved in 35 parts of acetone and the solution is poured into a stirred mixture of 100 parts of water and 100 parts of ice. To this cyanuric chloride suspension is added in a period of 20 minutes a solution of 14.3 parts of the tetrasodium salt of the above aminoazo compound in 300 parts of water, the temperature of the mixture being held below 5° by addition of ice. The mixture is stirred for a further hour and then neutralized to pH 6.8 by addition of 34 parts of a 10% aqueous sodium carbonate solution. Ten parts of sodium diethylmetanilate, 0.66 part of sodium bisulfate, and 50 parts of sodium chloride are then added, the precipitated dyestuff is filtered off, washed with 200 parts of acetone, and dried.

The resulting dye contains 1.81 atoms of organically bound chlorine to every monoazo molecule present. Reddish yellow shades with good

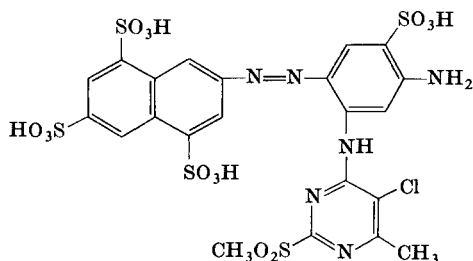
fastness to washing and light are obtained on cellulosic textiles when this dyestuff is used in combination with a treatment with an acid-binding agent.

(3) Dyestuff of formula (LIV)³⁷

With 4,5-dichloro-2-methylsulfonyl-6-methylpyrimidine as reactive component.

Nineteen parts by weight of 1,3-diaminobenzene-4-sulfonic acid is dissolved in 200 parts by volume of water at 60° with sodium carbonate solution at pH 6. To this solution is added at 60° 25 parts by weight of 2-methylsulfonyl-4,5-dichloro-6-methylpyrimidine, the pH of the reaction mixture being maintained at 5–6 by gradual addition of a 20% sodium carbonate solution. When condensation is completed, the reaction product is precipitated by addition of 60 parts by weight of sodium chloride and isolated as a pale yellow paste.

This condensation product is dissolved in 400 parts by volume of water at 40°, filtered after addition of a little activated carbon and kieselguhr, and the filtrate cooled to 10–15° by addition of ice. To this solution is added the solution of the diazonium compound obtained by the usual methods from 38.3 parts by weight of 2-naphthylamine-4,6,8-trisulfonic acid in 450 parts by volume of water and the mixture is treated with 140 parts by volume of a 20% sodium acetate solution. Coupling takes place quickly and completely at pH 4. After 15 minutes the dyestuff is precipitated in crystalline form. It is isolated and vacuum-dried at 60°. The resulting monoazo dyestuff corresponds to the formula



and is obtained, when dry, as an orange powder which dissolves in water to give a yellow solution. It produces reddish yellow shades on cotton when applied by the usual reactive printing or reactive dyeing methods.

(4) Dyestuff of formula (LXVI)⁴⁴

With aminochlorotriazine as reactive component.

Nineteen parts of cyanuric chloride is finely dispersed in 300 parts of

ice water. To this dispersion is added, after neutralization with sodium carbonate, a solution of 72.1 parts of the aminodisazo dyestuff, produced by coupling of the diazo compound from aniline-2,5-disulfonic acid with 1-naphthylamine-6-sulfonic acid, further diazotization of the resulting aminoazo dyestuff and coupling in a weak acid medium (pH 4–5) with 1-naphthylamine-8-sulfonic acid, in 500 parts of water. The mixture is stirred for 2 hours at 5°–8°, the pH of the solution being maintained between 5 and 7 by gradual addition of a dilute sodium hydroxide solution. When condensation is completed, the resulting solution of the dichlorotriazine dyestuff is mixed with 50 parts of a 10% aqueous ammonia solution and is heated for 2–3 hours at 30°–40°. The monochlorotriazine dyestuff thus obtained is salted out, filtered off, and dried. It dissolves in water to give a red-brown solution and dyes very fast red-brown shades on cotton.

(5) Dyestuff of formula (LXXVI)⁵¹

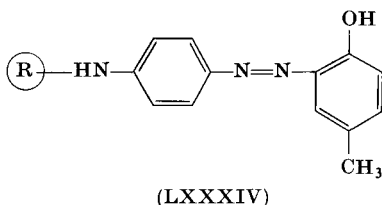
With cyanuric chloride as reactive component.

Cyanuric chloride, 18.6 parts, is finely dispersed in 300 parts of ice and 200 parts of ice water. To this dispersion is added a solution of 59.1 parts of the aminodisazo dyestuff, obtained by coupling of the diazo compound from 4-aminoazobenzene-3,4'-disulfonic acid with 1-naphthylamine-6-sulfonic acid, in 500 parts of water and condensation is carried out for 1 hour at a pH of 7–9 and a temperature of about 10°. The neutral solution of 48.9 parts of 1-amino-4-(4'-aminophenylamino)anthraquinone-2,3'-disulfonic acid in 500 parts of water is then added and the mixture is stirred for 48 hours at 40° and a pH between 6 and 8, precipitated and dried. The resulting dyestuff produces very fast khaki shades on cellulosic fibers by the so-called pad-dyeing process.

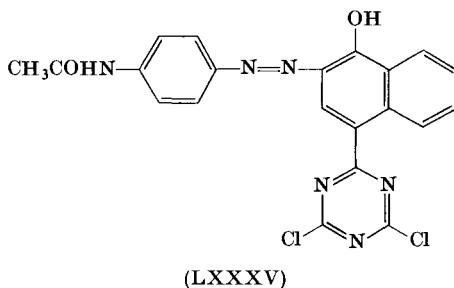
C. COUPLING PRODUCTS OF PHENOLS AND NAPHTHOLS

Coupling products of phenols and naphthols are used to a limited extent in the production of orange, scarlet, and red reactive dyes. These are almost entirely *o*-hydroxyazo compounds. Coupling products of *p*-substituted phenols have attained a little practical importance up to the present in the production of reddish yellow shades in the field of reactive disperse dyes. As an example, a coupling product of *p*-cresol (LXXXIV) may be mentioned.⁵⁷

⁵⁷ S, *SP* 340,927 (2.6.1955); CIBA, *BeP* 563,862 (11.1.1957).

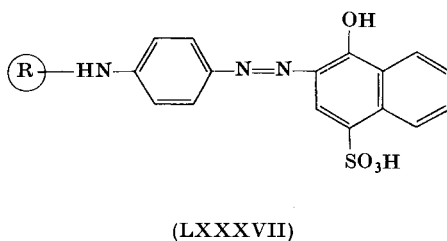
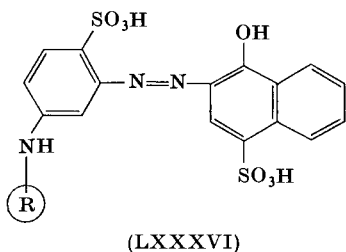


Reactive dyes of similar properties with red shades were synthesized by use of compounds obtained from cyanuric chloride or trichloropyrimidine and 1-naphthol in the presence of aluminum chloride as coupling component, e.g.,⁵⁸



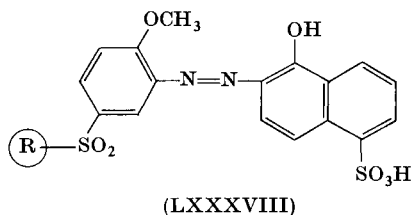
When the diazonium compounds reacted with such coupling components contain several sulfonic groups, the reactive dyes are suitable for cotton or regenerated cellulose.

The most important reactive dyes with aromatic hydroxy compounds as coupling components are obtained mainly by coupling of naphthol-sulfonic acids with diazonium components carrying reactive groups. 1-Naphthol-4- and 5-sulfonic acids are important.⁵⁹

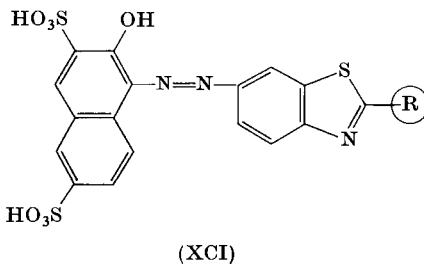
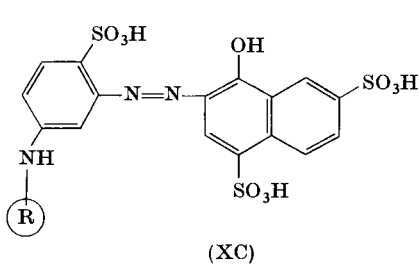
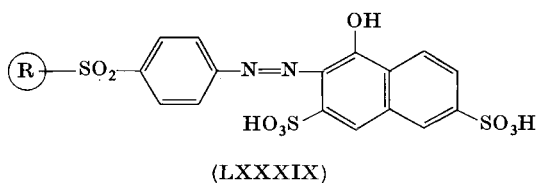


⁵⁸ ICI, *BP* 1,029,211; 1,029,212 (1.3.1962); G, *USP* 3,293,238 (30.12.1963).

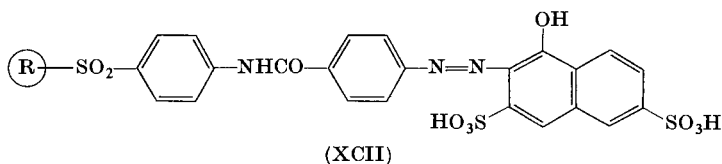
⁵⁹ S, *BeP* 578,742 (28.5.1958); BASF, *BeP* 593,868 (8.8.1959); FH, *DBP* 960,534 (9.1.1950).



Among naphtholdisulfonic acids, 1-naphthol-3,6-, 4,6-, and 4,7-disulfonic acids, as well as 2-naphthol-3,6- and 6,8-disulfonic acids, are particularly important, e.g.,⁶⁰



As an example of extended systems of this type may be mentioned dyestuffs obtained by the coupling of amides of aminobenzoic acid.



These are mainly yellowish red reactive dyestuffs. On the other hand, azo derivatives of 2-naphthol-8-sulfonic acids often give orange shades.⁶¹

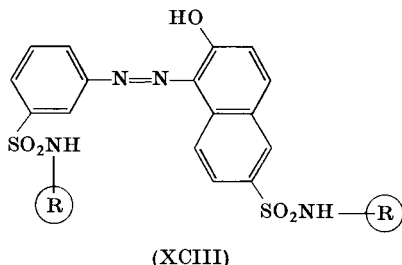
In addition to synthesis from diazonium compounds bearing reactive

⁶⁰ FH, *BeP* 629,713 (16.3.1962); S, *USP* 3,170,911 (14.5.1959); FBy, *FP* 1,480,931 (24.5.1965); FH, *FP* 1,534,414 (18.8.1966).

⁶¹ S, *BeP* 578,742 (28.5.1958); 666,524 (7.7.1964); CIBA, *BeP* 604,068 (23.5.1960).

groups, these dyes can also be obtained by primary coupling of diazonium compounds containing nitro or acylamino groups with naphtholsulfonic acids, conversion of the nitro or acylamino group to the free amine function, and subsequent condensation with the reactive component.

In the range of bifunctional reactive dyestuffs, mention may also be made of an example of this type in which linkage with the reactive residue takes place in both cases through the sulfamide group.⁶²



Methods of Production

(1) Dyestuff of formula (LXXXIV)⁵⁷

With cyanuric chloride as reactive component.

The coupling product obtained from 15 g of diazotized 1-amino-4-acetylaminobenzene and 10.8 g of *p*-cresol is stirred into 250 ml of 10% caustic soda and heated at 90–95° for 1 hour to split off the acetyl group. The saponification product is isolated and then suspended in 200 ml of water. This suspension is adjusted to pH 5–5.5 with acetic acid and cooled to 5°–10° by addition of ice; at that temperature a suspension of 18.4 g of cyanuric chloride is added in a little ice water. The hydrochloric acid liberated during the reaction is neutralized with a solution of 8.4 g of sodium bicarbonate in 30 ml of water. Condensation is completed after 1 hour, when the dyestuff is isolated and dried. As a fine dispersion, it gives yellow shades on polyamide fibers, such as nylon or Perlon.

The same dyestuff can be obtained by diazotization and coupling of the condensation product of cyanuric chloride and *p*-phenylenediamine with *p*-cresol.

(2) Dyestuff of formula (XC)⁶⁰

With trichloropyrimidine as reactive component.

1,3-Diaminobenzene-4-sulfonic acid, 94 parts, is dissolved in 550 parts of water at 45°–55° with the addition of sodium hydroxide solution. After

⁶² FBy, DOS 1,419,565 (21.12.1960).

addition of 92 parts of 2,4,6-trichloropyrimidine, the reaction mixture is stirred for about 8 hours at 45°–55° and a constant weak acid reaction is maintained by adding drop by drop a dilute sodium carbonate solution. On completion of condensation, the mass is stirred for a few hours at room temperature. The crystallized reaction product is then filtered off. It can be dried under vacuum at 70°–80°.

Sodium 1-amino-3-(dichloropyrimidylamino)benzene-6-sulfonate, 35.7 parts, produced as described in the foregoing paragraph, is dissolved with gentle heating in 1000 parts of water with an addition of dilute sodium carbonate solution to give a weak alkaline reaction. A solution of 7 parts of sodium nitrite in 30 parts of water is added and the mixture is stirred into 30 parts of concentrated hydrochloric acid and 50 parts of ice, further ice being added so that the temperature of the reaction mass does not exceed 5°. After stirring for some time, any excess nitrous acid is destroyed by addition of sulfamic acid.

Diazotization of 1-amino-3-(dichloropyrimidylamino)benzene-6-sulfonic acid can also be carried out directly at about 15°–20°. The diazonium salt dispersion is run slowly with vigorous stirring into a mixture, cooled to 10°, of 35 parts of the neutral sodium salt of 1-hydroxynaphthalene-4,7-disulfonic acid, 25 parts of sodium bicarbonate, and 600 parts of water.

An orange-red monoazo dyestuff is formed. On completion of coupling, the dyestuff is salted out with sodium chloride and after some time it is filtered off. The filter cake is washed with sodium chloride solution and dried under vacuum at 80°. On grinding, it is obtained as a brown-red powder which dissolves in water to give an orange-red solution.

(3) Dyestuff of formula (XCI)⁶⁰

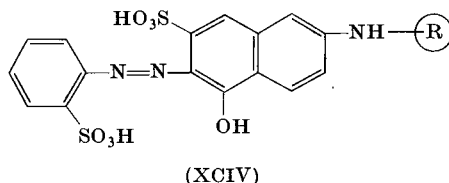
With 2-methylsulfonyl-6-aminobenzothiazole as reactive diazonium component.

2-Methylsulfonyl-6-aminobenzothiazole, 13.2 parts, is stirred into 100 parts by volume of ice water and 16 parts by volume of concentrated hydrochloric acid; to this mixture is added a solution of 4.1 parts of sodium nitrite in 10 parts by volume of water. The diazo compound dissolves to give a yellow solution. When any excess nitrous acid has been removed, the diazo solution is added to a solution of 17.6 parts of R-acid and 10 parts of soda ash in 200 parts of ice water. Coupling is quickly completed. The dyestuff is suctioned off and dried at 50°. A red powder is obtained. The resulting dye has formula (XCI) ($R = SO_2Me$). On cellulose it gives red shades with very good fastness properties, in particular very good wet-fastness.

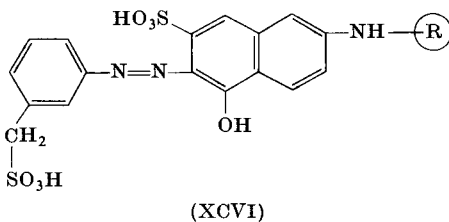
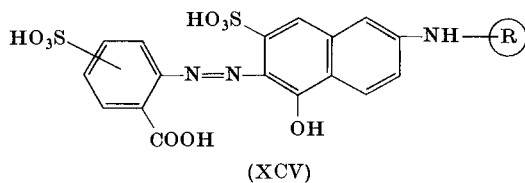
D. COUPLING PRODUCTS OF AMINONAPHTHOLS

The coupling products of aminonaphtholsulfonic acids possess by far the greatest importance in the production of reactive dyes. They comprise a range of shades from orange to black. Outstanding are the particularly brilliant red shades, which have contributed considerably to the promotion of reactive dyes. The versatility of aminonaphtholsulfonic acids is due to the large number of position-isomeric compounds and to the ability to couple these compounds selectively to *o*-amino or *o*-hydroxyazo dyestuffs. Moreover, aminohydroxydisazo dyestuffs can often be obtained. The following selection considers primarily derivatives which have been found interesting in practice.

The first triazinyl reactive dyestuffs to be marketed also included the following coupling product of J-acid⁶³



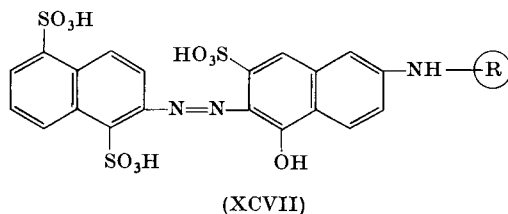
which gives brilliant yellowish orange shades on cotton. There are numerous variants of this type, of which the following are examples⁶⁴:



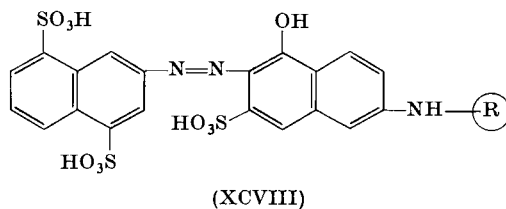
⁶³ ICI, *DAS* 1,019,025 (29.11.1954).

⁶⁴ S, *FP* 1,246,743 (10.11.1958); FB_y, *BeP* 631,962 (7.5.1962).

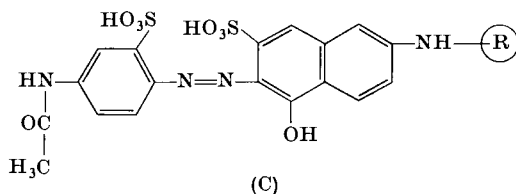
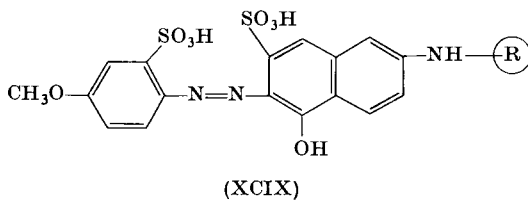
Medium to reddish orange shades are obtained by the use of diazonium compounds of 2-naphthylamine-1-sulfonic acid and its derivatives.⁶⁵



If the sulfonic group in the 1-position is absent from the diazonium component, a marked bathochromic shift occurs, which may result in the production of yellowish red shades.⁶⁶



Dyestuffs in this range of shades are, however, obtained mainly by the use of diazonium compounds of the benzene series with electron-donor substituents in the *p*-position.⁶⁷

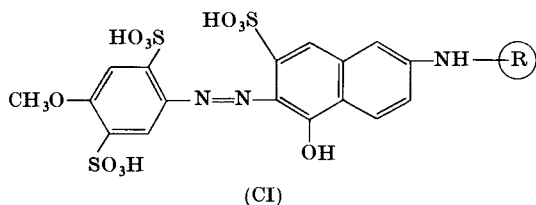


⁶⁵ ICI, *USP* 2,951,071 (27.10.1958).

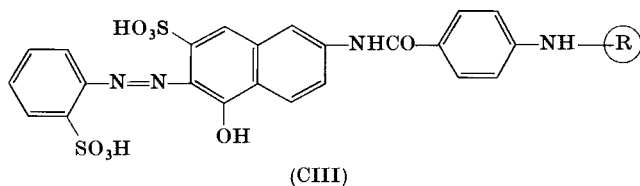
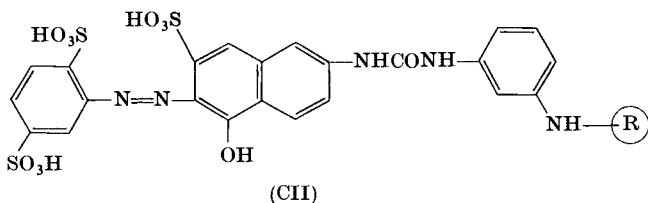
⁶⁶ CFM, *DAS* 1,246,905 (22.4.1962).

⁶⁷ ICI, *DAS* 1,113,050 (26.3.1958); CIBA, *DAS* 1,101,657 (14.9.1956).

To increase solubility in dyestuffs of this type 2-amino-5-hydroxy-naphthalene-1,7-disulfonic acid is used as coupling component, or 1-amino-4-methoxybenzene-2,5-disulfonic acid as diazonium component.⁶⁸



To synthesize dyestuffs with a higher affinity for cotton, which are particularly suitable for dyeing from a long liquor, reactive component and dyestuff component are separated by amide or urea groups. The following compounds are examples of this dyestuff type⁶⁹:

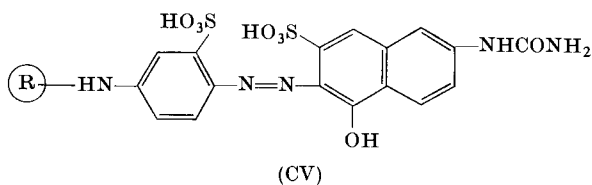
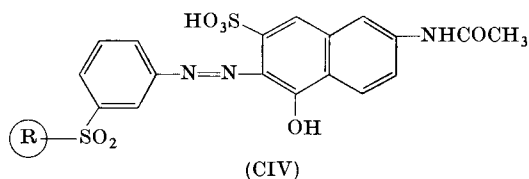


In addition to dyestuffs which carry the reactive residue on the amino group of J-acid, compounds are described in which diazonium compounds bearing reactive groups are coupled with *N*-acylated J-acid.⁷⁰

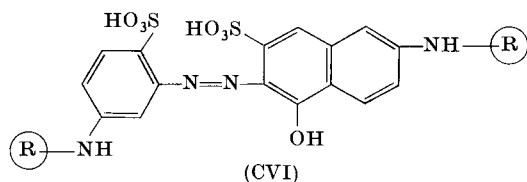
⁶⁸ FBy, *BeP* 741,344 (6.11.1968).

⁶⁹ Gy, *SP* 460,205 (17.3.1961); CIBA, *DAS* 1,101,657 (14.9.1956); S, *SP* 370,855 (19.9.1958).

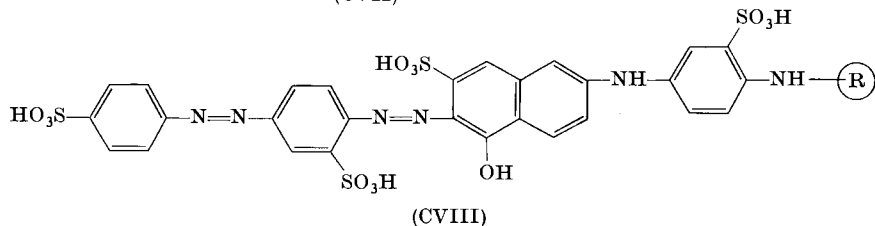
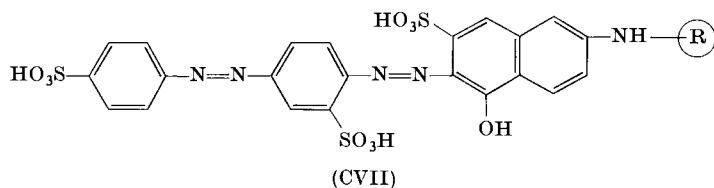
⁷⁰ J. Panchartek, Z. J. Allan, and J. Poskocil, *Collect. Czech. Chem. Commun.* **27**, 268 (1962); CIBA, *DAS* 1,112,225 (14.9.1957).



If reactive components are used as acylating agents, "bifunctional" dyestuffs are obtained, which are generally notable for a higher fixation yield in the reaction with the fiber.⁷¹



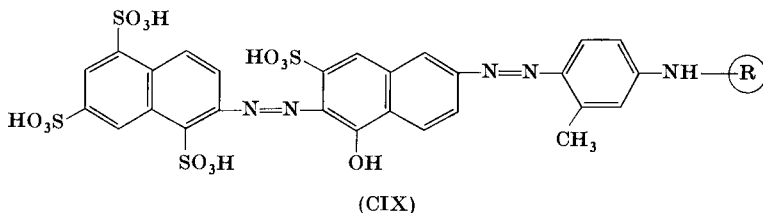
Disazo dyes containing J-acid as a middle or end component give predominantly bluish red to blue shades.⁷²



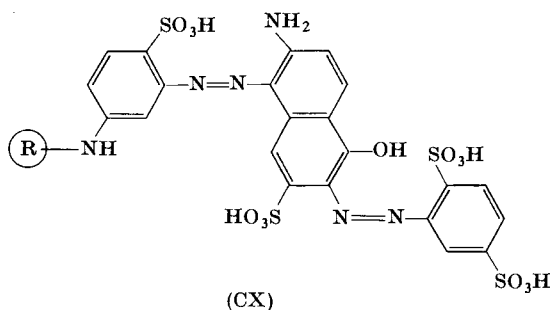
⁷¹ S, *BeP* 590,451 (6.5.1959); Fran, *FP* 1,308,044 (22.9.1961); ICI, *BeP* 591,077 (11.3.1959).

⁷² CIBA, *SP* 350,388 (3.7.1956); *DAS* 1,151,625 (14.9.1956); ICI, *FP* 1,264,022 (20.5.1959).

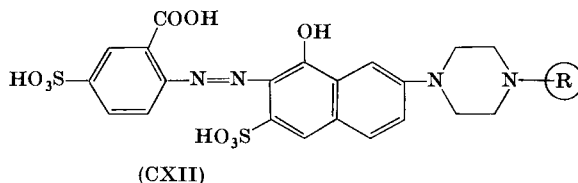
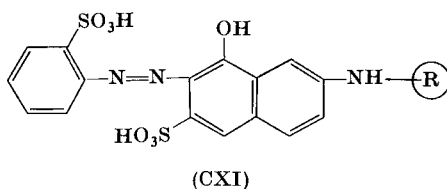
If 2-amino-6-aryldazo derivatives obtained by coupling in the 6-position are diazotized and coupled with aniline derivatives, very heavy red shades are obtained.⁷³



Similar shades are possessed by *o*-amino-*o*-hydroxydisazo dyes obtained by double coupling.⁷⁴



Compared with *o*-hydroxyazo derivatives of J-acid, the corresponding dyes from γ -acid have less practical importance.⁷⁵

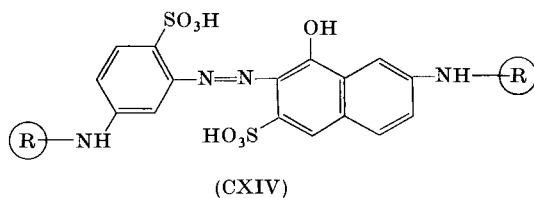
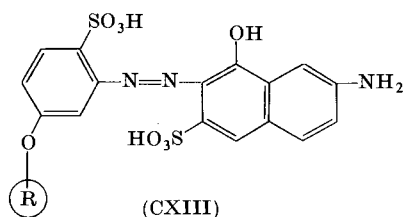


⁷³ Gy, *BeP* 654,651 (22.10.1963).

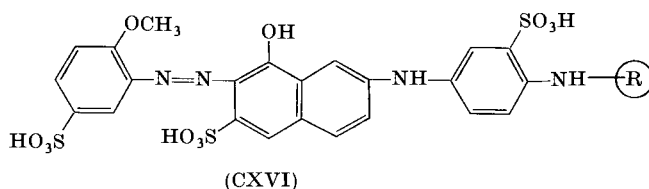
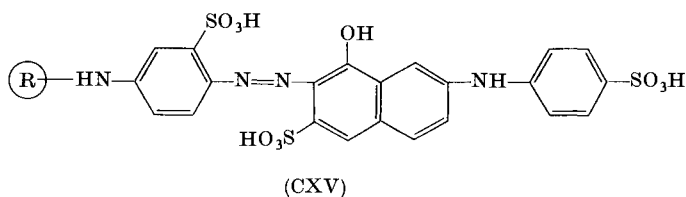
⁷⁴ ICI, *FP* 1,365,387 (15.5.1962).

⁷⁵ S, *BP* 916,094 (28.5.1958); ICI, *BP* 957,445 (10.4.1961).

This also applies to derivatives obtained by coupling with diazonium compounds containing reactive groups, and also to the bifunctional dyes of this range.⁷⁶



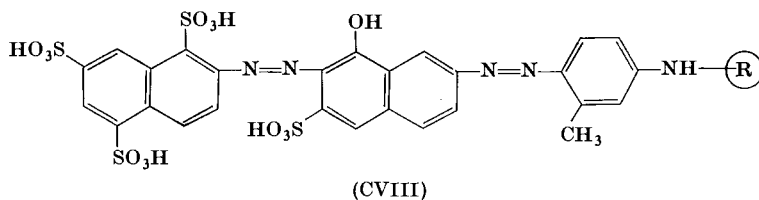
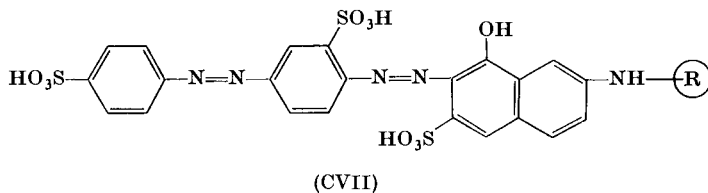
Only the coupling products of 2-arylamino-8-hydroxynaphthalene-6-sulfonic acid, which are used in the production of bright brown shades,⁷⁷ are outstanding.



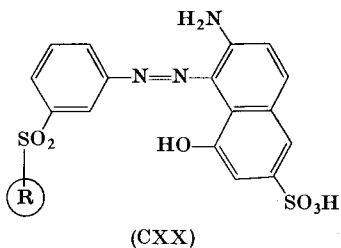
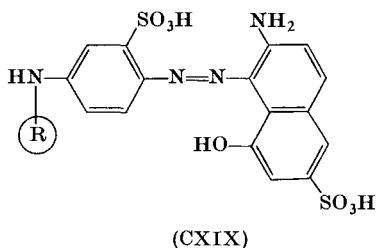
⁷⁶ S, BP 916,094 (28.5.1958).

⁷⁷ ICI, BP 923,887 (24.3.1959); FP 1,264,094 (19.5.1959).

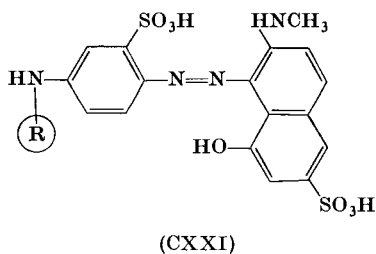
Finally, the following disazo dyes, with which bright red shades can be obtained, may also be mentioned⁷⁸:



Of much more practical importance are the *o*-aminoazo dyestuffs from γ -acid as reactive dyes for synthetic and natural polyamides.⁷⁹



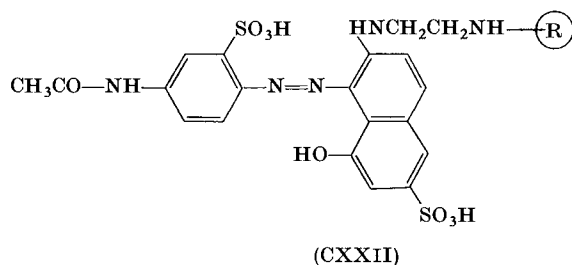
The derivatives substituted in the amino group are also often used.⁸⁰



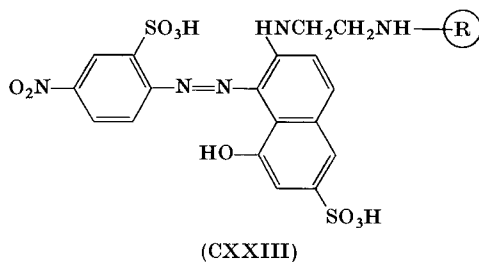
⁷⁸ CIBA, *SP* 350,052 (29.8.1956); Gy, *BeP* 654,651 (22.10.1963).

⁷⁹ ICI, *SP* 228,212 (11.11.1940); CIBA, *BP* 879,642 (19.2.1959); *DAS* 1,058,467 (11.1.1957); BASF, *BeP* 573,862 (13.12.1957); FH, *BP* 1,033,267 (28.2.1963).

⁸⁰ CIBA, *BeP* 693,749 (8.2.1966); BASF, *DAS* 1,127,016 (7.12.1957).

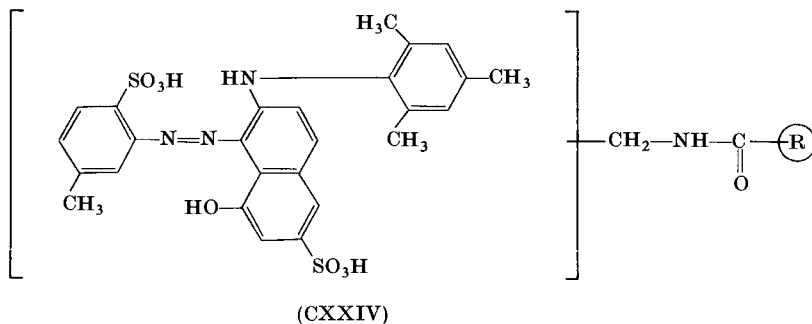


The use of nitroaniline derivatives as diazonium components, e.g., of 4-nitroaniline-2-sulfonic acid, leads to the synthesis of blue reactive dyes.⁸¹



As a further possibility of introducing the reactive residue, the Einhorn reaction may be mentioned, according to which reactive systems containing methylolcarbamide groups can be condensed in sulfuric acid with azo compounds.

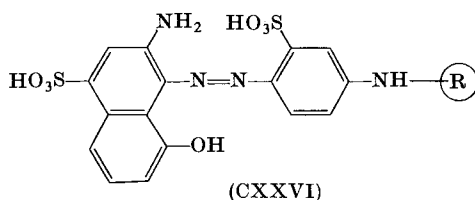
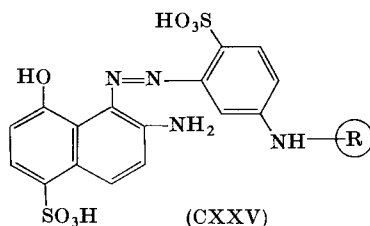
In many cases, no precise information is given regarding the type of substitution.⁸²



⁸¹ BASF, DAS 1,127,016 (7.12.1957).

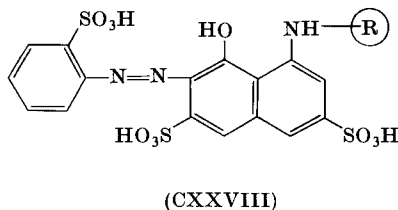
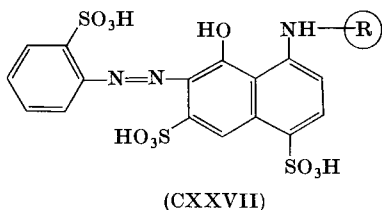
⁸² S, USP 3,158,597 (24.6.1960).

Of the various isomers and derivatives of 2-amino-8-hydroxynaphthalenesulfonic acid, dyes from the 4- and 5-sulfonic acids must also be mentioned,⁸³



as well as coupling products of 2-amino-8-hydroxynaphthalene-3,6-disulfonic acid.⁸⁴

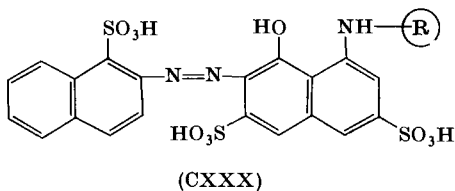
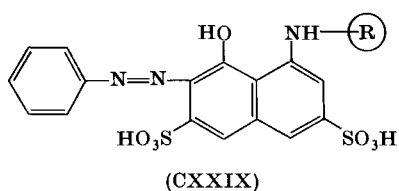
The hard core of most commercial reactive ranges in the field of brilliant red dyes is found in the coupling products of 1-amino-8-naphtholdisulfonic acids, those of 1-amino-8-naphthol-3,6- and 4,6-disulfonic acids being mainly used. The coupling products of 1-amino-8-naphthol-4,6-disulfonic acid give predominantly more yellowish and more brilliant dyes than the corresponding derivatives of the 3,6-disulfonic acid,⁸⁵



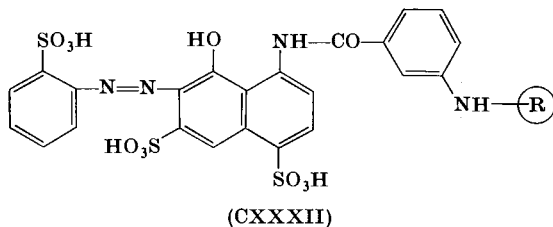
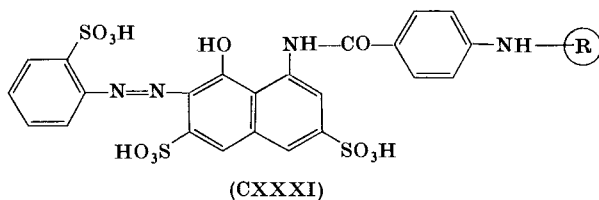
⁸³ FBY, *BeP* 683,357 (30.6.1965); *DOS* 1,937,361 (23.7.1969).

⁸⁴ CFM, *DAS* 1,092,144 (22.2.1958).

⁸⁵ ICI, *USP* 2,892,829 (29.11.1954); *DAS* 1,103,483 (23.4.1957); CIBA, *GE* 436,179 (9.1.1923); ICI, *DAS* 1,088,633 (26.6.1957).



while the fastness to light and chlorine of the dyestuffs derived from 2-naphthylamine-1-sulfonic acid as diazonium component are particularly outstanding.⁸⁶ Synthesis of these dyes is generally effected by coupling diazonium salts with 1-amino-8-naphtholdisulfonic acids substituted "reactively" in the amino group, but can also be achieved by final condensation of the aminoazo compound with the reactive component. If a separation of dyestuff and reactive component is required, for example, for reasons associated with brightness of shade or modification of the reactivity, this can be achieved by introduction of bridge links. In this connection, aminobenzoylamino compounds obtained by acylation of the amino groups with *m*- or *p*-nitrobenzoyl chloride and subsequent reduction of the nitro group are mainly used, as in the dyestuffs⁸⁷ (CXXXI) and (CXXXII),

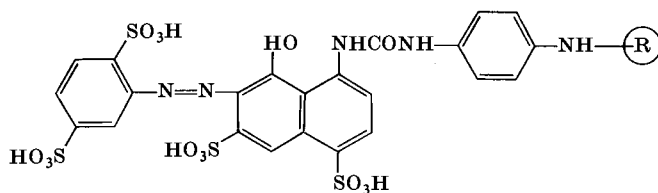


or linking takes place through a urea group.⁸⁸

⁸⁶ E. Siegel, *Chimia (Aarau)* Suppl., p. 100 (1968).

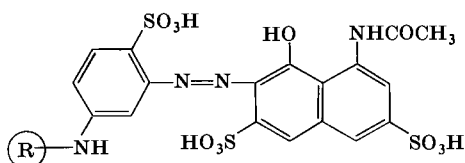
⁸⁷ S, *FP* 1,246,743 (10.11.1958); *SP* 370,855 (19.9.1958).

⁸⁸ Gy, *BeP* 615,215 (17.3.1961).

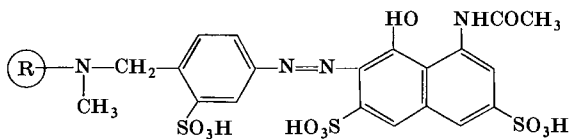


(CXXXIII)

Moreover, brilliant red dyes of this type are produced by coupling of diazonium compounds containing reactive groups with *N*-acyl H-acid⁸⁹:

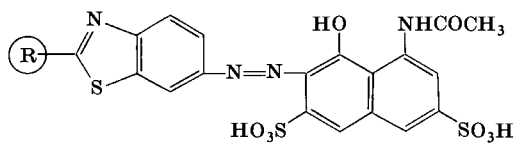


(CXXXIV)

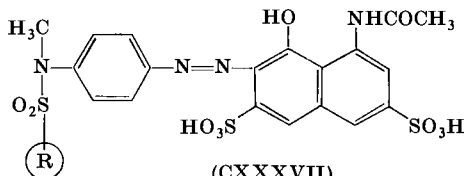


(CXXXV)

This method of synthesis is particularly important for those reactive dyes which contain aromatic-bound amino groups, e.g., in the following dyestuffs⁹⁰:



(CXXXVI)



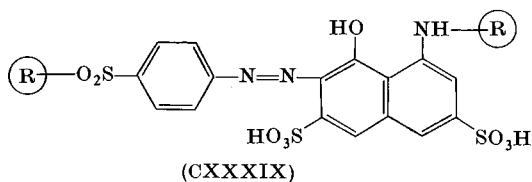
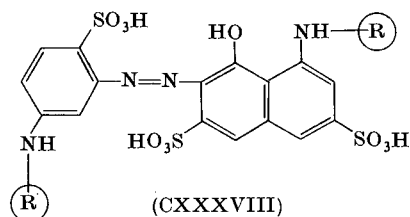
(CXXXVII)

⁸⁹ ICI, *BeP* 568,297 (5.6.1957); CIBA, *FP* 1,203,681 (26.3.1957); FBY, *BeP* 652,741 (12.9.1963).

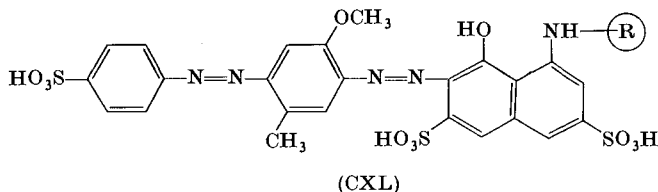
⁹⁰ FBY, *FP* 1,480,931 (24.5.1965); FH, *DAS* 1,204,762 (22.7.1960).

If in this case condensed aromatic heterocyclic compounds are used as diazonium components, the shade undergoes a marked change to bluish red.

Combination of both types of linkage—reactive group in the diazonium and in the coupling components—also leads to the production of dye-stuffs which react with the fiber with very high yields. In the synthesis of these reactive dyes, the same or different reactive components may be used.⁹¹



H-acid derivatives as end components in disazo dyestuffs give violet to blue shades.⁹²

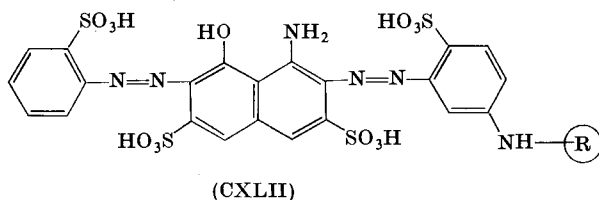
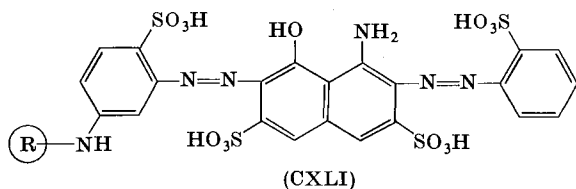


These dyes have, however, not yet achieved any considerable importance. On the other hand, from disazo dyes containing H-acid as middle component are derived the reactive black brands with the highest turnover. Diazonium compounds containing reactive groups may be coupled in the *o*-position both to the amino and the hydroxy group.⁹³

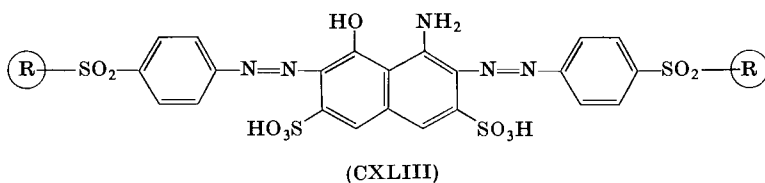
⁹¹ ICI, OS 1,469,778 (7.4.1964); BASF, FP 1,228,601 (10.6.1958).

⁹² ICI, DAS 1,102,319 (12.8.1958).

⁹³ FBy, BeP 707,573 (5.12.1966); CIBA, BeP 617,936 (22.5.1962); BP 959,314 (16.2.1960).



Moreover, the combination of two diazonium compounds containing reactive groups with H-acid is noteworthy.⁹⁴



Methods of Production

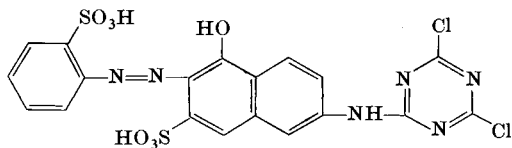
(1) Dyestuff of formula (XCIV)⁶³

With cyanuric chloride as reactive component.

A solution of 18.5 parts of cyanuric chloride in 100 parts of acetone is poured into a stirred mixture of 400 parts of water and 400 parts of crushed ice, and 2 parts of 2 *N* hydrochloric acid is added. To the suspension of cyanuric chloride thus obtained are added during 40 minutes, and at a temperature below 5°, 26.1 parts of the sodium salt of J-acid as a solution in 480 parts of water, made slightly alkaline to Brilliant Yellow by addition of sodium carbonate. The mixture is stirred at a temperature below 5° for 1 hour and then 6 parts of 2 *N* sodium carbonate is added and stirring is continued at the same temperature for another 20 minutes. A suspension of the diazo compound from 16.45 parts of aniline-2-sulfonic acid, obtained by diazotizing in a mixture of 200 parts of water and 18 parts of hydrochloric acid (specific gravity 1.18) at a temperature between 0° and 2° with 6.55 parts of sodium nitrite, is then

⁹⁴ FH, GE 960,534 (9.1.1950).

added to the mixture during 5 minutes at a temperature between 0° and 4°. Forty parts of sodium acetate crystals are added during 10 minutes and the mixture is stirred at 0–4° for 90 minutes, after which time sufficient anhydrous sodium carbonate is gradually added during a further 90 minutes to render the aqueous medium slightly alkaline to litmus. Sufficient sodium chloride to give a concentration of 200 g/liter is added and the mixture is stirred for 30 minutes, while the temperature is maintained between 0° and 4°; the mixture is filtered, the solid on the filter is washed with 20% brine and then with acetone, and dried at 20°–45°. The product forms a red-brown solid which dissolves in water to give an orange solution and in concentrated sulfuric acid to give a bluish red solution. This product in the form of its free acid has the formula



(2) Dyestuff of formula (CXX)⁷⁹

With the β -sulfatoethyl sulfone group as reactive residue.

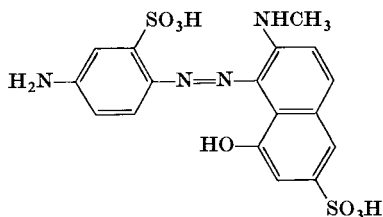
3-Aminophenyl β -hydroxyethyl sulfone sulfuric acid ester, 562 parts, is added to 2000 parts of water. By slow addition of a mixture of 206 parts of 33% potassium hydroxide solution and 206 parts of water the bulk of the acid ester is neutralized, the temperature being maintained at 0°–5° by adding about 1000 parts of ice. Subsequently, by introducing about 70 parts of sodium bicarbonate the pH is adjusted to 6.8–7.2 and the solution clarified. The filtrate is mixed with 600 parts of concentrated hydrochloric acid and then cooled to 5–8° by adding about 2000 parts of ice. At this temperature 400 parts by volume of 5 *N* sodium nitrite solution is added during 90 minutes, the mixture stirred for 1 hour, and the excess nitrous acid decomposed by addition of a small amount of sulfamic acid. The diazonium salt suspension is added to a suspension of the coupling component obtained by dissolving 478 parts of γ -acid in a mixture of 3000 parts of water and 242 parts of 33% sodium hydroxide solution and subsequent precipitation by means of a mixture of 294 parts of concentrated hydrochloric acid and 1300 parts of water. The pH of the mixture is adjusted to 1.0 by adding a small amount of sodium acetate and the temperature maintained at 16°. The mixture is stirred for 16 hours, the temperature being slowly raised to 25°. The mineral acid liberated during the coupling causes the pH to decrease to 0.6–0.7. By addition of sodium acetate the pH is readjusted to 1.0, the

solution stirred for another 2 hours at 25°, and the pH then once more adjusted to 3.7–3.8 by means of sodium acetate. The dyestuff is precipitated with potassium chloride, filtered with suction, dried, and ground. Yield: 1708 parts of a brown-red powder containing 2.95% of azo nitrogen. The dyestuff dyes wool in an acid or neutral bath in clear red shades distinguished by excellent fastness properties, in particular by very good fastness to light, washing, perspiration, and milling.

(3) Dyestuff of formula (CXXI)⁸⁰

With dibromopropionyl chloride as reactive component.

Ninety grams of dyestuff of the formula



in 1000 ml of water is neutralized with sodium carbonate and 20 g of sodium bicarbonate is added. α,β -dibromopropionyl chloride, 56 g, is added with vigorous stirring at 5°–10° in 1 hour.

On completion of acylation, the pH is adjusted to 12 by addition of 30% caustic soda solution, the temperature being maintained below 15°. After stirring for a further 30 minutes, neutralization is obtained with 30% hydrochloric acid, the dyestuff is completely precipitated by salting out with sodium chloride and then isolated. The dyestuff paste is washed subsequently with 15% sodium chloride solution and vacuum-dried at 70°–80°. The bluish red powder obtained dissolves in water and gives bluish red shades on wool.

(4) Dyestuff of formula (CXXIV)⁸²

With the chloroacetyl group as reactive residue.

The red dye, 54.1 parts, obtained by acid coupling of diazotized 1-aminobenzene-2-sulfonic acid with 2-(2',4',6'-trimethylphenylamino)-8-hydroxynaphthalene-6-sulfonic acid, is dissolved with stirring in 300 parts of 96% sulfuric acid at 15–20°. On cooling to 0–5°, 25 parts of *N*-hydroxymethylchloroacetamide are added in portions and the temperature is increased to 20° in 1 hour. The mass is run into 1200 parts of ice and stirred until the temperature decreases to 10°. The precipitated dye is filtered off, dissolved twice in 2000 parts of water, and reprecipi-

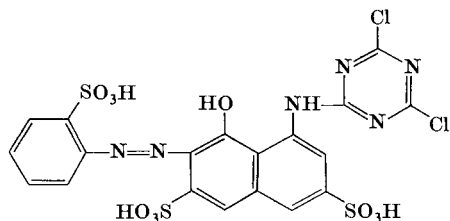
tated with 400 parts of common salt. It is filtered, washed with 20% common salt solution, dried under vacuum at room temperature over sulfuric acid, or at 35°–40° without a siccative. A red dye is obtained which dyes wool and nylon in shades fast to light and wet treatments.

(5) Dyestuff of formula (CXXVIII)⁸⁵

With cyanuric chloride as reactive component.

A solution of 18.5 parts of cyanuric chloride in 100 parts of acetone is poured into a stirred mixture of 300 parts of water and 300 parts of crushed ice, and 2 parts of 2 *N* hydrochloric acid is added. To the suspension of cyanuric chloride thus obtained is added during 1 hour a solution of 36.3 parts of the disodium salt of H-acid in 160 parts of water, which has been made slightly alkaline to Brilliant Yellow by addition of aqueous sodium carbonate solution, the temperature of the mixture during and subsequent to the addition being kept below 5°. The reaction mixture is stirred until no unchanged H-acid remains in the resulting solution.

A suspension of the diazo compound from 16.45 parts of aniline-2-sulfonic acid, obtained by diazotizing a mixture in 200 parts of water and 22 parts of hydrochloric acid (density 1.18) at a temperature between 0° and 2° with 6.55 parts of sodium nitrite, is added to the mixture during 5 minutes while the temperature is maintained between 0° and 5°. Fifty parts of sodium acetate crystals is added during 10 minutes and the mixture is then stirred for about 20 hours at a temperature between 0° and 4°, after which time sufficient anhydrous sodium carbonate is added to render the aqueous medium slightly alkaline to litmus. Sufficient sodium chloride to give a concentration of 200 g/liter is added and the mixture is stirred for 30 minutes and then filtered. The solid on the filter is washed with 20% aqueous sodium chloride solution and dried at 20°–45°. The product forms a bluish red powder which dissolves in water to give a yellowish red solution and in concentrated sulfuric acid to give a reddish violet solution. This dyestuff has, in the form of its free acid, the formula

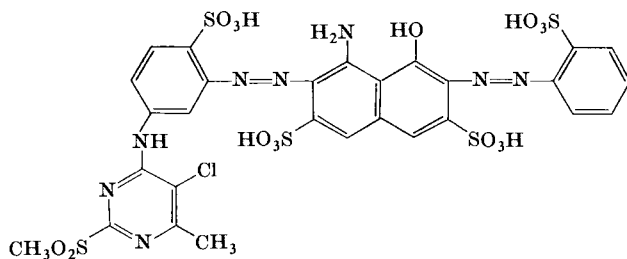


When applied to cellulosic fibers, e.g., cotton, with subsequent treatment with an acid-binding agent, yellowish red shades are obtained possessing very good fastness to repeated washing and good fastness to light.

(6) Dyestuff of formula (CXLII)⁹³

With 2-methylsulfonyl-4,5-dichloro-6-methylpyrimidine as reactive component.

One-tenth of a mole of the condensation product obtained (according to the specifications of example 356 of Belgian patent 673,572) from 19 parts by weight of 1,3-diaminobenzene-4-sulfonic acid and 24 parts by weight of 2-methylsulfonyl-4,5-dichloro-6-methylpyrimidine is dissolved in 700 parts by volume of cold water, treated with 28 parts by volume of hydrochloric acid, and diazotized by addition of 25 parts by volume of 30% sodium nitrite solution. The suspension of the diazonium compound thus obtained is added to the freshly prepared suspension of 0.1 mole of H-acid in 800 parts by volume of water and 20 parts by volume of concentrated hydrochloric acid. After thorough mixing of the suspensions, 150 parts by volume of a 20% sodium acetate solution is added in 15 minutes. The reaction mixture is stirred for 4 hours at a pH of 2-3. After completion of coupling, the solution of the monoazo compound thus obtained is treated with a suspension of the diazonium compound produced in the usual way from 0.1 mole of 1-aminobenzene-2-sulfonic acid. A further 200 parts by volume of a 20% sodium acetate solution is then added and the reaction mixture is stirred for 12 hours. When the second coupling is completed, the dyestuff is precipitated with 500 parts by weight of sodium chloride and 350 parts by weight of potassium chloride, isolated, and vacuum-dried at 60°. The disazo dyestuff obtained has the following formula:



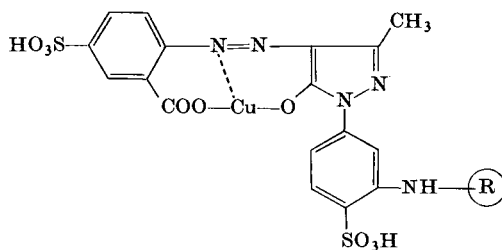
The dried product is a dark powder which dissolves in water to give a blue-gray solution. It produces blue-gray shades on cotton when applied by the usual reactive printing or reactive dyeing processes.

E. METAL COMPLEX DYES

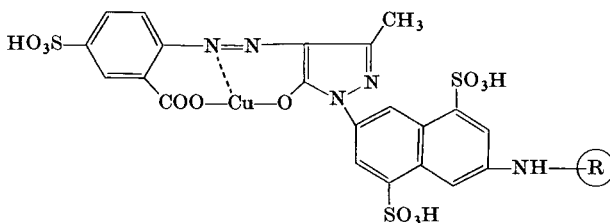
To produce highly lightfast reactive dyes in the shade range of yellow, rubine, violet, blue, brown, olive, and black, metal complexes obtained from *o,o'*-disubstituted azo compounds are mainly used. Reactive dyestuffs are synthesized not only from copper complexes, which are used mainly as direct cotton dyes, but also from chrome and cobalt complexes used up to the present almost exclusively as wool dyestuffs. These less substantive dyes are often used in textile printing and in continuous processes, while the planar copper complexes are also suitable for dyeing from a long liquor.

1. *Copper Complexes*

Copper complexes of azo dyestuffs derived from pyrazolone give yellow and brown shades, the yellow range being obtained through the coupling products of anthranilic acids⁹⁵



(CXLIV)

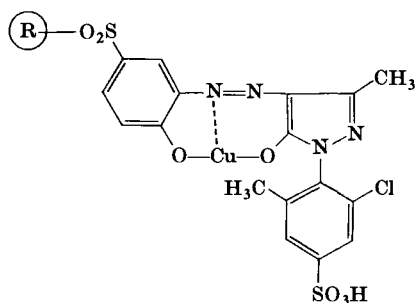


(CXLV)

or by use of aminophenol sulfones⁹⁶

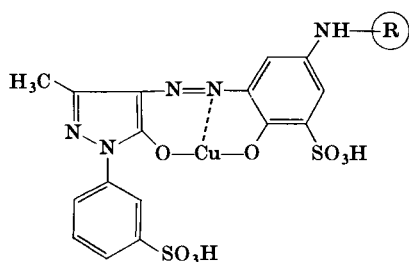
⁹⁵ ICI, *BP* 878,726 (10.4.1959); FBy, *FP* 1,388,578 (18.4.1963).

⁹⁶ FH, *DAS* 1,126,542 (26.3.1958).

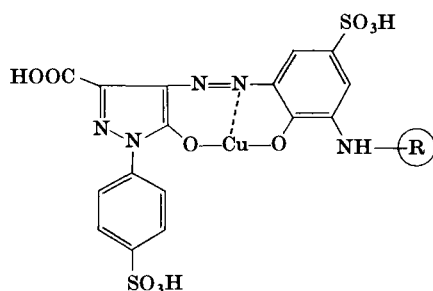


(CXLVI)

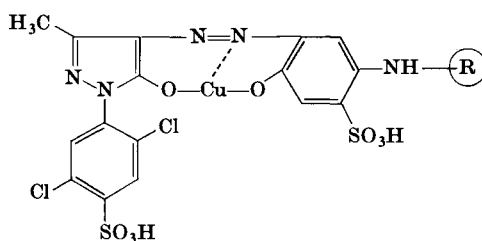
On the other hand, diaminophenol derivatives as diazo components generally lead to browner shades, e.g.,⁹⁷



(CXLVII)



(CXLVIII)



(CXLIX)

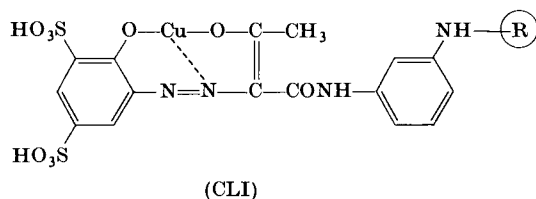
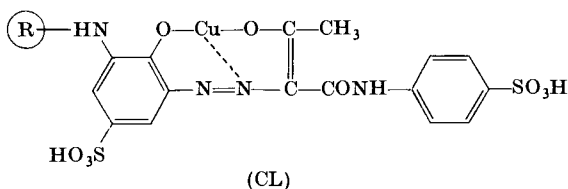
These dyestuffs are synthesized mainly by condensation of the aminoazo metal complexes with the reactive components, the amines being produced either by hydrolysis of acylamino compounds or by reduction of dyestuffs containing nitro groups. The use of *o*-hydroxydiazonium compounds containing reactive groups is, however, also described.⁹⁸

⁹⁷ S, *DAS* 1,248,189 (10.2.1961); FBy, *DAS* 1,230,944 (1.2.1963).

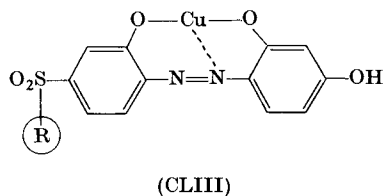
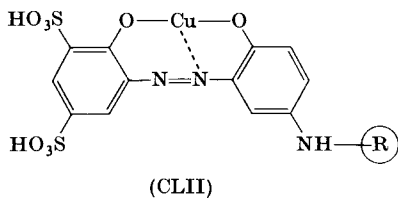
⁹⁸ FBy, *DAS* 1,230,944 (1.2.1963); FH, *DAS* 1,126,542 (26.3.1958).

Copper complexes produced from coupling products of acetoacetic arylides have not attained much practical importance up to the present.

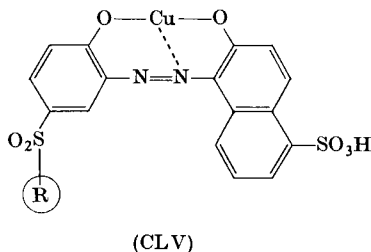
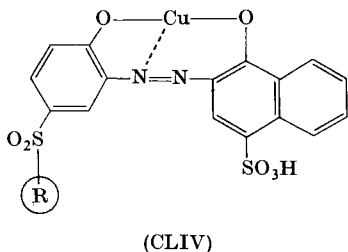
The following compounds are examples of the dyestuffs described in patent literature⁹⁹:



The practical importance of copper complexes of the *o,o'*-dihydroxyazo-benzene type is also not very great. The shades of these dyestuffs are generally violet to brown.¹⁰⁰



Red and violet dyestuffs of greater practical importance can be obtained by use of 1- or 2-naphtholsulfonic acids.¹⁰¹



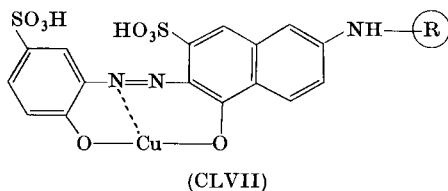
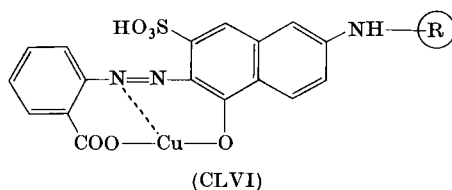
⁹⁹ ICI, *FP* 1,240,423 (28.11.1958); *BP* 878,726 (10.4.1959).

¹⁰⁰ S, *BeP* 608,445 (11.10.1960); FH, *BeP* 652,985 (11.9.1963).

¹⁰¹ FH, *DAS* 1,126,542 (26.3.1958).

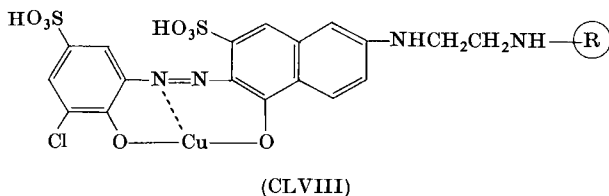
These dyestuffs are obtained by coupling diazonium compounds containing reactive groups with the appropriate coupling components and subsequent conversion to the copper complex. In this case, in addition to the direct copper treatment of *o,o'*-dihydroxyazo compounds, copper treatment by oxidation plays a greater rôle since it can proceed under conditions which do not impair the reactive component.¹⁰¹ The most important copper complex reactive dyestuffs are obtained with aminonaphtholsulfonic acids as coupling components.

Diazonium compounds of the benzene series and J-acid as coupling component give orange-brown and violet shades.¹⁰²



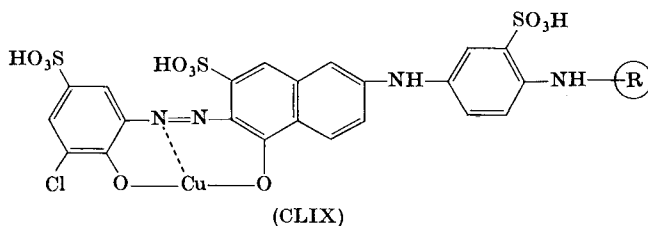
These dyes are generally synthesized by condensation of the aminoazo metal complex dyestuff with the reactive component.

In addition to the dyestuffs which contain the reactive component directly linked to the amino group, those compounds which have a bridge member between amino group and reactive component are also of practical importance. Alkyl, aryl, and acyl groups are described as bridge members, e.g.,¹⁰³

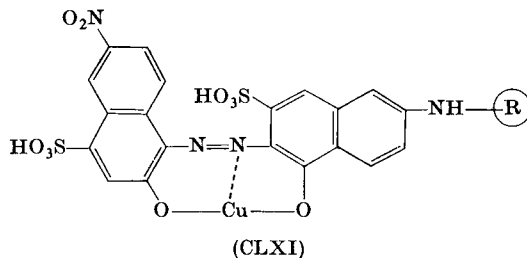
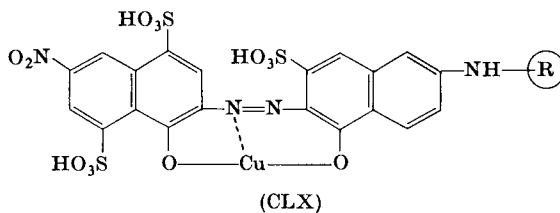


¹⁰² ICI, *DAS* 1,135,591 (5.7.1957); CIBA, *DRP* 528,166 (8.10.1927).

¹⁰³ Gy, *DAS* 1,227,587 (30.11.1960); ICI, *DAS* 1,175,809 (20.5.1959).



Much bluer shades are obtained with copper complex reactive dyes of the azonaphthalene series.¹⁰⁴



In addition to the analogous dyestuffs derived from 2-amino-5-hydroxynaphthalene-1,7-disulfonic acid,¹⁰⁵ 2-amino-8-hydroxynaphthalene-6-sulfonic acid,¹⁰⁶ 2-amino-8-hydroxynaphthalene-3,6-disulfonic acid,¹⁰⁷ 1-amino-5-hydroxynaphthalene-7-sulfonic acid,¹⁰⁸ and from 2-amino-3-hydroxynaphthalene-7-sulfonic acid and 2-amino-3-hydroxynaphthalene-6-sulfonic acid or -6,8-disulfonic acid,¹⁰⁹ 2-amino-5-hydroxynaphthalene-4,8-disulfonic acid and 2-amino-6-hydroxynaphthalene-8-sulfonic acid are also of practical importance in the production of blue reactive dyestuffs.¹¹⁰

¹⁰⁴ FBy, *BeP* 619,107 (22.6.1961); CIBA, *DAS* 1,106,896 (10.10.1957).

¹⁰⁵ ICI, *DAS* 1,089,098 (5.7.1957); 1,175,809 (20.5.1959).

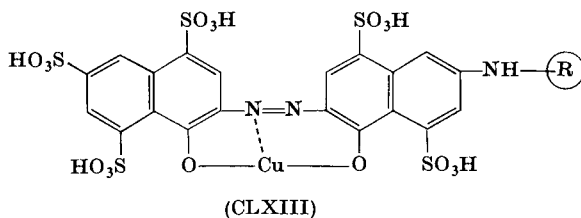
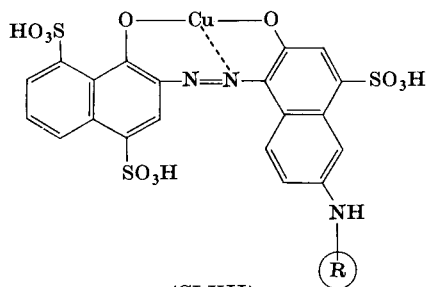
¹⁰⁶ ICI, *DAS* 1,135,591 (5.7.1957).

¹⁰⁷ FBy, *DAS* 1,186,160 (17.2.1961).

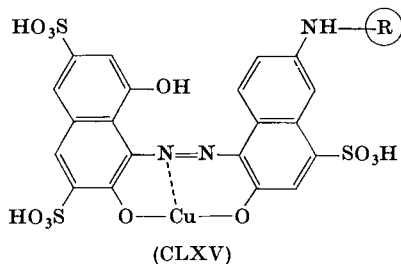
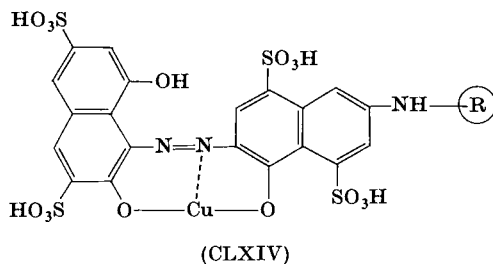
¹⁰⁸ CIBA, *DAS* 1,134,169 (13.10.1958).

¹⁰⁹ S, *DAS* 1,226,729 (14.10.1960).

¹¹⁰ Gy, *BeP* 596,941 (13.11.1959); CIBA, *DAS* 1,136,437 (27.8.1958); FBy, *BeP* 619,104 (22.6.1961); S, *BeP* 598,831 (29.1.1960).



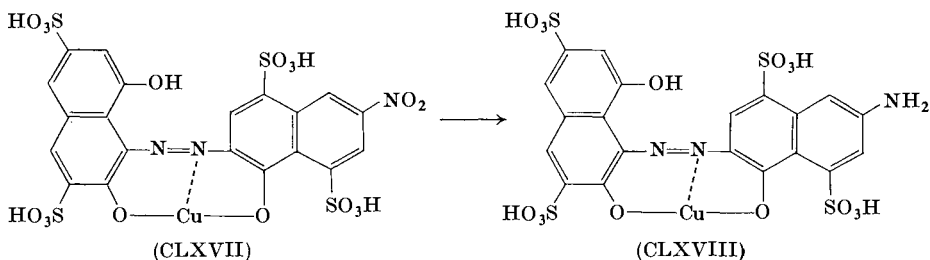
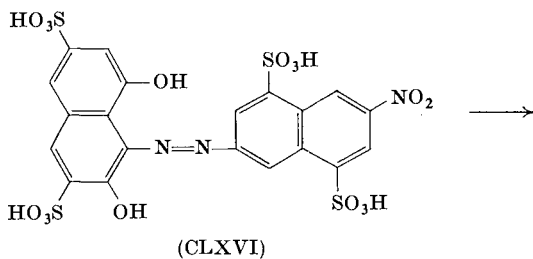
Particularly bright, greenish blue dyestuffs are obtained when 1-azonaphthalene copper complexes carry a hydroxyl group in the 8-position.¹¹¹



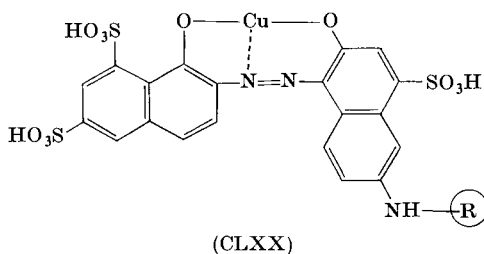
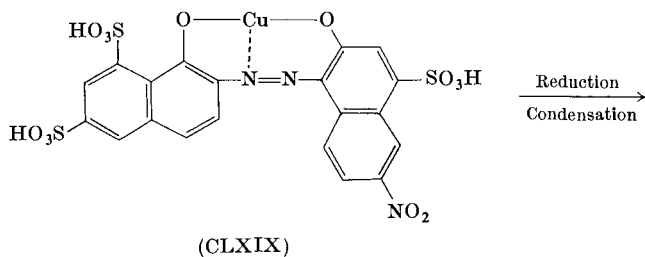
In addition to the synthesis of these dyestuffs by coupling of diazonium compounds of the naphthalene series with aminonaphtholsulfonic acids, conversion to the copper complex, and final condensation with the

¹¹¹ FBy, *BeP* 626,035 (14.12.1961).

reactive component, synthesis by coupling of nitronaphthalenediazonium compounds with hydroxynaphthalenesulfonic acids, conversion to the copper complex, reduction of the nitro group, and condensation with the reactive component also possesses practical importance¹¹¹:

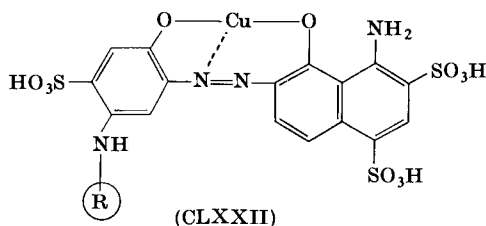
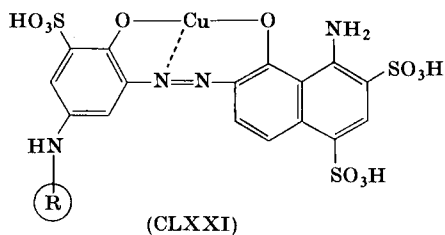


This procedure is adopted almost exclusively for dyes derived from 2-hydroxy-6-aminonaphthalene-4-sulfonic acid. In this case, 1-diazo-2-hydroxy-6-nitronaphthalene-4-sulfonic acid is used as diazonium component.¹¹²

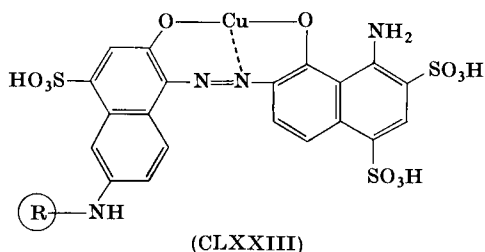


¹¹² Gy, *BeP* 596,941 (13.11.1959); CIBA, *DAS* 1,136,437 (27.8.1958).

An outstanding position in the production of bright blue dyestuffs—particularly of the navy blue type—is occupied by 1-amino-8-naphthol-2,4-disulfonic acid (Chicago acid).¹¹² Reddish blue dyes are obtained with diazonium compounds of the benzene series¹¹³

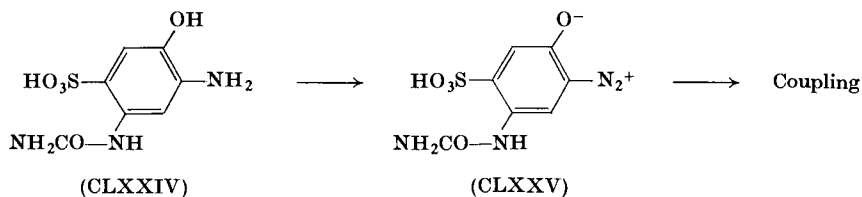


while diazonium components of the naphthalene series give more greenish dyestuffs.¹¹²



The reduction of these primarily formed nitroaminoazo copper complexes often gives rise to difficulties.

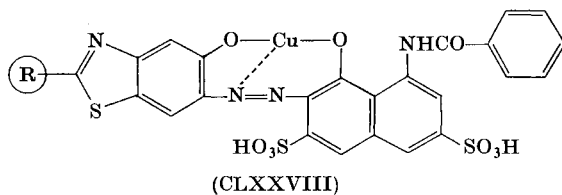
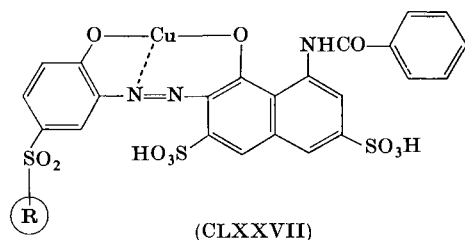
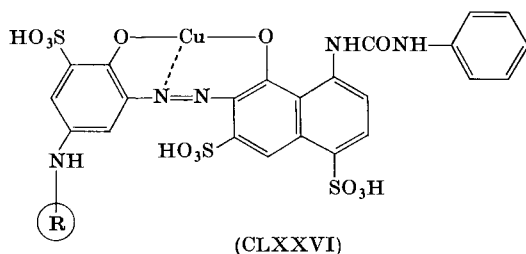
To avoid this step in the dyestuff synthesis ureidoaminohydroxybenzenesulfonic acids, for example, are used as diazonium component.¹¹⁴



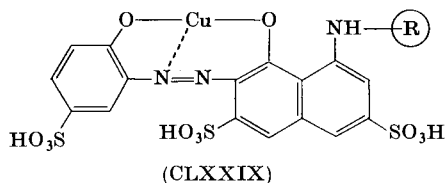
¹¹³ FBy, *DAS* 1,230,944 (1.2.1963); Gy, *BeP* 597,730 (4.12.1959).

¹¹⁴ FBy, *DAS* 1,230,944 (1.2.1963).

The change to bluer shades in the copper complexes with a 1-amino-8-hydroxynaphthalene configuration is also utilized in the copper complex derivatives of H-acid and K-acid. In this case, the reactive component can be incorporated either into the diazonium or the coupling component. The combination of both principles in the synthesis of bifunctional reactive dyes is also described. Suitable for the production of bluish violet dyestuffs are both the first type, in which the reactive residue is linked to a benzenoid diazonium component,¹¹⁵



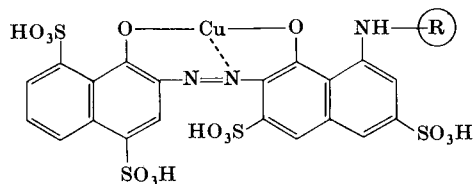
and also dyestuffs of the second type, in which the reactive residue is linked to the coupling component.¹¹⁶



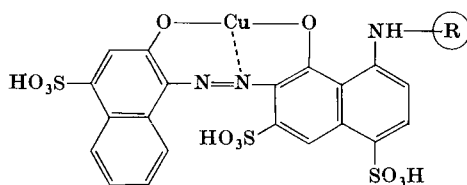
¹¹⁵ Gy, *BeP* 615,215 (17.3.1961); FH, *DAS* 1,126,542 (26.3.1958); Kuhlmann, *FP* 87,166/1,290,839 (12.1.1965); BASF, *FP* 1,390,080 (24.4.1963).

¹¹⁶ ICI, *DAS* 1,089,098 (5.7.1957); *BeP* 569,115 (15.7.1957).

In this case, however, it is primarily the copper complex compounds of the azonaphthalene series which are of practical importance in the production of navy blue reactive dyes¹¹⁷:



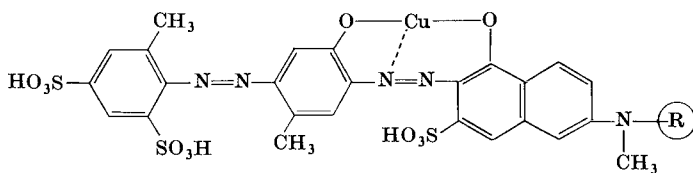
(CLXXX)



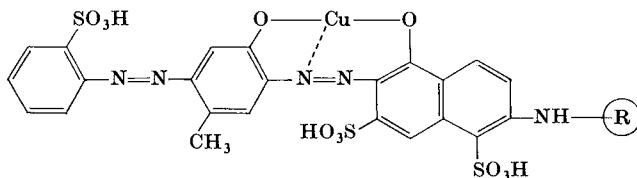
(CLXXXI)

a. Disazo Copper Complex Reactive Dyes. Disazo copper complex dyestuffs have practical importance for the synthesis of navy blue, gray, and brown reactive dyes. Among the large number of possible combinations the following types are outstanding:

(1) Coupling products of diazotized aminoazobenzene derivatives with aminonaphtholsulfonic acids¹¹⁸:



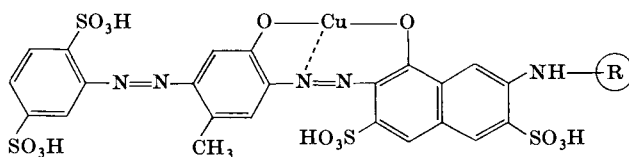
(CLXXXII)



(CLXXXIII)

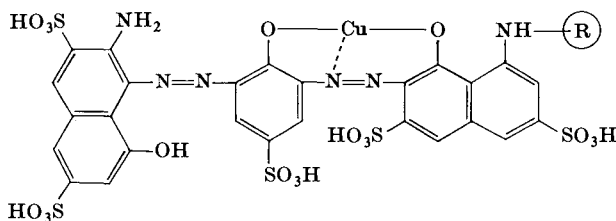
¹¹⁷ CIBA, DAS 1,223,971 (28.1.1960); Gy, BP 944,300 (27.1.1960).

¹¹⁸ FBy, BeP 642,886 (1.2.1963); ICI, DAS 1,156,914 (28.11.1958); FBy, DAS 1,186,160 (7.2.1961).



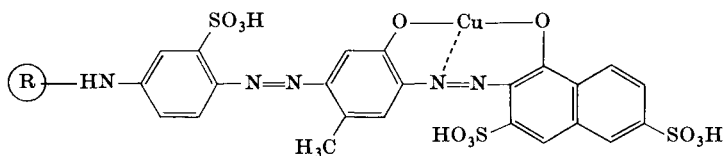
(CLXXXIV)

These dyes are generally synthesized by condensation of the aminodisazo copper complex dyestuff with the reactive component. Another sequence in the procedure is to apply, for example, the copper treatment by oxidation. An analogous dyestuff type with a *m*-disazo linkage in the middle component can be obtained, for example, by tetrazotization of 2,6-diaminophenol-4-sulfonic acid and coupling with azo components, one of which, at least, accepts a reactive residue.¹¹⁹

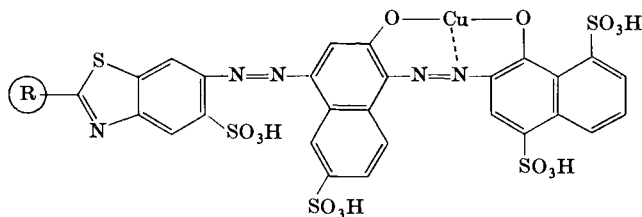


(CLXXXV)

(2) Coupling products of diazotized aminoazo compounds with naphthol-sulfonic acids¹²⁰:



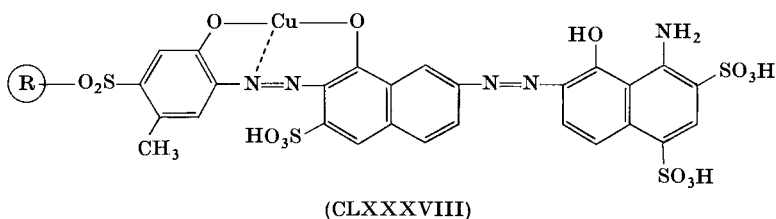
(CLXXXVI)



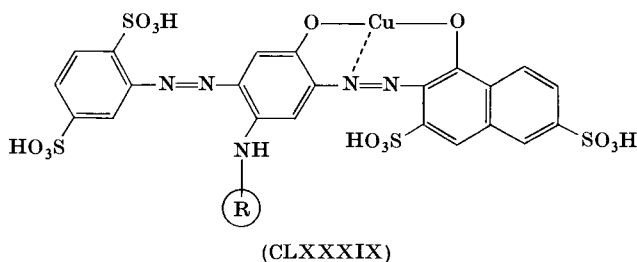
(CLXXXVII)

¹¹⁹ Gy, *FP* 1,288,305 (18.3.1960).

¹²⁰ Gy, *DP* 6,410,848 (18.9.1963); *BeP* 653,180 (18.9.1963); *FBY*, *DP* 6,607,156 (24.5.1965); *FH*, *BeP* 686,104 (28.8.1965).

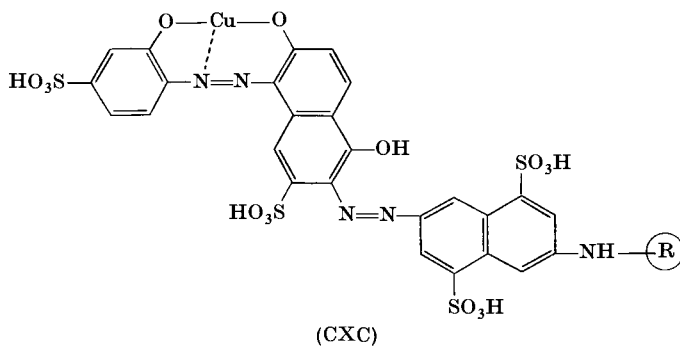


Dyestuffs of this type can be synthesized in such a manner that the middle component carries the reactive group.¹²¹



Moreover, these dyestuffs are starting products in the synthesis of Ni, Co, and Cr complex dyes.

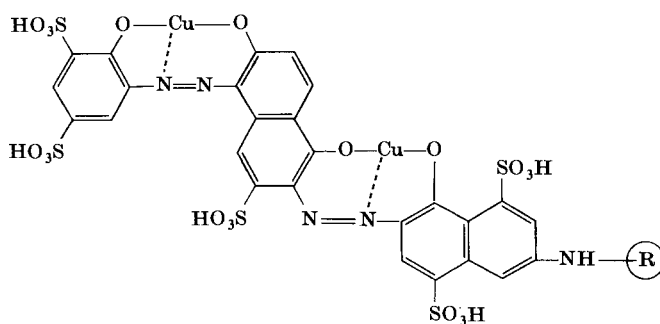
(3) Coupling products of diazotized amines containing reactive groups with copper complexes containing hydroxy groups¹²²:



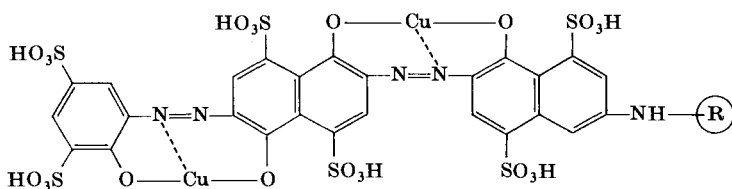
¹²¹ S, *SP* 473,874 (29.10.1965).

¹²² S, *FP* 1,486,850 (16.7.1965).

(4) Disazo dyestuffs in which each azo group participates in a copper complex group¹²³:



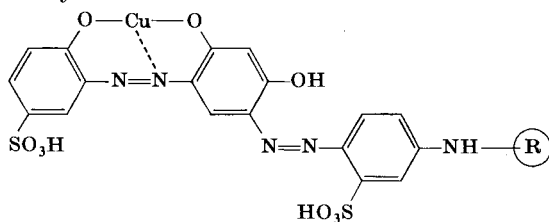
(CXCI)



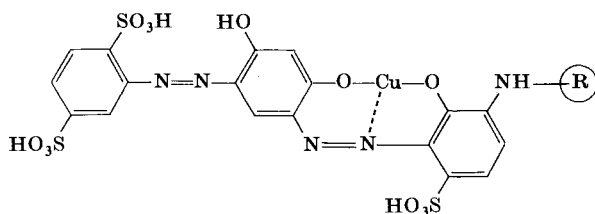
(CXCII)

The last two are blue-gray to greenish gray reactive dyes.

Resorcinazo copper complexes are also used in the production of brown reactive dyes.¹²⁴



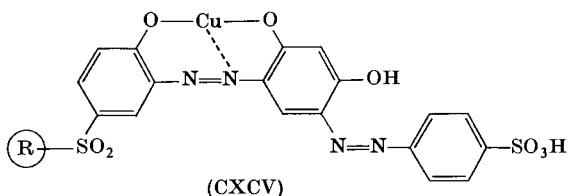
(CXCIII)



(CXCIV)

¹²³ S, *FP* 1,468,474 (19.2.1965); FBy, *DAS* 1,298,662 (7.9.1961).

¹²⁴ Gy, *DAS* 1,112,229 (23.5.1958); S, *BeP* 612,668 (13.2.1961); FH, *DAS* 1,233,963 (8.8.1963); S, *BeP* 600,169 (4.3.1960).

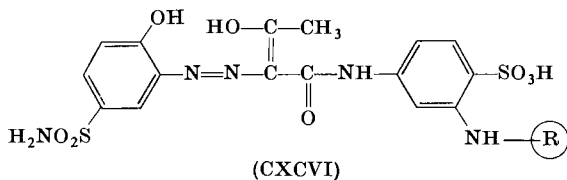


These dyestuffs are best synthesized by coupling of the hydroxymonoazo copper complex with the respective diazonium compounds.

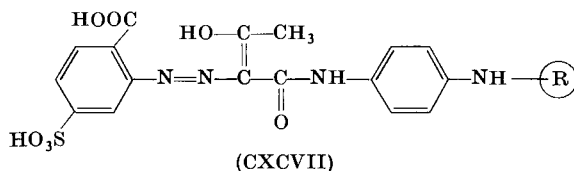
2. Chromium and Cobalt Complexes

Compared with copper complex dyes, chromium and cobalt complex dyestuffs are used mainly in the production of reactive dyes of heavier shades, predominantly brown, gray, and black shades. These reactive dyes are synthesized more often than in the case of corresponding copper complex derivatives through the metal complex aminoazo compounds, which are finally condensed with the reactive component. This is due to the reaction conditions in the metal complex formation. Although mainly symmetric 1:2 chromium and cobalt complex reactive dyes are represented in commercial ranges, numerous unsymmetrical complex dyestuffs of this type are also described. Intramolecular color mixtures can therefore be achieved, e.g., in olive dyestuffs, and also a better adaptation of reactive and dyestuff components.

Yellow chromium and cobalt complex dyes can be obtained from the coupling products of acetoacetic arylides.¹²⁵



1:2 Co complex

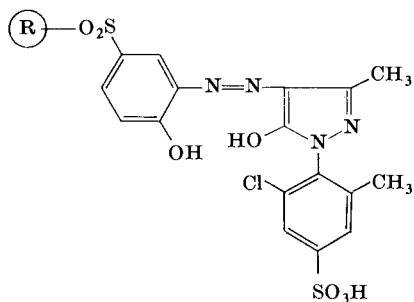


1:2 Cr complex

The color strengths of these products are often unsatisfactory.

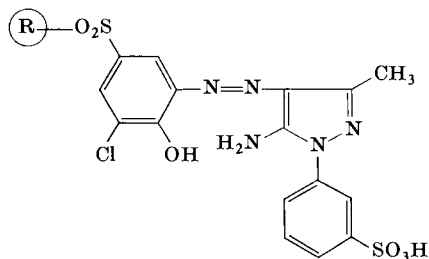
¹²⁵ CIBA, *BeP* 621,676 (24.8.1961); 570,122 (6.8.1957); S, *DAS* 1,222,607 (13.11.1961).

On the other hand, orange to brown shades are obtained from coupling products of pyrazole derivatives.¹²⁶



(CXC VIII)

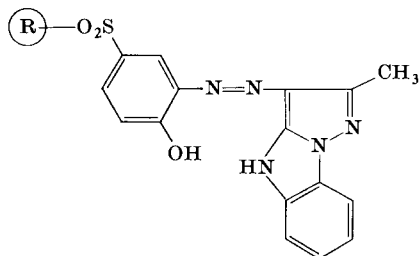
1:2 Cr complex



(CXC IX)

1:2 Co complex

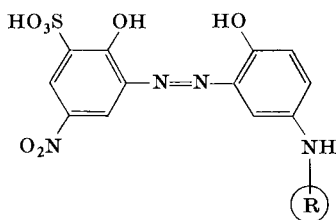
Conversion of the aminopyrazole type to the tricyclic system gives red-brown shades.¹²⁷



(CC)

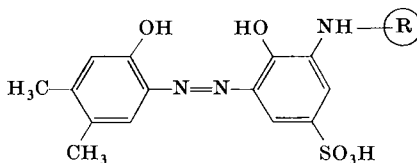
1:2 Co complex

In a similar manner, brown reactive dyes are obtained from chromium and cobalt complex compounds of *o,o'*-dihydroxyazobenzene.¹²⁸



(CCI)

1:2 Cr complex



(CCII)

1:2 Co complex

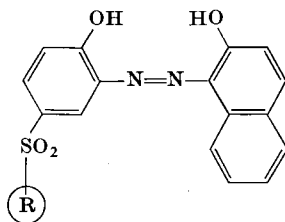
¹²⁶ FH, *FP* 1,219,489 (26.3.1958); FBy, *FP* 1,293,555 (29.3.1960).

¹²⁷ FBy, *DAS* 1,218,088 (23.12.1960).

¹²⁸ S, *BeP* 608,445 (11.10.1960); CIBA, *BeP* 570,122 (6.8.1957).

More important are, however, chromium and cobalt complex dyestuffs derived from benzeneazonaphthalene and from azonaphthalene.

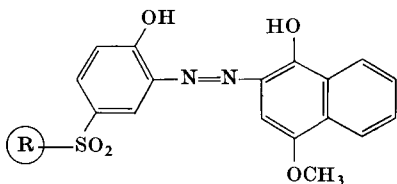
Coupling products of naphthol derivatives with *o*-hydroxydiazonium compounds of the benzene series give deep-bordeaux cobalt complex compounds,¹²⁹



(CCIII)

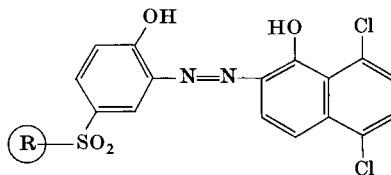
1:2 Co complex

while chromium complex dyestuffs of this type give blue shades.¹³⁰



(CCIV)

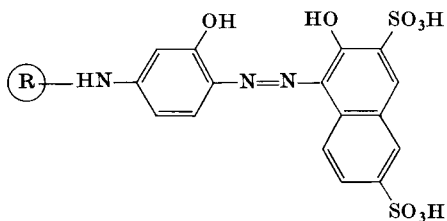
1:2 Cr complex



(CCV)

1:2 Cr complex

These dyestuffs, which are free from sulfonic groups, are used mainly for the dyeing of polyamide fibers, while the corresponding sulfonic acids also dye cotton.¹³¹



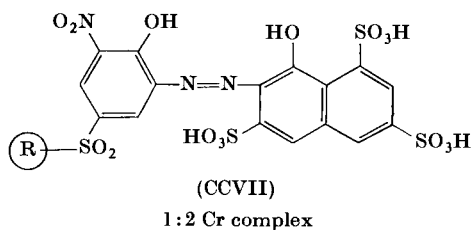
(CCVI)

1:2 Cr complex

¹²⁹ FH, *BeP* 661,236 (21.3.1964).

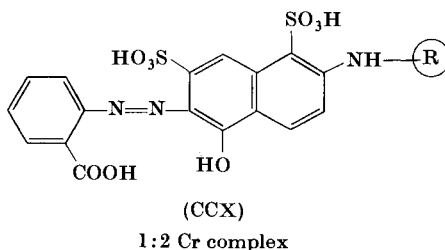
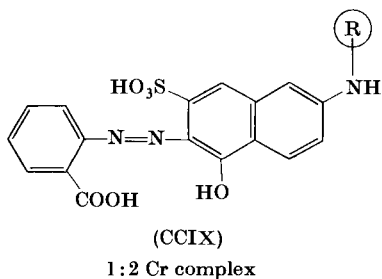
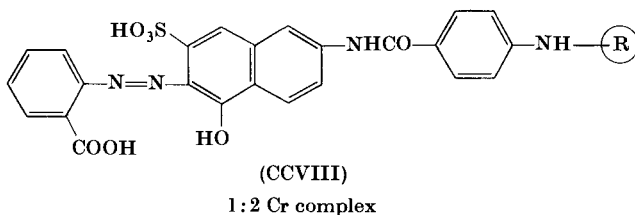
¹³⁰ FH, *BeP* 661,236 (21.3.1964).

¹³¹ Gy, *BeP* 597,730 (4.12.1959); FH, *DAS* 1,126,542 (26.3.1958).



The most important chromium and cobalt complex reactive dyes are derived from coupling products of aminonaphtholsulfonic acids. In this case also, mainly brown, gray, and black dyestuffs are to be found in the commercial ranges.

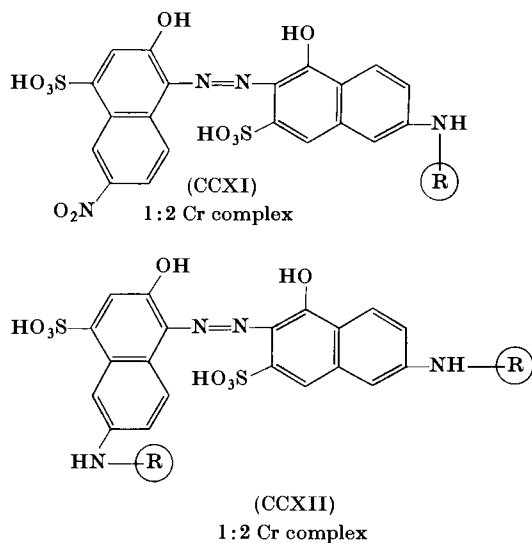
Interesting brown chromium complex dyestuffs are obtained with J-acid or its 1-sulfonic acid as coupling component and anthranilic acid as diazo component,¹³²



while with diazotized 1-amino-2-hydroxy-6-nitronaphthalene-4-sulfonic acid gray or black chromium complexes are obtained.¹³³

¹³² ICI, BP 878,527 (23.2.1959); FP 1,273,224 (9.11.1959); S, DAS 1,222,607 (13.11.1961).

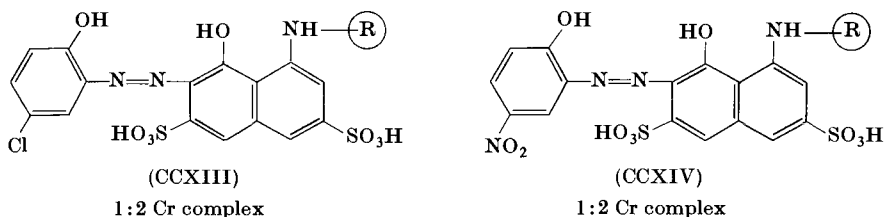
¹³³ CIBA, BeP 571,893 (10.10.1957); DAS 1,136,437 (27.8.1958).



Redder shades can often be produced by mixture with the corresponding cobalt complex.

The chromium and cobalt complex dyestuffs derived from γ -acid or 2-amino-8-naphthol-3,6-disulfonic acid (2R-acid) have not attained much practical importance up to the present.¹³⁴

With diazotized *o*-aminophenol derivatives, H-acid gives blue-gray to black chromium complex dyestuffs.¹³⁵

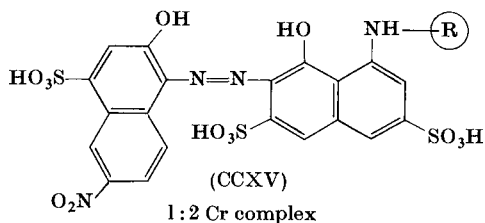


In this case also, 1-amino-2-hydroxy-6-nitronaphthalene-4-sulfonic acid is used as diazonium component¹³⁶

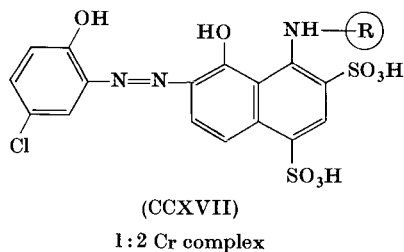
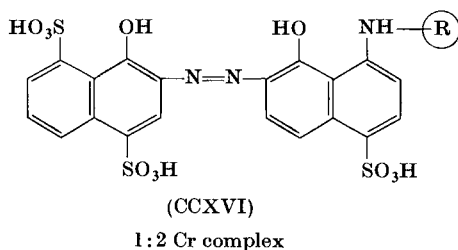
¹³⁴ ICI, *BP* 878,527 (23.2.1959); 970,120 (31.1.1961); Gy, *BeP* 615,215 (17.3.1961); S, *DAS* 1,226,728 (10.4.1959).

¹³⁵ S, *DAS* 1,226,728 (10.4.1959); FBy, *DAS* 1,202,415 (27.2.1961); ICI, *BP* 985,481 (22.9.1960); S, *BeP* 589,104 (10.4.1959).

¹³⁶ CIBA, *BeP* 571,893 (10.10.1957).

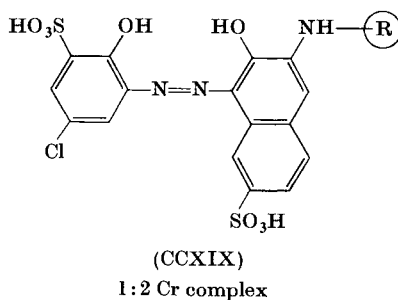
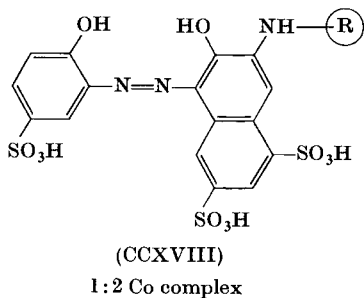


Shading can also be carried out in this case with the corresponding cobalt complex dyestuffs to obtain a redder shade. As a variant of this 1-amino-8-hydroxynaphthalene chromium complex type, mention may also be made of dyestuffs derived from 1-amino-8-naphthol-4-sulfonic acid and 1-amino-8-naphthol-2,4-disulfonic acid¹³⁷



which also give navy blue to blue-gray shades.

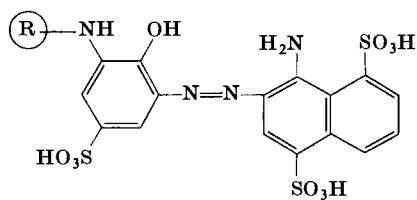
If the amino and hydroxyl groups are not in the peri position to each other in the naphthalene nucleus, but are in the *o*-position, as in derivatives of 2-amino-3-hydroxynaphthalene, mainly violet chromium complex dyes are obtained, while the corresponding cobalt complexes give interesting reddish brown reactive dyes.¹³⁸



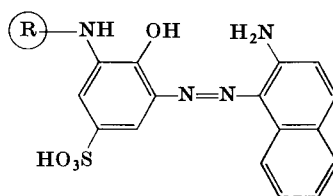
¹³⁷ CIBA, *BeP* 599,581 (28.1.1960); S, *DAS* 1,226,728 (10.4.1959).

¹³⁸ S, *DAS* 1,226,729 (14.10.1960).

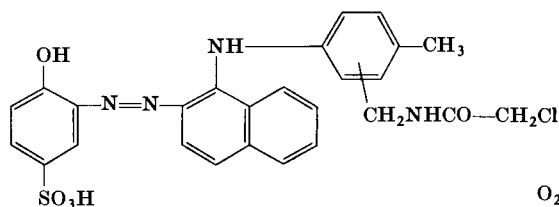
Finally, mention must also be made of symmetric 1:2 cobalt and chromium complex dyestuffs in which *o*-hydroxy-*o*'-aminoazo groups function as ligands. These dyestuffs generally give blue to green shades.¹³⁹



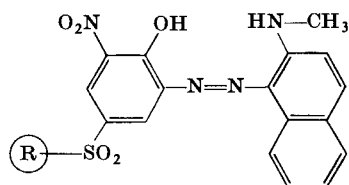
(CCXX)
1:2 Co complex



(CCXXI)
1:2 Co complex
1:2 Cr complex



(CCXXII)
1:2 Co complex



(CCXXIII)
1:2 Co complex

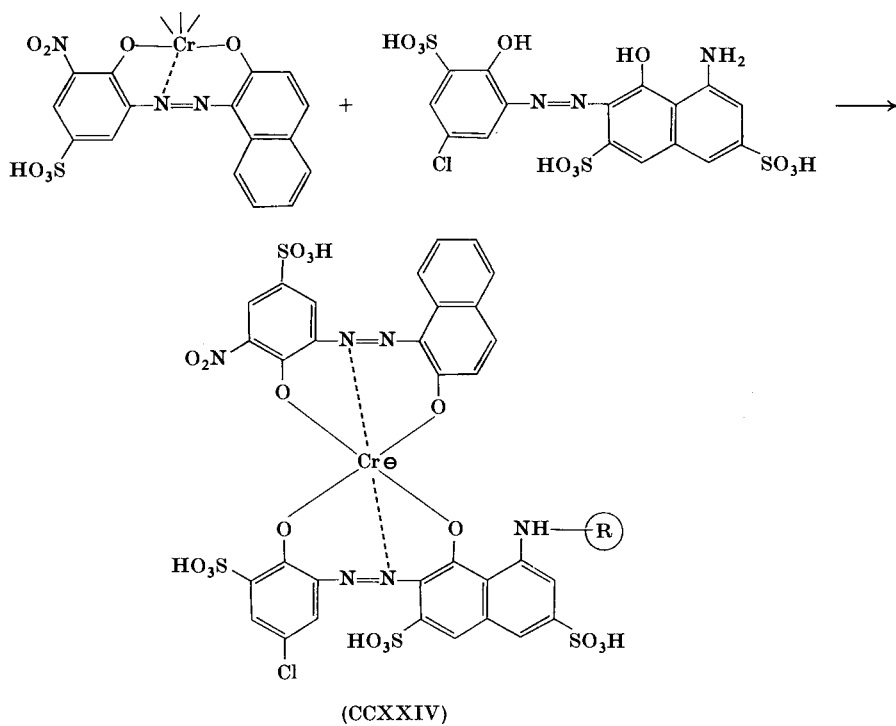
3. Unsymmetrical Chromium or Cobalt Complexes

To obtain certain intramolecular color mixtures, to improve the adaptation of reactive and dyestuff components, or else to synthesize particularly economical metal complex dyestuffs, unsymmetrical 1:2 chrome complex dyestuffs may be used.

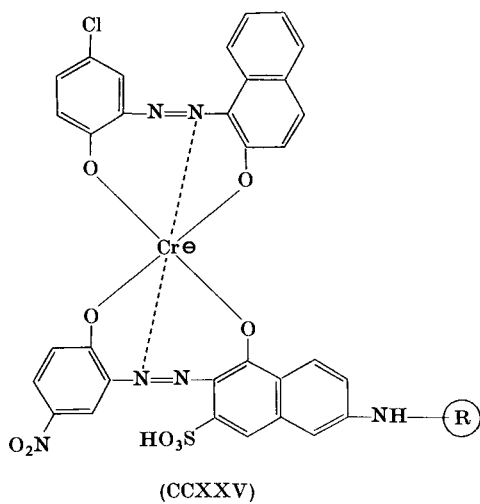
Gray or black reactive dyestuffs which contain only one reactive component in the dyestuff molecule can be obtained, for example, by reaction of a 1:1 chrome complex dyestuff free from amino groups with an *o,o*'-dihydroxyazo dyestuff containing amino groups and subsequent condensation with the reactive component.¹⁴⁰

¹³⁹ CIBA, USP 2,931,794 (6.8.1957); S, BeP 618,069 (7.6.1961); FH, FP 1,219,489 (26.3.1958).

¹⁴⁰ FBy, BeP 664,682 (3.6.1964).

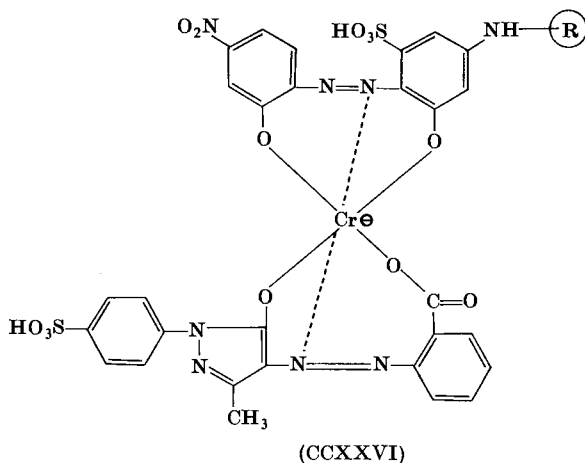


Corresponding chromium complex dyestuffs with J-acid are also described.¹⁴¹

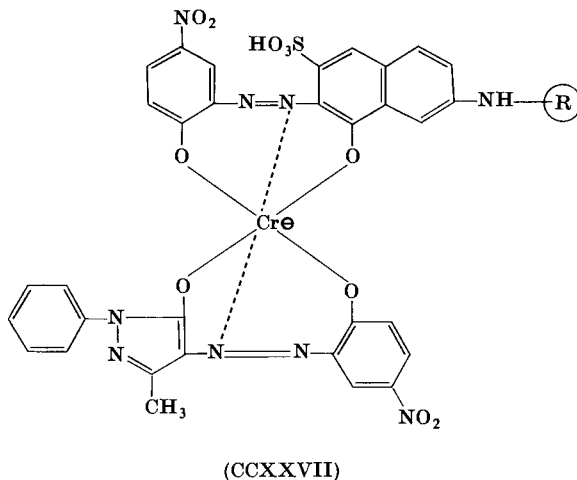


¹⁴¹ ICI, *BeP* 636,099 (13.8.1962).

As examples of intramolecular color mixtures may be mentioned the combination of a pyrazolone dyestuff component with a 4-amino-4'-nitro-2,2'-dihydroxyazobenzene¹⁴² to give a green reactive dye,



and the combination of a pyrazolone dyestuff component with a coupling product of γ -acid¹⁴³



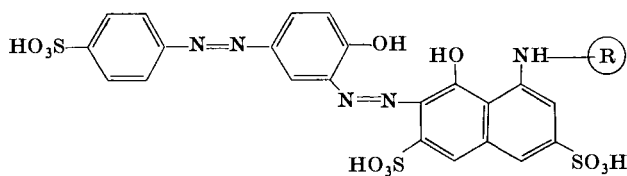
giving a brown chromium complex dye.

¹⁴² CIBA, *DAS* 1,112,228 (14.8.1957).

¹⁴³ ICI, *BeP* 636,099 (13.8.1962).

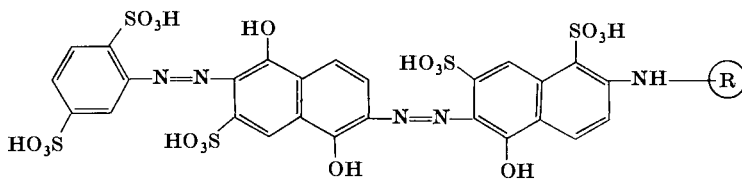
4. *Disazo Chromium and Cobalt Complexes*

Disazo chromium and cobalt complexes are only used occasionally in the production of blue, gray, or black reactive dyes. As end components bearing reactive groups, aminonaphthol mono- or disulfonic acids are mainly used.¹⁴⁴



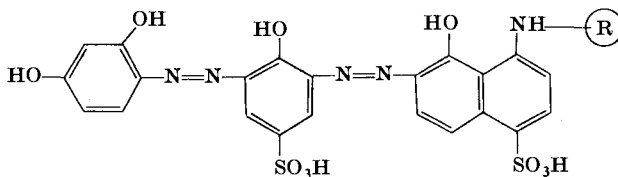
(CCXXVIII)

1:2 Co complex



(CCXXIX)

1:2 Co complex



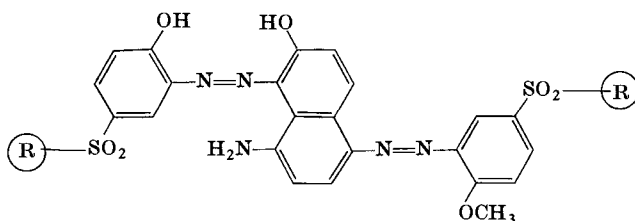
(CCXXX)

1:2 Co complex

An aminonaphthol is used as middle component for two diazonium compounds containing reactive groups in the black dyestuff¹⁴⁵ (CCXXXI).

¹⁴⁴ S, *BeP* 613,106 (27.1.1961); ICI, *BP* 951,471 (26.5.1961); Gy, *FP* 1,288,305 (22.12.1959).

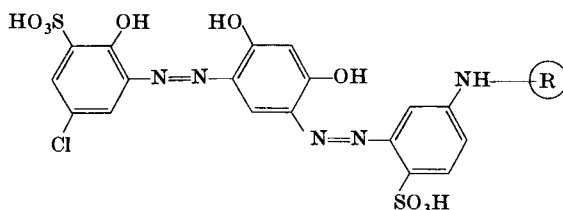
¹⁴⁵ FBy, *DAS* 1,116,846 (31.1.1958).



(CCXXXI)

1:2 Co complex

(CCXXXII) is an example of brown disazo cobalt complex dyestuffs with resorcin as middle component.¹⁴⁶



(CCXXXII)

1:2 Co complex

Dyestuffs of this type are obtained by coupling of the hydroxy cobalt complex dyestuffs with diazonium compounds bearing reactive groups. Finally, mention must also be made of the use of disazo compounds in unsymmetrical 1:2 chromium complex dyestuffs, which are generally suitable for black shades.¹⁴⁷ They are synthesized mainly by reaction of the 1:1 chromium complex monoazo compound with the metal-free *o,o'*-dihydroxydisazo compound, the reactive component being introduced both before and after formation of the 1:2 chromium complex.

5. Formazans^{147a}

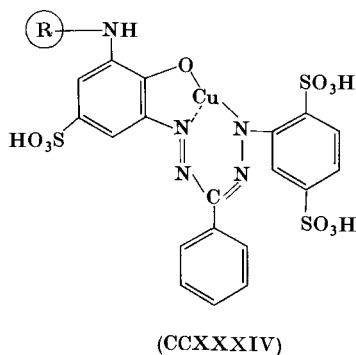
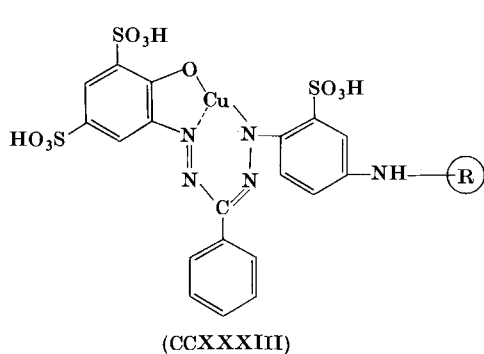
In the production of bright bluish red, blue to green metal complex reactive dyestuffs, derivatives of formazan continue to gain in importance. The simplest type of this dyestuff group contains a ligand in the

¹⁴⁶ S, *BeP* 600,169 (4.3.1960).

¹⁴⁷ Gy, *BeP* 654,038 (7.10.1963).

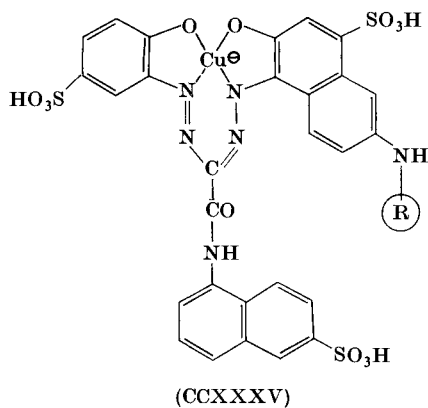
^{147a} For a discussion of the structures of metal complexes of formazans, see R. Price, *CSD* III, p. 373.

o-position to the formazan system, hydroxy, carboxy, or sulfonamide groups being particularly suitable.¹⁴⁸



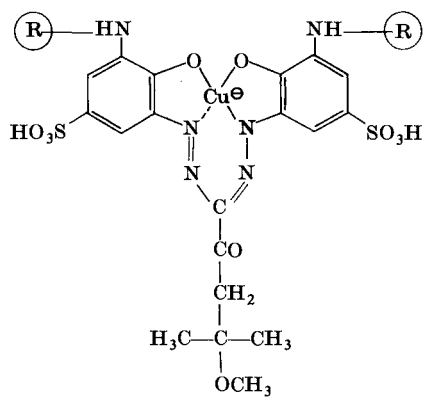
Of the formazan dyestuffs with two ligand groups in the *o,o'*-positions to the formazan system the following combinations are noteworthy:

(1) *o,o'*-Dihydroxyformazan compounds¹⁴⁹



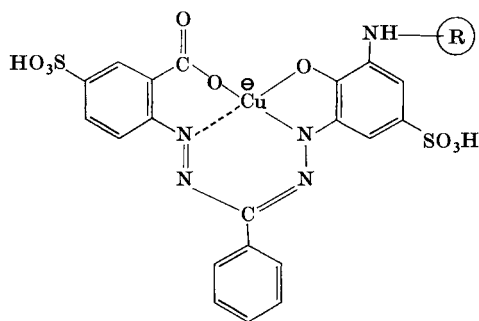
¹⁴⁸ Gy, *DAS* 1,155,872 (15.1.1960); *USP* 3,068,219 (13.11.1959).

¹⁴⁹ S, *BeP* 620,342 (8.8.1961); Gy, *BeP* 606,068 (12.7.1961); S, *BeP* 615,407 (30.3.1961).

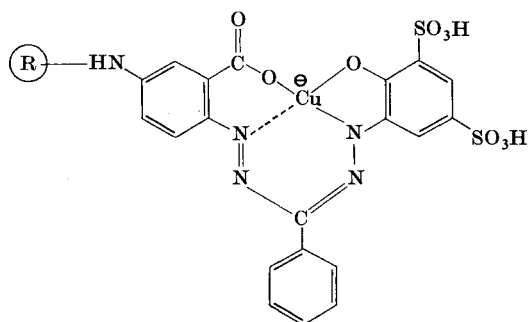


(CCXXXVI)

(2) *o*-Hydroxy-*o'*-carboxyformazan compounds¹⁵⁰

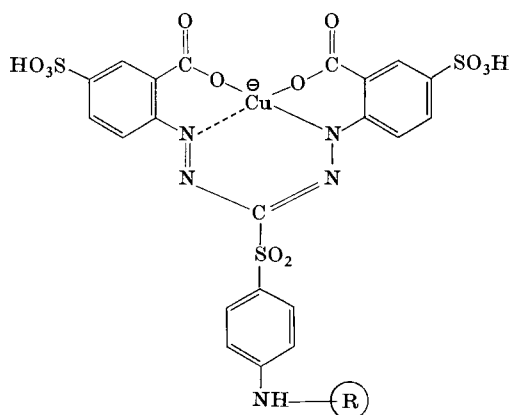


(CCXXXVII)



(CCXXXVIII)

¹⁵⁰ Gy, *BeP* 650,328 (10.7.1963); 701,656 (21.7.1966).

(3) *o,o'*-Dicarboxyformazan compounds¹⁵¹

(CCXXXIX)

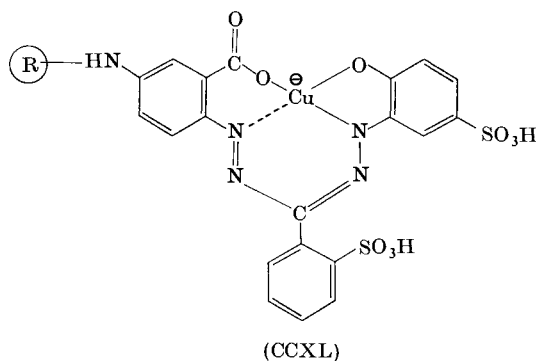
The synthesis of this formazan system, e.g., by coupling of aldehydehydrazones, β -dicarbonyl compounds, or derivatives of sulfonylacetic acid, is described in several reviews.¹⁵² The reactive components can be introduced in a final condensation with formazan complex dyes containing amino groups [e.g. (CCXXXVIII)], or by use of diazonium compounds containing reactive groups for coupling with aldehydehydrazones [e.g. (CCXL)] or compounds with reactive methylene or methyl groups, and conversion to the metal complex as the final step of the reaction. The use of hydrazones containing reactive groups as coupling components is also described.¹⁵³ Moreover, the dependence of the shade of the *C*-phenylformazan metal complexes on the substitution in the *C*-phenyl nucleus is noteworthy. The greenish blue shade of the dyestuff (CCXXXVIII), for example, is changed to a strong reddish blue shade by introduction of a sulfonic group in the *o*-position to the formazan system.¹⁵⁴

¹⁵¹ S, *BeP* 600,697 (26.2.1960).

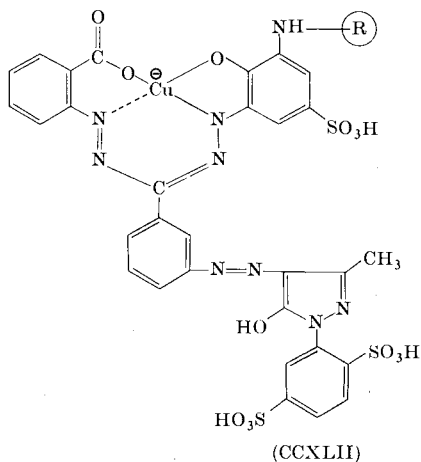
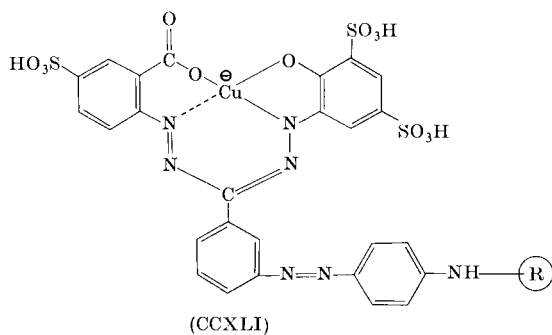
¹⁵² R. Pütter, in "Houben-Weyl, Methoden der organischen Chemie," Vol. X, Part 3, p. 627. Thieme, Stuttgart, 1965; R. Wizinger, *Chimia (Aarau)* Suppl., p. 82 (1968); H. Baumann and H. R. Hensel, *Fortschr. Chem. Forsch.* 7, No. 4 (1967).

¹⁵³ Gy, *BeP* 701,656 (21.7.1966).

¹⁵⁴ Gy, *BeP* 701,656 (21.7.1966).



The chromophore system of the formazan metal complexes has been used in the synthesis of various intramolecular color mixtures. Green azoformazan dyestuffs, for example, are obtained by combination of blue formazan copper complexes with yellow azo systems.¹⁵⁵



Methods of Production

(1) Dyestuff of formula (CXLVI)⁹⁶

With β -sulfatoethyl sulfone as reactive residue.

2-Aminophenol-4- β -hydroxyethyl sulfone, 221 parts (parts by weight throughout this procedure) (98%), is stirred into 650 parts of 90% sulfuric acid and stirring is continued until complete solution is obtained.

¹⁵⁵ Gy, BP 1,161,006 (22.4.1966); BeP 727,611 (29.1.1968).

The sulfuric acid solution is then poured into 1400 parts of ice and 270 parts of water and the mixture neutralized at 0°–5° with a solution of 1150 parts of caustic soda (33%) and 3450 parts of water, 2700 parts of ice being added simultaneously. The solution is subsequently diazotized at 0°–5° with 172.5 parts of 40% sodium nitrite solution and delta-neutralized (i.e., to a pH of about 6) with sodium bicarbonate.

1-(2'-Chloro-6'-methyl-4'-sulfophenyl)-3-methyl-5-pyrazolone, 510 parts (60%), is stirred with 500 parts of water, and caustic soda is then added until a neutral reaction is obtained. The diazo solution and the pyrazolone solution are subsequently combined. After a short time coupling is completed. The mixture is neutralized with acetic acid, 280 parts of crystallized sodium acetate and 250 parts of crystallized copper sulfate are added, and the mixture is heated to 60–65°. The copper-containing dyestuff is salted out, suctioned off, and dried. It is a brown powder which gives a yellow shade with good to very good wet-fastness properties and excellent fastness to light when printed on cotton in the presence of sodium bicarbonate.

(2) Dyestuff of formula (CLXI)¹⁰⁴

With cyanuric chloride as reactive component.

The nitrated diazo compound obtained from 1-amino-2-naphthol-4-sulfonic acid, 29.5 parts, is added as sodium salt to 23.9 parts of J-acid and 100 parts by volume of 2 *N* sodium hydroxide solution and coupled at 15°–20°. On completion of coupling, the dyestuff is precipitated by addition of sodium chloride, filtered off, and purified by washing with 5% sodium chloride solution. The dyestuff thus prepared, 53.4 parts, is dissolved in 1500 parts of water, and 50 parts of sodium acetate is added. After addition of 25 parts of crystallized copper sulfate, the mixture is heated for 1 hour at 60°–80°. The copper complex is salted out and filtered. The resulting paste is dissolved in 2000 parts of water and the solution is rendered slightly alkaline. Cyanuric chloride, 18.5 parts dissolved in 100 parts of acetone, is added at 5–10° and the reaction mixture is neutralized by addition of a dilute sodium carbonate solution. After completion of condensation, the dichlorotriazine dyestuff is precipitated by addition of sodium chloride, filtered off, then mixed with 5 parts of monosodium phosphate and 5 parts of disodium phosphate and vacuum-dried at 40°. The dyestuff obtained produces wash-fast violet shades on cotton from an alkaline, salt-containing bath.

(3) Dyestuff of formula (CLXXIII)¹¹²

With tetrachloropyrimidine as reactive component.

6-Nitro-1-diazo-2-naphthol-4-sulfonic acid, 29.5 g, is coupled at 20°–25° with 31.9 g of 1-amino-8-naphthol-2,4-disulfonic acid (Chicago acid) in the presence of 40 g of sodium carbonate. After completion of coupling, the mixture is heated to 90°–95°, 43 g of crystallized sodium sulfide is added, and stirring is continued for 1 hour at that temperature. The dyestuff is precipitated at room temperature by addition of acid and salting out, and is then isolated and washed with sodium chloride solution acidified with hydrochloric acid.

The dyestuff paste is dissolved at 40°–45° in 200 ml of water containing sodium acetate. After addition of activated carbon and clarification, a solution of 25 g of crystallized copper sulfate in 100 ml of water is added to the filtrate, and the reaction mixture is stirred for 1 hour at 40°–45°. The pH of the solution is then adjusted to 6–6.5 with sodium carbonate. Tetrachloropyrimidine, 21.8 g, is added to this solution in 3 hours, the pH being maintained at 6–6.5 by addition of sodium carbonate. When free amino groups can no longer be detected, 20% (by volume) of sodium chloride and 10% of potassium chloride are added, the precipitated dyestuff is isolated, and vacuum-dried at 40°.

The copper complex dyestuff obtained in the form of a dark powder gives a blue solution in water and produces bright blue shades on cotton.

(4) Dyestuff of formula (CLXXX)¹¹⁷

With aminochlorotriazine as reactive residue.

The diazo compound produced in the usual way from 30.3 parts of 2-naphthylamine-4,8-disulfonic acid is coupled in the presence of sodium acetate with 36.1 parts of *N*-acetyl H-acid. The resulting monoazo dyestuff is salted out, filtered, and dissolved in 1200 parts of water at 40°. To this solution are added 1 part of acetic acid, 30 parts of crystallized sodium acetate, and 100 parts by volume of a 1 M aqueous copper sulfate solution; 180–230 parts by volume of a 6% hydrogen peroxide solution is then added gradually in 1–2 hours. A change of shade from red to blue takes place in the reaction solution. The resulting copper complex is isolated and heated for 1 hour at 90° with a 3% sodium hydroxide solution to split out the acetyl group. After cooling and subsequent neutralization with hydrochloric acid, the dyestuff is isolated and dried. A solution of 74 parts of the resulting copper-containing aminoazo dyestuff (sodium salt) in 1000 parts of water is added to a fine suspension of 19 parts of cyanuric chloride in 400 parts of ice water and 50 parts of acetone. Condensation is carried out at 0°–5°, the liberated mineral acid being neutralized by gradual addition of a 2 N sodium hydroxide solution (pH 5–7). On completion of the reaction, 50 parts by volume of

10% aqueous ammonia is added and the mixture is stirred for 2 hours at 40°. The dyestuff is then salted out, filtered, and dried. It gives a blue solution in water and dyes reddish blue shades on cellulosic fibers.

(5) Dyestuff of formula (CLXXXIII)¹¹⁸

With cyanuric chloride as reactive component.

Diazotized orthanilic acid is coupled with 2-methoxy-5-methylaniline, the resulting aminoazo compound is diazotized, and under alkaline conditions coupled with a molar quantity of 2-amino-5-naphthol-1,7-disulfonic acid. A mixture of 18 parts of the trisodium salt of the aminodisazo compound, 400 parts of water, 10 parts of diethanolamine, 30 parts of 2 *N* aqueous copper sulfate solution, and 15 parts of concentrated aqueous ammonia solution is stirred for 15 hours at 95–100°. Forty parts of sodium chloride are then added and the precipitated metal complex filtered and dried. A solution of 21 parts of this metal complex in 200 parts of water is stirred into a suspension of 5.2 parts of cyanuric chloride in a mixture of 50 parts of acetone, 100 parts of ice, and 50 parts of water, the temperature being maintained between 0 and 5° by cooling from the outside. The mixture is stirred for 1 hour and then 11 parts of a 10% aqueous sodium carbonate solution added. After addition of 9 parts of sodium diethylmetanilate, 1 part of sodium hydrogen sulfate, and 15 parts of sodium chloride, the precipitated dyestuff is filtered off. The dyestuff paste is washed with 400 parts of acetone, then mixed with 1.8 parts of sodium diethylmetanilate and 0.2 part of sodium hydrogen sulfate and dried at 20°. Analysis shows that the resulting dyestuff mixture contains 2.1 atoms of organically bound chlorine for each disazo molecule. When applied to cellulosic textiles in conjunction with an acid-binding agent, the dyestuff gives blue shades with excellent fastness to washing and fastness to light.

(6) Dyestuff of formula (CCXIII)¹³⁵

With 2,4,5,6-tetrachloropyrimidine as reactive component.

The dyestuff obtained from diazotized 2-amino-4-chlorophenol and H-acid, 47.3 parts, is stirred into 300 parts of water. To the dyestuff suspension are added 30 parts of crystallized sodium acetate and 30 parts of crystallized chromium-potassium sulfate at 80° and the mixture is heated under reflux for 24 hours. Subsequently, the dyestuff solution is cooled to 80°, 21.8 parts of 2,4,5,6-tetrachloropyrimidine is added, and the mixture is stirred for several hours at 80°. During this time, the pH of the solution is maintained at 5 by gradual addition of a dilute sodium carbonate solution. After completion of condensation, the dyestuff is

precipitated by addition of sodium chloride at 80° and is then filtered off. The dried and ground dyestuff is a black powder which gives a dark blue solution in water.

(7) Dyestuff of formula (CCXVIII)¹³⁸

With 2,4,5,6-tetrachloropyrimidine as reactive component.

2-Amino-4-nitrophenol-6-sulfonic acid, 23.4 parts, is stirred into 80 parts of water and 15 parts of 30% hydrochloric acid and diazotized at 0°–5° with a solution of 7 parts of sodium nitrite in 25 parts of water. The diazo solution, neutralized to Congo Red by addition of sodium bicarbonate, is added gradually at 0°–5° to a solution of 23.9 parts of 2-amino-3-hydroxynaphthalene-6-sulfonic acid and 10.5 parts of 30% sodium hydroxide solution in 200 parts of water, the pH of the coupling mixture being maintained between 8.5 and 9 by a further addition of 28 parts of 30% sodium hydroxide solution. Coupling is completed after stirring for 1 hour. The dyestuff is completely precipitated by addition of sodium chloride and is then filtered off and washed with sodium chloride solution. The filter cake is suspended in 160 parts of water at 70°. A solution of 15 parts of cobalt sulfate in 40 parts of water is added gradually in 30 minutes at 70°–75°. The pH is maintained between 5.0 and 6.0 by simultaneous addition of a dilute sodium carbonate solution. After addition of the cobalt sulfate solution, the complex solution is again stirred for 30 minutes at 70°. The cobalt complex is precipitated by addition of sodium chloride, then filtered and washed with sodium chloride solution.

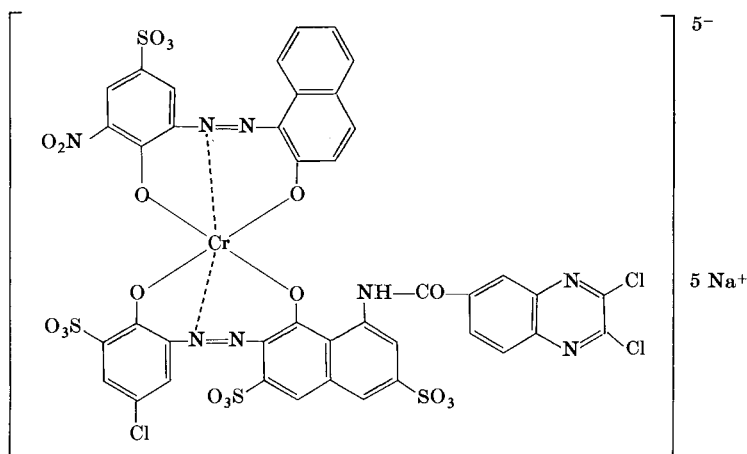
The dyestuff paste is dissolved in 150 parts of water at 80°, then mixed with 21.8 parts of 2,4,5,6-tetrachloropyrimidine and stirred for 4 hours at 80°. During this time, the pH of the solution is maintained between 4 and 5 by addition of a dilute sodium carbonate solution. On completion of condensation, the dyestuff is precipitated at 80° by addition of sodium chloride and filtered off. The dried dyestuff is a dark powder which gives a dark brown solution in water.

(8) Dyestuff of formula (CCXXIV)¹⁴⁰

With 2,3-dichloroquinoxaline-6-carbonyl chloride as reactive component.

Thirty-eight and nine-tenths parts of the dyestuff obtained by coupling 6-nitro-2-diazophenol-4-sulfonic acid and 2-naphthol in a soda alkaline medium are stirred into 200 parts of water at pH 8 and 70°–80°. To this suspension is added 67.9 parts of the chromium complex of the azo dyestuff containing 1 chromium atom to 1 molecule of dyestuff produced

from 4-chloro-2-diazophenol-6-sulfonic acid and H-acid, the pH being maintained between 7 and 9 by gradual addition of soda solution. After 20 minutes at 70°–80° a dark blue solution has formed. The paper chromatogram shows that a homogeneous mixed complex has developed. The mixed complex is acylated in 30 minutes at 45° and pH 4–6 with 26 parts of 2,3-dichloroquinoxaline-6-carbonyl chloride, the pH being maintained in the specified range by gradual addition of a soda solution. The acylated dyestuff is salted out with 20% potassium chloride, filtered and dried at 50°. The dark powder obtained gives a blue-gray solution in water. As pentasodium salt the dyestuff has the formula



It dyes gray to black shades on cotton.

(9) Dyestuff of formula (CCXXXIII)¹⁴⁸

With cyanuric chloride as reactive component.

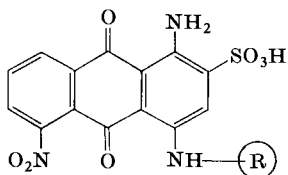
Sixty-three and three-tenths parts of the copper complex of *N*-(2-hydroxyphenyl-3,5-disulfonic acid)-*N'*-(4'-aminophenyl-2'-sulfonic acid)-*ms*-phenylformazan (obtained by coupling equimolecular quantities of diazotized 2-amino-phenol-4,6-disulfonic acid and diazotized 4-aminoacetanilide-3-sulfonic acid with ethyl phenylformyl acetate in the presence of copper salts by the usual method and subsequent saponification of the acetyl amino group with dilute caustic soda) are dissolved in 1200 parts of water with neutral reaction. This solution is gradually added in 2 hours at 0°–2° to an aqueous, finely dispersed suspension of 22.2 parts of cyanuric chloride, obtained by pouring on to ice-water a solution of cyanuric chloride in 150 parts of acetone, at a pH of 2.0–2.5. When the starting material can no longer be detected, the dyestuff is

precipitated by addition of sodium chloride, filtered off, washed with dilute sodium chloride solution, and finally vacuum-dried. The dyestuff gives a blue solution in water.

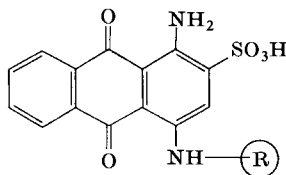
III. Anthraquinonoid Dyes

Anthraquinonoid dyestuffs are used extensively in the production of water-soluble reactive dyes. Most important are derivatives of 1-amino-4-arylaminoanthraquinone-2-sulfonic acid, which give brilliant blue dyes with good fastness to light, shades ranging from bluish violet to bluish green also being obtained by changing the various substituents.

The direct condensation of 1,4-diaminoanthraquinone-2-sulfonic acid with heterocyclic reactive components gives blue-violet to reddish blue reactive dyes which up to the present have not attained any great practical importance.¹⁵⁶

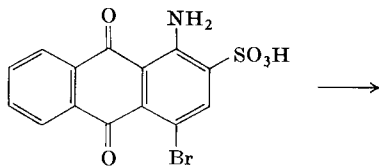


(CCXLIII)



(CCXLIV)

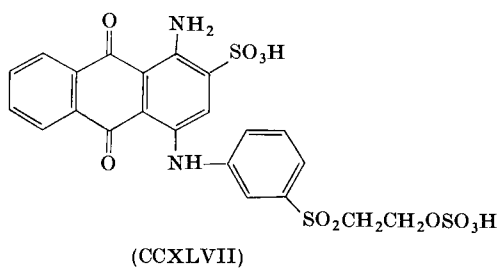
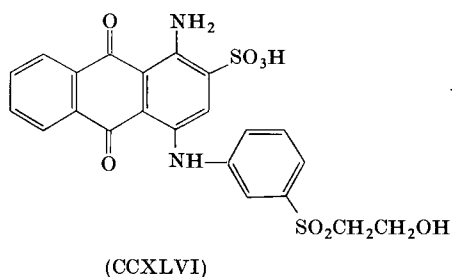
The combination of 1-amino-4-anilinoanthraquinone-2-sulfonic acid with reactive groups, as in the case of azo dyes, is of practical importance, when it is through amino groups of the phenyl residue or through a sulfonyl group. Dyestuffs of the latter type are generally synthesized by condensation of phenyl sulfones containing amino groups with 1-amino-4-bromoanthraquinone-2-sulfonic acid and subsequent conversion into reactive groups.¹⁵⁷



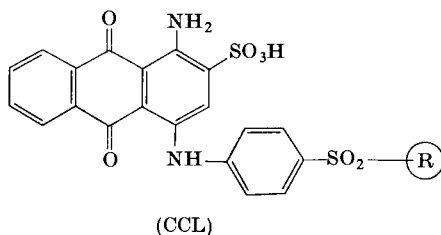
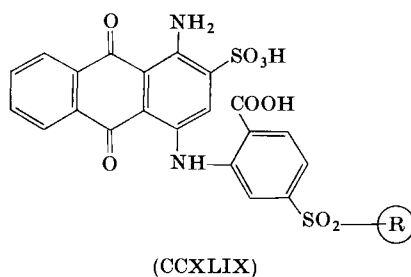
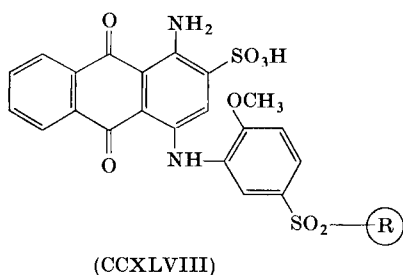
(CCXLV)

¹⁵⁶ CIBA, *DAS* 1,117,245 (12.9.1956).

¹⁵⁷ FH, *DAS* 1,268,756 (29.10.1963).



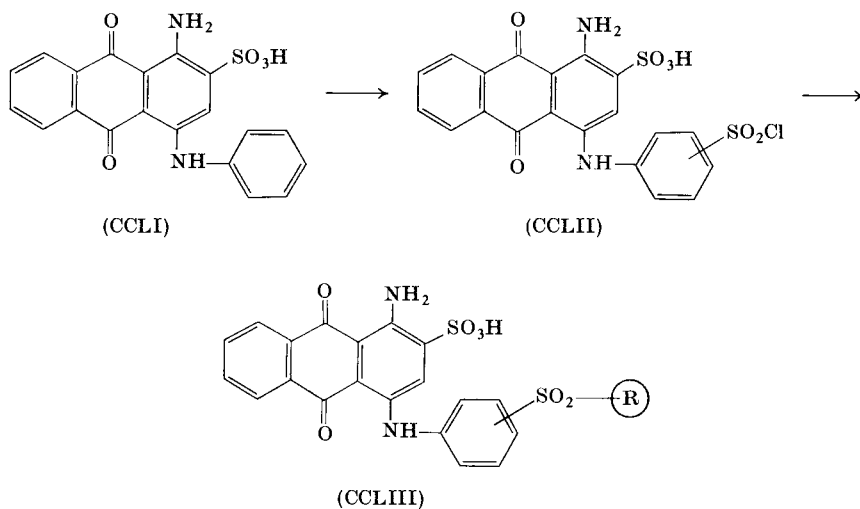
In an analogous manner, numerous dyestuffs substituted in the phenyl nucleus have been obtained, for example,¹⁵⁸



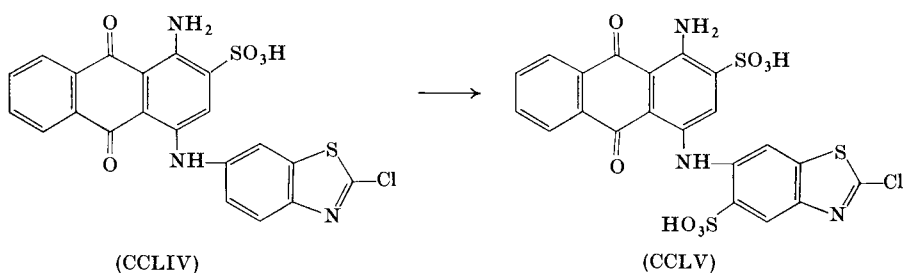
Another method of synthesis starts from 1-amino-4-anilinoanthraquinone-2-sulfonic acid, which can be easily converted into a sulfonyl

¹⁵⁸ FH, GE 960,534 (9.1.1950); 965,902 (18.7.1949); BeP 655,035 (29.10.1963).

chloride. The sulfonyl chloride group can then be transformed into residues containing reactive groups.¹⁵⁹



In a similar manner, condensation of 6-amino-2-chlorobenzothiazole with 1-amino-4-bromoanthraquinone-2-sulfonic acid gives the 4-benzothiazolylanthraquinone derivative, which is subsequently sulfonated to improve the solubility.¹⁶⁰

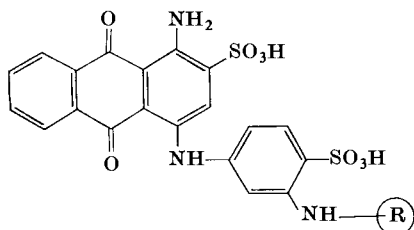


For condensation with heterocyclic reactive components or with carbonyl chlorides with substituted reactive groups, 1-amino-4-aminophenyl-aminoanthraquinone-2-sulfonic acids are widely used. The simplest dyestuffs of this type are obtained from the condensation products of

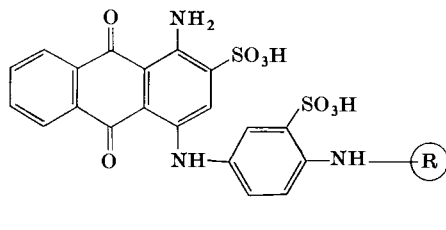
¹⁵⁹ FH, BP 1,013,442 (1.12.1960).

¹⁶⁰ BASF, DOS 1,444,573 (11.4.1962).

1-amino-4-bromoanthraquinone-2-sulfonic acid with 1,3-diaminobenzene-4-sulfonic acid or 1,4-diaminobenzene-2-sulfonic acid,¹⁶¹



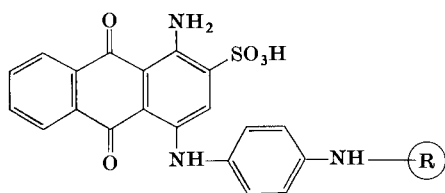
(CCLVI)



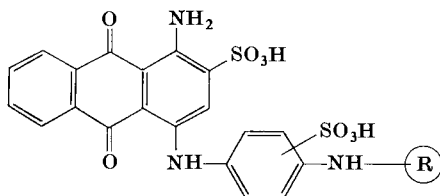
(CCLVII)

the 4'-amino-substituted compounds generally possessing a greener shade.

Isomeric compounds of the 4'-aminophenylaminoanthraquinone type can be obtained by sulfonation of 1-amino-4-(4'-aminophenyl)aminoanthraquinone-2-sulfonic acid and subsequent condensation with reactive components or by aftersulfonation of the anthraquinone derivatives free from sulfonic acid groups in the 4-phenyl nucleus condensed with a reactive group.¹⁶²



(CCLVIII)

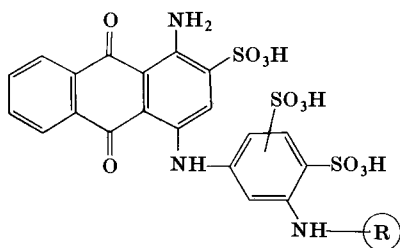


(CCLIX)

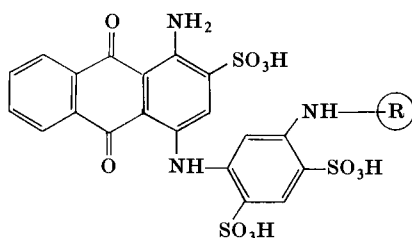
¹⁶¹ CIBA, DAS 1,117,245; 1,128,939 (12.9.1956).

¹⁶² CIBA, FP 1,498,813 (11.11.1965).

Dyestuffs containing two sulfonic acids in the phenyl residue can be obtained either by condensation of reactive components with corresponding amines or by stronger aftersulfonation of the compound free from sulfonic acid groups.¹⁶³

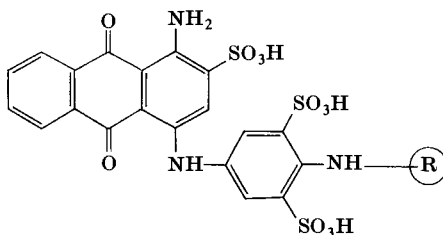


(CCLX)



(CCLXI)

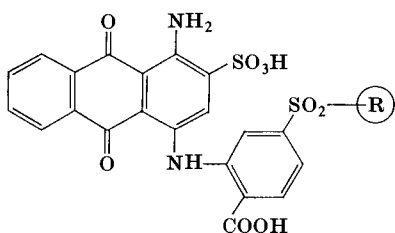
The compound



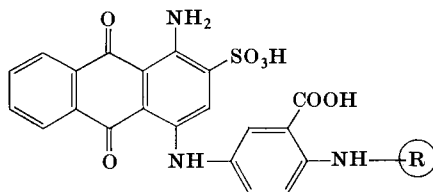
(CCLXII)

is produced by condensation of 1,4-diaminobenzene-2,6-disulfonic acid with 1-amino-4-bromoanthraquinone-2-sulfonic acid and conversion to the reactive dyestuff.¹⁶⁴

Carboxyl groups in the phenylamino residue of this dyestuff type are also patented, but are only of minor practical importance.¹⁶⁵



(CCLXIII)



(CCLXIV)

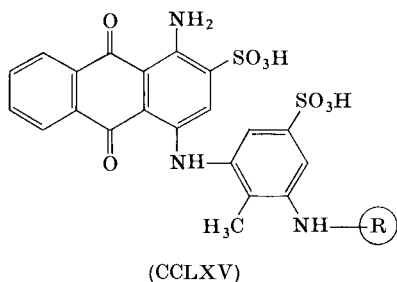
¹⁶³ BASF, *DAS* 1,198,469 (27.2.1961); 1,200,980 (14.1.1961); S, *SP* 401,312 (27.7.1961).

¹⁶⁴ BASF, *FP* 1,268,154 (22.9.1959).

¹⁶⁵ FH, *BeP* 655,035 (29.10.1963); CIBA, *DAS* 1,117,245 (12.9.1956).

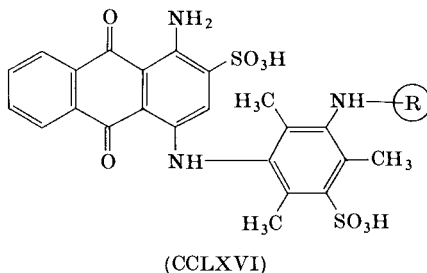
On the other hand, 1-amino-4-arylaminoanthraquinone-2-sulfonic acid dyestuffs alkyl-substituted in the aryl group have been developed extensively. Particularly outstanding are the 2'-alkyl- or 2',6'-dialkyl-substituted derivatives, which because of the steric hindrance of the coplanar arrangement of anthraquinone and aryl residue generally possess redder blue shades.

The following dyestuff (CCLXV) may be mentioned as an example of an *o*-monoalkyl dye of this type.



It is synthesized by condensation of 1-amino-4-bromoanthraquinone-2-sulfonic acid with 2,6-diaminotoluene-4-sulfonic acid and subsequent treatment with reactive components.¹⁶⁶

In an analogous manner, 1-amino-4-(2',4',6'-trimethyl-3'-amino-5'-sulfophenyl)aminoanthraquinone-2-sulfonic acid can also be obtained and then converted with reactive components to reddish blue reactive dyes.¹⁶⁷

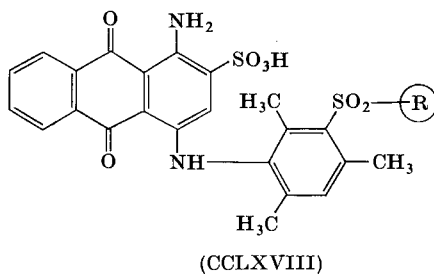
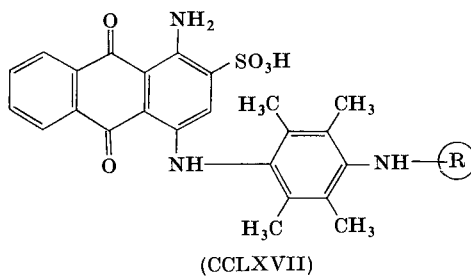


Further possibilities of varying this dyestuff type are suggested in the following examples¹⁶⁸:

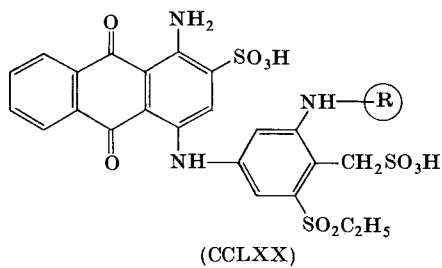
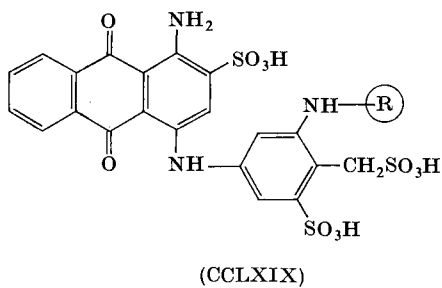
¹⁶⁶ FBy, DOS 1,544,505 (28.12.1964); BP 995,795 (7.2.1961).

¹⁶⁷ S, FP 1,238,515 (9.9.1958); CFM, BP 1,017,616 (25.10.1962); CIBA, DOS 1,644,507 (7.7.1965); ICI, FP 1,546,109 (29.11.1966).

¹⁶⁸ CIBA, DOS 1,644,508 (7.7.1965); S, DAS 1,218,636 (13.5.1960).

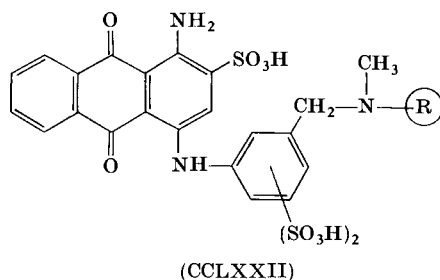
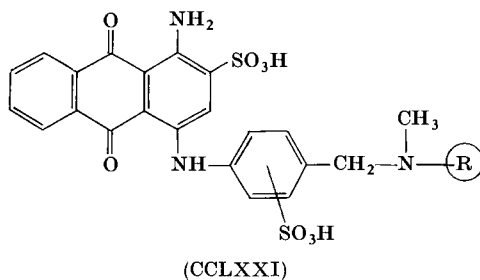


Attention is also drawn to the use of alkylenesulfonic acid residues in the aryl nucleus of 1-amino-4-arylaminoanthraquinone-2-sulfonic acid dyestuffs.¹⁶⁹

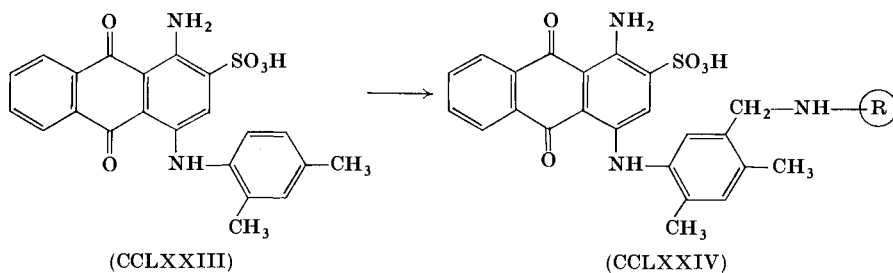


¹⁶⁹ CFM, BP 1,017,616 (25.10.1962).

In comparison with the 1-amino-4-arylaminoanthraquinone dyestuffs 2,4,6-trialkyl-3-amino-substituted in the aryl residue, alkyleneamino derivatives are of greater practical importance.¹⁷⁰



The sulfonic groups are generally introduced into the phenyl residue of these dyestuffs by sulfonation of the condensation product obtained from aminobenzylamines,¹⁷⁰ while to introduce the aminomethylene group an aminomethylation reaction may also be applied to the aryl-aminoanthraquinone dyestuff.¹⁷¹



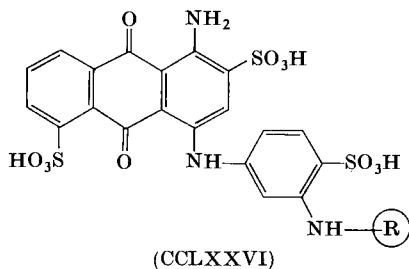
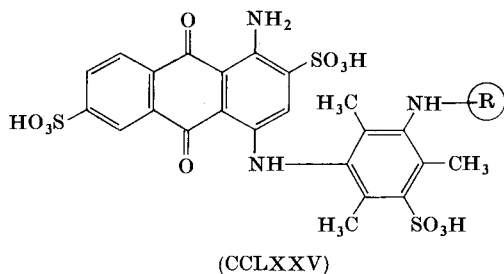
In addition to the 1-amino-4-arylaminoanthraquinone-2-sulfonic acid reactive dyes, numerous reactive dyestuffs substituted in the anthra-

¹⁷⁰ FBy, *BeP* 622,569 (23.9.1961); S, *DAS* 1,297,258 (26.6.1964).

¹⁷¹ Gy, *DAS* 1,148,341 (23.4.1958).

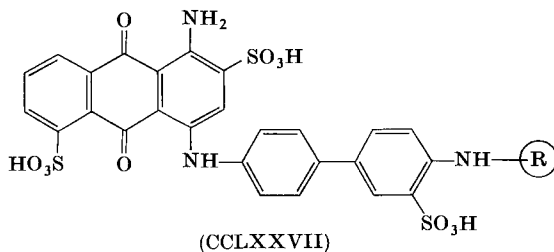
quinone system by further sulfonic groups have been similarly described.¹⁷²

The sulfonic group substitution generally leads to greener blue shades.^{173, 174}



The condensation of polynuclear arylamines with 1-amino-4-bromo-anthraquinone-2-sulfonic acids is particularly important in practice for the production of very greenish blue and green dyes.

As amines, derivatives of benzidine,¹⁷⁴ 4,4'-diaminostilbene,¹⁷⁵ and 4,4'-diaminoazobenzene¹⁷⁶ are mainly used.



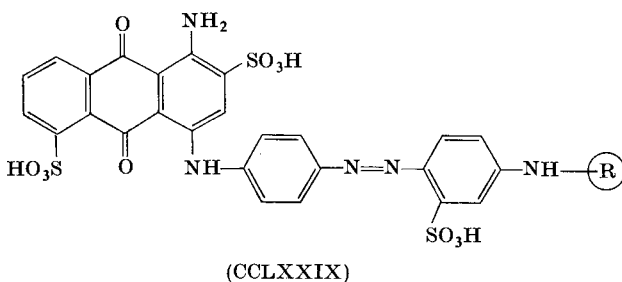
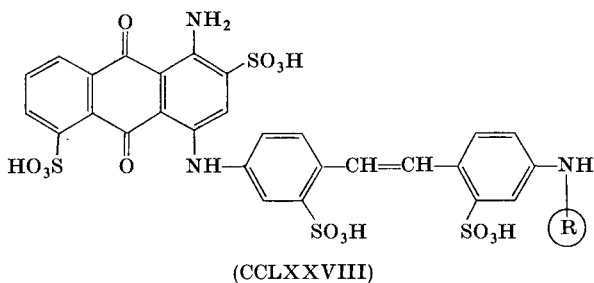
¹⁷² Gy, *FP* 1,238,515 (9.9.1958); 76,971/1,238,515 (31.10.1958); ICI, *BP* 781,930 (29.11.1954); 874,508 (9.11.1955).

¹⁷³ Gy, *FP* 76,971/1,238,515 (31.10.1958).

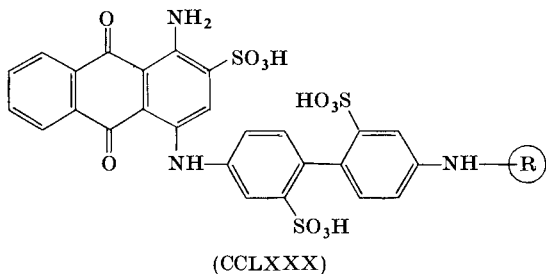
¹⁷⁴ ICI, *BP* 781,930 (29.11.1954).

¹⁷⁵ ICI, *BP* 874,508 (9.11.1955).

¹⁷⁶ ICI, *BP* 781,930 (29.11.1954).



Corresponding dyestuffs bearing only one sulfonic group in the anthraquinone residue are also described.¹⁷⁷

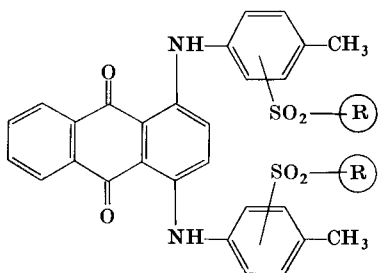


Derivatives of 1,4-bis(anilino)anthraquinone are also used in the production of blue-green and green reactive dyes. In this case, linking with the reactive component may take place either through sulfone functions in the phenyl residues¹⁷⁸ or through amino groups in the anthraquinone system.¹⁷⁹

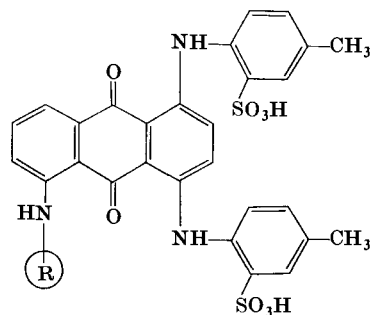
¹⁷⁷ Gy, *DAS* 1,150,770 (6.2.1959); FBy, *BP* 995,795 (7.2.1961).

¹⁷⁸ FBy, *FP* 1,217,738 (28.1.1958).

¹⁷⁹ FBy, *BP* 1,147,110 (30.11.1966).

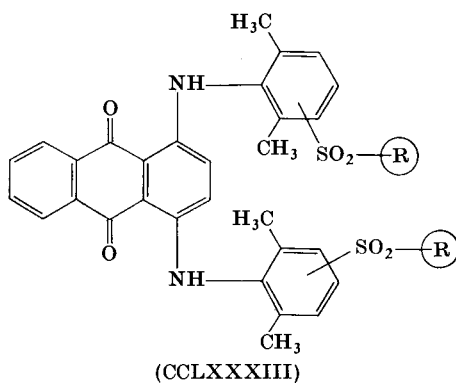


(CCLXXXI)

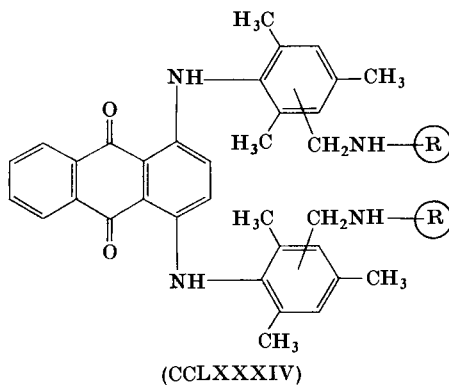


(CCLXXXII)

Moreover, in this dyestuff type a change to redder blue shades is observed as a result of 2',6'-alkyl substitution of the phenyl nuclei, as in the following blue dyes¹⁸⁰:



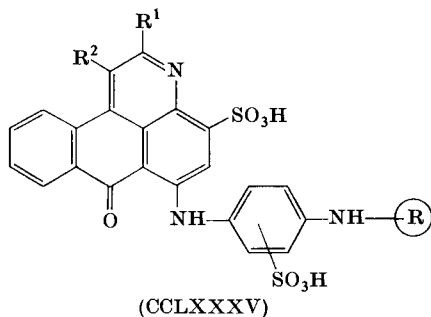
(CCLXXXIII)



(CCLXXXIV)

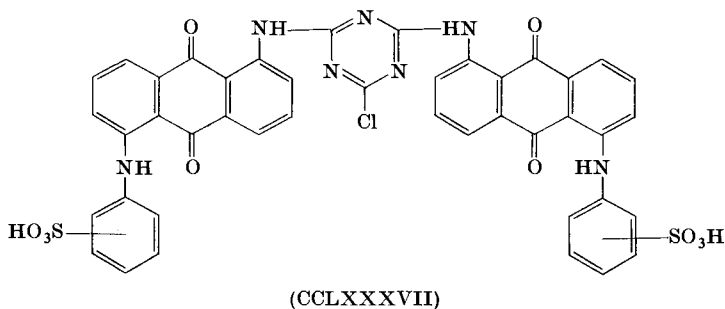
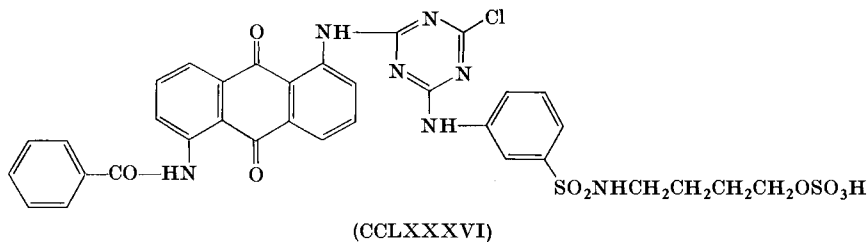
¹⁸⁰ FBy, DOS 1,419,808 (28.3.1959); S, DAS 1,227,588 (10.1.1961).

Numerous other anthraquinonoid and more highly condensed quinonoidal systems are not discussed in detail, since up to the present they have achieved very little practical importance. As examples, only the compounds (CCLXXXV) are mentioned



in which R^2 generally stands for a hydroxyl group and R^1 for an aliphatic or aromatic acyl residue.¹⁸¹ Compounds of this type are red reactive dyestuffs which are often notable for a high fastness to light.

Finally, there are certain vat dyes carrying reactive residues, which under the conditions of application may possibly react with the fiber. The following triazine derivatives are examples¹⁸²:



¹⁸¹ S, USP 2,962, 497 (31.1.1958).

¹⁸² CIBA, DAS 1,222,463 (2.2.1960); 1,266,423 (19.3.1962).

Methods of Production

(1) Dyestuff of formula (CCXLVII)¹⁵⁷

With the β -sulfoethyl sulfone group as reactive residue.

Thirty-four parts by weight of 90 wt % of 1-amino-4-*N*-(3'- β -hydroxyethylsulfonyl)phenylaminoanthraquinone-2-sulfonic acid is added to 150 parts by volume of pyridine and the mixture is heated to 75–80°. Then, 21 parts by weight of sulfamic acid is added. The temperature of the reaction mixture rises in a few minutes to 95–100°, at which it is maintained for $\frac{1}{2}$ hour by application of external heat after the heat of reaction has subsided. The esterification mixture is then poured into 1500 parts by volume of water, previously adjusted to pH 5 with hydrochloric acid. The ester is salted out from its aqueous solution by addition of potassium chloride at 60°–65°, filtered, washed with 8% potassium chloride solution and dried. Dyestuff (CCXLVII) is obtained in a high degree of purity and with a yield of 33.5 parts by weight, corresponding to 94% of theory. The dyestuff is identical with that isolated according to the process described in German patent 965,902 by esterification with concentrated sulfuric acid. Pyridine may be replaced as solvent by quinoline, dimethylaniline, dimethylformamide, dimethyl sulfoxide, picoline, or lutidine, or by mixtures of these solvents.

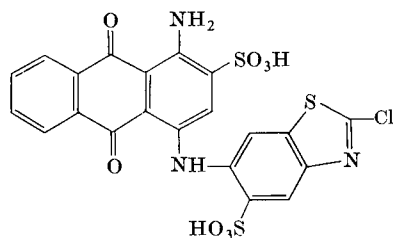
(2) Dyestuff of formula (CCLV)¹⁶⁰

With 6-amino-2-chlorobenzothiazole-5-sulfonic acid as reactive component.

To a suspension of 40.4 parts of the sodium salt of 1-amino-4-bromoanthraquinone-2-sulfonic acid in 400 parts of water is added a solution of 27.7 parts of 2-chloro-6-aminobenzothiazole in 50 parts by volume of dioxane, and then 24 parts of sodium hydrogen carbonate and 3 parts of copper(I) chloride are added. The mixture is heated for about 9 hours at 60° until the chromatogram of the colored starting material has disappeared, and is then filtered, washed with water until the effluent runs slightly blue, and the resulting product dried.

Thirty-nine parts of the new dyestuff, which crystallizes in blue needles, is dissolved at 5°–10° in 1 hour in 240 parts by volume of oleum with a 10% sulfur trioxide content and the mixture is stirred for about 2 hours at room temperature. It is then poured onto ice, and the sulfonation product is suctioned off and washed with water until a neutral effluent is obtained.

The new dyestuff, probably of the formula



gives bright blue shades on cotton with very good wet-fastness properties in the presence of basic agents.

(3) Dyestuff of formula (CCLVI)¹⁶¹

With the 2-chloro-4-(3'-sulfophenylamino)triazinyl group as reactive residue.

To a solution of 19 parts of cyanuric chloride in 80 parts of acetone are added 100 parts of ice. The resulting suspension of cyanuric chloride is added to a solution, cooled to 5°, of 53.3 parts of the disodium salt of 1-amino-4-(3'-aminoanilino)anthraquinone-2,4'-disulfonic acid in 2000 parts of water. The reaction mixture is stirred for 1 hour at 5–7°. During this time, 50 parts by volume of 2 *N* sodium carbonate solution is added gradually.

On completion of monocondensation, a solution of 19.5 parts of the sodium salt of metanilic acid in 300 parts of water is added. The reaction mixture is heated to 60°, while 55 parts by volume of 2 *N* sodium carbonate solution is added gradually so that the pH remains between 5.0 and 7.0, stirring then being continued for 1 hour at that temperature. The resulting dyestuff is precipitated by the addition of sodium chloride, filtered off, and vacuum-dried at 90°. It is a dark-colored substance which dyes reddish blue shades with good fastness to washing and high fastness to light on cotton and regenerated cellulose.

(4) Dyestuff of formula (CCLXVIII)¹⁶⁸

With trichloropyrimidine as reactive component.

3-Aminobenzyl alcohol, 12.3 parts, is dissolved in 150 parts of water, and 42 parts of caustic soda (30%) is added. The solution is cooled to 2° by the addition of ice. A solution of 18.3 parts of 2,4,6-trichloropyrimidine in 22 parts of toluene is added dropwise over 3 hours while stirring, the temperature being maintained at 0°–3°. The mixture is stirred for 10–15 hours at 0°–3° and 35.5 parts of hydrochloric acid (30%) is then added.

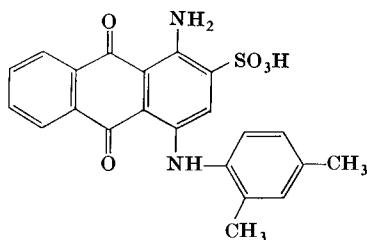
After a further hour, filtration is carried out, and the residue is washed with a common salt solution and vacuum-dried at 35–40°. One hundred percent 1-amino-4-(2',4',6'-trimethyl)phenylaminoanthraquinone-2-sulfonic acid, 43.6 parts, is added at 20–30° to 270 parts of chlorosulfonic acid. After complete solution, 80 parts of sulfonyl chloride are added drop by drop, and the mixture is heated in about 30 minutes to 50°. After 16 hours at 50°–55°, the mixture is cooled and poured into a mixture of 2000 parts of ice, 1000 parts of water, and 200 parts of sodium chloride. The precipitate is suctioned off, washed with 10% sodium chloride solution and pasted up in 500 parts of water. The suspension is adjusted to pH 7 and 33 parts of finely pulverized 3-amino-1-(dichloropyrimidylhydroxymethyl)benzene are sprinkled in. The mixture is stirred for several hours at 20–30°, the pH being maintained at 7.0–7.5 by the addition of dilute sodium carbonate solution. On completion of condensation, the mixture is strongly acidified with hydrochloric acid, the precipitated dyestuff is suctioned off, washed with 1% hydrochloric acid to remove the slight excess of 3-amino-1-(dichloropyrimidylhydroxymethyl)benzene, the dyestuff paste is neutralized carefully with sodium carbonate, and vacuum-dried at 50°.

The ground dyestuff is a dark blue powder, which gives a blue solution in water. It dyes brilliant blue shades on wool with very good fastness to light, washing, milling, water, perspiration, crocking, and dry cleaning.

(5) Dyestuff of formula (CCLXXIV)¹⁷¹

With *N*-methylethchloroacetamide as reactive component.

The sodium salt, 17.76 parts, of the dyestuff of formula



obtained by condensation of 1 mole of 1-amino-4-bromoanthraquinone-2-sulfonic acid with 1 mole of 1-amino-2,4-dimethylbenzene, is dissolved at 10°–15° in 320 parts of 96% sulfuric acid. To this solution is added 5.46 parts of *N*-methylethchloroacetamide and stirring is continued for 24 hours at the same temperature. The mixture is then poured onto ice. The precipitated dyestuff is suctioned off, suspended in water, and

the suspension adjusted carefully to pH 7 with caustic soda, the dyestuff then being separated with sodium chloride as sodium salt. The dyestuff obtained gives blue shades on wool from a slightly acid bath. The dyeing possesses very good fastness properties.

(6) Dyestuff of formula (CCLXXVIII)¹⁷⁵

With cyanuric chloride as reactive component.

A solution of 2.43 parts of cyanuric chloride in 12 parts of acetone is poured gradually into 120 parts of ice-cold water with stirring. To the suspension of cyanuric chloride, a solution of 10.5 parts of the tetrasodium salt of 1-amino-4-4'-(4''-aminophenylvinyl)phenylaminoanthraquinone-2,5,3',2''-tetrasulfonic acid in 250 parts of water is added during 30 minutes, the temperature of the mixture being maintained at 0° to 4°, and the pH at approximately 4.5 by addition of 10% sodium carbonate solution. The mixture is stirred for a further hour under these conditions. The pH is then adjusted to approximately 6.0, and a solution of 2 parts of anhydrous disodium hydrogen phosphate and 4 parts of anhydrous potassium dihydrogen phosphate in 30 parts of water is added. Fifty parts of sodium chloride is added to the stirred mixture and the dyestuff so precipitated is filtered and washed on the filter with a solution of 24 parts of sodium chloride, 3 parts of anhydrous disodium hydrogen phosphate, and 6 parts of anhydrous potassium dihydrogen phosphate in 200 parts of water. The dyestuff is finally mixed intimately with a mixture of 0.5 part of anhydrous disodium hydrogen phosphate and 1.0 part of anhydrous potassium dihydrogen phosphate and dried at room temperature.

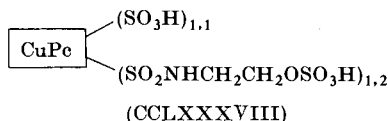
IV. Phthalocyanines

The use of soluble phthalocyanine reactive dyes permits primarily the dyeing of bright turquoise shades on cotton, with high fastness to washing and also satisfactory fastness to crocking. This fact has promoted considerably the introduction of reactive dyestuffs.

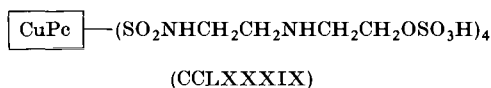
Copper and nickel phthalocyanine reactive dyes remain among the most commercially important reactive dyestuffs. In addition to their application as homogeneous dyestuffs, they also play an important rôle in the production of bright green shades in mixtures with yellow dyestuffs. Synthesis of these dyes generally starts from phthalocyanine tri- or tetrasulfonyl chlorides or the corresponding sulfonyl chloride-sulfonic acids obtained by sulfonation or sulfochlorination of Cu or Ni phthalocyanine. Conversion into reactive dyestuffs can be achieved either by

condensation with amines or diamines and subsequent transformation into the reactive dyestuff, or by condensation of a reactive component containing amino groups with the sulfonyl chlorides.

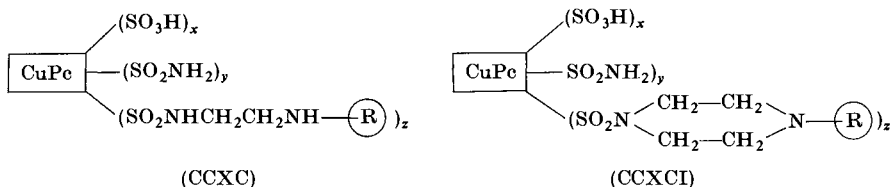
The first method is adopted, for example, in the production of turquoise dyes with aliphatic reactive residues, in which the sulfonyl function of the sulfonyl chloride is used to synthesize the reactive residues.¹⁸³



Further variations in the side chain of this dyestuff type are described, e.g.,¹⁸⁴



Of more practical importance are phthalocyanine reactive dyes in which reactive component and phthalocyanine sulfonic acid are linked through an aliphatic, araliphatic, or aromatic bridge member. Ethylenediamine and its analogs are most often used as aliphatic bridge links.¹⁸⁵



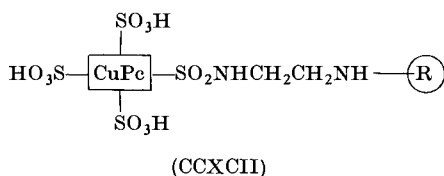
These compounds are synthesized mainly by condensation of Cu phthalocyanine tri- or tetrasulfonyl chlorides, or the mixed sulfonyl chloride-sulfonic acids, with monoacylalkylenediamines and simultaneous hydrolysis of excess sulfonyl chloride groups or their conversion to sulfonamides, hydrolysis of the acylamino group or groups, and subsequent condensation with the reactive component. The ratio of the separate substituents may vary according to reaction conditions and the quantity of amines used. The sum of these substituents is at most 4.

¹⁸³ ICI, *DAS* 1,091,259 (14.12.1956).

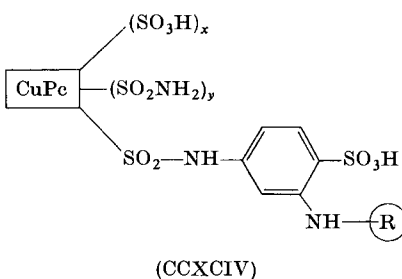
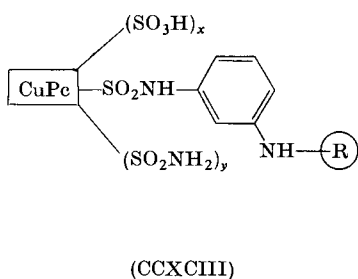
¹⁸⁴ FBy, *DAS* 1,237,242 (28.1.1958).

¹⁸⁵ S, *DAS* 1,215,842 (19.4.1962); CIBA, *DAS* 1,180,868 (17.8.1956); ICI, *FP* 1,471,782 (18.3.1965); 1,360,036 (7.5.1963); *DAS* 1,233,521 (4.12.1961).

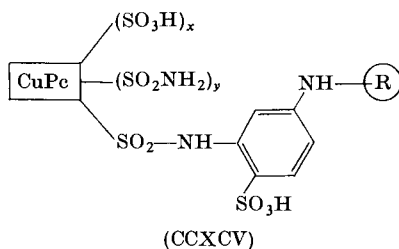
The use of ammonia, primary amines, or secondary amines to hydrolyze the sulfonyl chloride groups, forming sulfonamide groups simultaneously, generally gives bright bluer shades. The sulfonyl chloride groups are often hydrolyzed by treatment with aqueous alkalis so that in addition to the sulfonamide function carrying the reactive group, up to three sulfonic acid groups may be attached to the phthalocyanine.¹⁸⁶



Arylenediamines are also often used as bridge links between phthalocyanine and reactive component. 1,3-Diaminobenzene and its sulfonic acids are mainly used.¹⁸⁷



In the case of 1,3-diaminobenzene-4-sulfonic acid, the isomeric compound is produced by reaction of the condensation product obtained from diamine and reactive component with the phthalocyanine tetra-sulfonyl chloride or the sulfonyl chloride-sulfonic acid mixture.¹⁸⁸

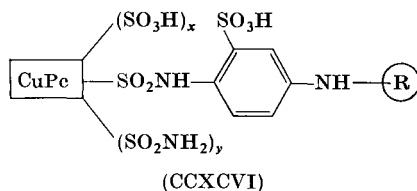


¹⁸⁶ CIBA, *DAS* 1,180,868 (17.8.1956).

¹⁸⁷ S, *FP* 1,248,155 (12.12.1958); CIBA, *FP* 1,464,923 (11.12.1964); S, *BP* 916,094 (28.5.1958).

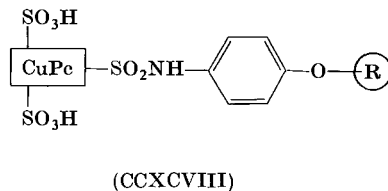
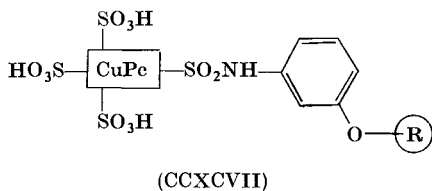
¹⁸⁸ CI 74460; CI Reactive Blue; J. Panchartek, Z. J. Allan, and F. Muzik, *Collect. Czech. Chem. Commun.* **25**, 2783 (1960).

The corresponding phthalocyanine derivatives containing 1,4-diaminobenzene-2-sulfonic acid as bridge link are also described, but up to the present have not attained much importance.¹⁸⁹

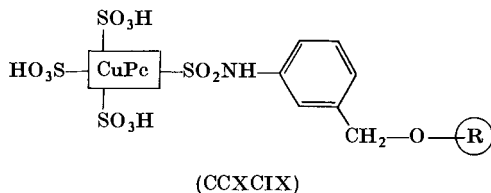


This dyestuff is synthesized by condensation of the 1,4-diaminobenzene-2-sulfonic acid, first condensed with the reactive component, with the phthalocyanine tetrasulfonyl chloride. The same applies to numerous other aromatic bridge links which are further substituted in the linking aryl residue or which consist of polynuclear systems.¹⁹⁰

In addition to diaminoaryls, aminophenol and its substitution products are also used as bridge links.¹⁹¹



The linking of reactive component and phthalocyanine residue through araliphatic bridge members is also described in the patent literature, e.g.,¹⁹²



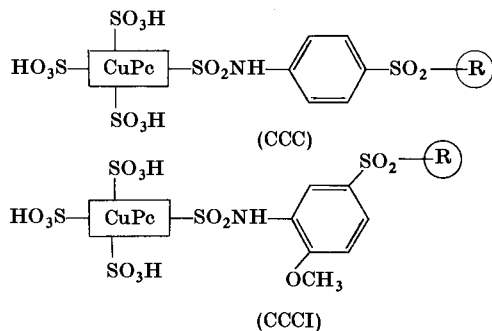
¹⁸⁹ ICI, *FP* 1,429,819 (7.4.1964); S, *FP* 1,248,155 (12.12.1958).

¹⁹⁰ ICI, *DAS* 1,202,420 (7.8.1957).

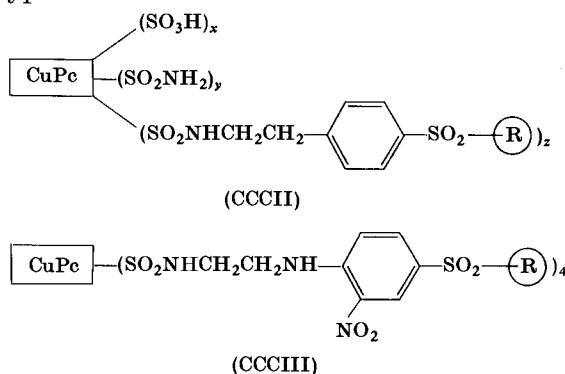
¹⁹¹ S, *DAS* 1,100,847 (29.11.1957).

¹⁹² S, *BP* 990,974 (13.5.1960).

Compared with phthalocyanine reactive dyes linked through aliphatic or aromatic diamines, these dyestuffs in which aminoaryl residues are carriers of the reactive systems possess more practical importance.¹⁹³

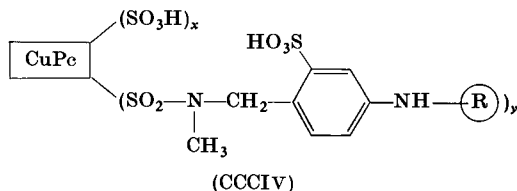


Mixtures of aliphatic and aromatic bridge links are also described for this dyestuff type.¹⁹⁴



These compounds are synthesized either by condensation of the sulfatoethyl aminophenyl sulfones with the Cu phthalocyanine sulfonyl chlorides or the sulfonyl chloride-sulfonic acids, or by sulfonation of the β-hydroxyethyl sulfone derivatives.

Aminobenzylamine sulfonic acids are also described as bridge links.¹⁹⁵

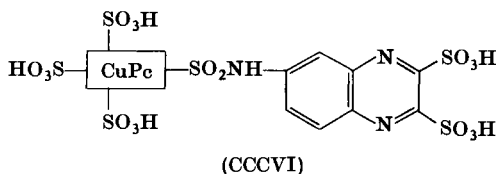
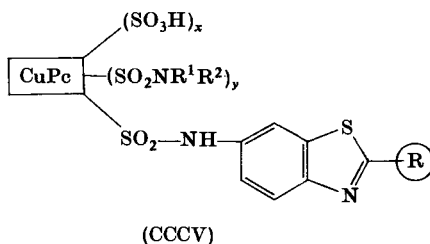


¹⁹³ FH, DAS 1,179,317 (15.3.1960); FP 1,462,722 (2.1.1965).

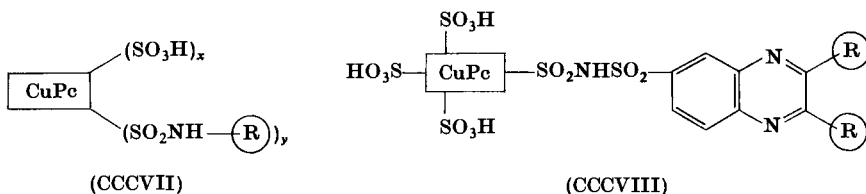
¹⁹⁴ FH, DAS 1,226,731 (3.10.1962).

¹⁹⁵ FBy, FP 1,467,293 (28.12.1964).

(CCCV) and (CCCVI) are further examples of phthalocyanine reactive dyes which are obtained by condensation of reactive components containing amino groups with phthalocyanine sulfonyl chlorides.¹⁹⁶



The direct linkage of reactive components with sulfonamides of the phthalocyanine range can also be achieved, but up to the present these dyestuffs have not attained much practical importance.¹⁹⁷



These dyes are generally synthesized by condensation of the phthalocyaninesulfonamides with the reactive components¹⁹⁸; in the case of the sulfimide linkage, a sulfamide of the reactive component can also be condensed with phthalocyanine sulfonyl chlorides.¹⁹⁹

The previously mentioned types of linkage between reactive component and phthalocyanine permit the synthesis of reactive dyestuffs containing the reactive residue several times in the molecule. Moreover,

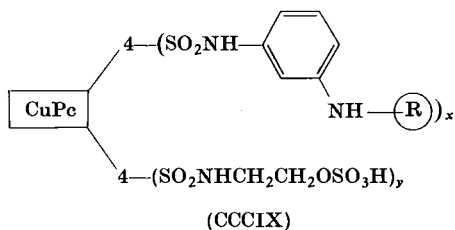
¹⁹⁶ FBy, *BeP* 689,380 (12.11.1965); ICI, *FP* 1,367,010 (21.6.1962).

¹⁹⁷ FBy, *DAS* 1,258,525 (14.10.1957); *BeP* 668,146 (12.8.1964); 716,585 (15.7.1967).

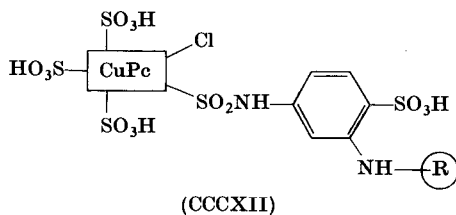
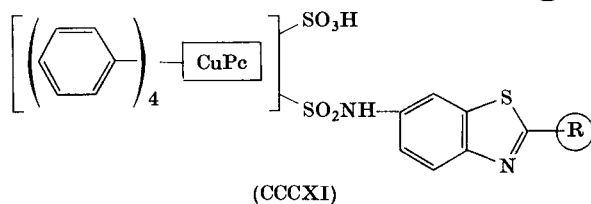
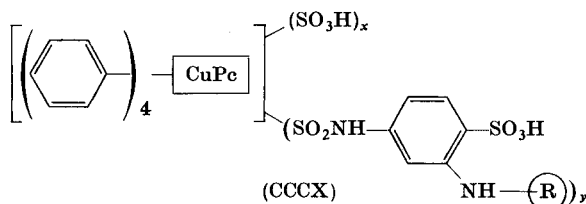
¹⁹⁸ FBy, *DAS* 1,258,525 (14.10.1957).

¹⁹⁹ FBy, *BeP* 668,146 (12.8.1964).

numerous combinations of different linkage types and different reactive components are described, e.g.,²⁰⁰



In addition to the simple phthalocyanine derivatives obtained by condensation of phthalic acid derivatives, mention must also be made of the phenyl-substituted or halogen-substituted derivatives which are used in the production of bluish green reactive dyes,²⁰¹

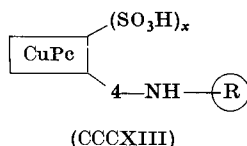


and the reactive dyes obtained from aminophthalocyanine sulfonic acids.²⁰²

²⁰⁰ S, *FP* 1,257,937 (6.5.1959).

²⁰¹ FBY, *BP* 995,795 (7.2.1961); BASF, *DOS* 1,444,573 (11.4.1962); *DAS* 1,123,065 (17.8.1959).

²⁰² ICI, *DAS* 1,152,493 (14.3.1956); 1,202,420 (7.8.1957).



Synthesis of these compounds starts from the corresponding substituted phthalic acids, which are condensed to the phthalocyanine and then converted into water-soluble reactive dyes. The same method of synthesis is used in the production of phthalocyanine-4-sulfonic acid or polysulfonic acid reactive dyestuffs obtained by condensation of 4-sulfophthalic acid derivatives.²⁰³

The copper phthalocyanine-4-sulfonyl chlorides can be linked with reactive components through the same variety of bridge members as the phthalocyanine-3-sulfonic acid derivatives obtained by sulfochlorination or sulfonation of the phthalocyanine. Moreover, 3,4-phthalocyanine polysulfonic acid derivatives can be obtained by sulfonation or sulfochlorination of phthalocyanine-4-mono- to trisulfonic acids.²⁰⁴

In addition to the substituent variations on the phthalic acid derivatives used as starting products, mention must also be made of the phthalocyanine dyes produced by condensation of heterocyclic *o,o'*-dicarboxylic acid derivatives, such as diazaphthalocyanine derivatives, which can be obtained by mixed condensation of equal parts of phthalic anhydride and pyridine-2,3-dicarboxylic anhydride.²⁰⁵

Compared with the reactive dyes derived from copper phthalocyanine, phthalocyanine reactive dyestuffs of other metals, e.g., Co or Ni phthalocyanine complexes, have only minor importance. Ni phthalocyanine reactive dyes generally possess greener shades than corresponding Cu phthalocyanine derivatives.²⁰⁶ Their importance is due to the higher fastness to light in the presence of moisture of the green dyeings or prints obtained by mixture with yellow reactive dyes. These reactive dyestuffs, which also generally contain sulfonamide groups, are synthesized in a similar manner to the corresponding Cu phthalocyanine derivatives.²⁰⁶

Mixtures of phthalocyanine residues with yellow components of the aminoazo or pyrazolone range, which give brilliant green dyestuffs, are described in Section II,A.

²⁰³ S, *FP* 1,257,937 (6.5.1959); ICI, *DAS* 1,202,420 (7.8.1957); S, *BeP* 645,855 (9.5.1963); ICI, *DAS* 1,152,493 (14.3.1956).

²⁰⁴ ICI, *DAS* 1,192,764 (18.11.1959); 1,233,521 (4.12.1961).

²⁰⁵ BASF, *DAS* 1,061,009 (15.3.1957).

²⁰⁶ ICI, *DAS* 1,202,420 (7.8.1957); 1,152,493 (14.3.1956).

Methods of Production

(1) Dyestuff of formula (CCXC)¹⁸⁵

With aminochlorotriazine as reactive residue.

Copper phthalocyanine, 57.5 parts, is stirred into 537 parts of chlorosulfonic acid in such a manner that the temperature does not rise above 30°. Stirring is then continued for 30 minutes at room temperature. The reaction mixture is heated in 1½ hours to 130°–133° and maintained at this temperature for 4 hours. After stirring until cold, it is added to a mixture of 500 parts of water, 280 parts of sodium chloride, and 3000 parts of crushed ice with constant stirring. After stirring for a further short time and filtration, washing on the suction filter is carried out with 600 parts by volume of a saturated sodium chloride solution and 200 parts of ice. In this way, a copper phthalocyanine sulfonyl chloride is obtained, which is further processed as a moist, acid paste (starting product) and which most probably consists of a mixture of copper phthalocyanine-3,3',3''-trisulfochloride-3'''-monosulfonic acid with the corresponding copper phthalocyanine disulfochloride disulfonic acid. Half of the product obtained as described (about 0.05 mole) is neutralized at 0°–3°.

Monoacetythylenediamine, 6.78 parts, is dissolved in 250 parts of water. Eleven parts of sodium carbonate is sprinkled into the well-stirred neutral sulfonyl chloride suspension and the amine solution is added. The mixture is stirred for 24 hours at 20°–22°. For saponification, 60 parts of sodium hydroxide (100%) is added, the volume is made up to 1000 parts, and heating is continued for 2½ hours at 85°–90°. At 40° the alkalinity is reduced with conc. hydrochloric acid to a pH of 8.5, and excess amine is removed by steam distillation. The dyestuff can be precipitated from slightly alkaline solution by addition of sodium chloride.

Half of the dyestuff obtained is dissolved in water, cooled to 0°–2°, and condensed at 6°–8° with 4.6 parts of cyanuric chloride, which has previously been dissolved in acetone, poured on to ice water, and filtered. The reaction solution is maintained between pH 5.5 and 7.5 by gradual addition of 25 parts of 1 *N* sodium hydroxide solution. On completion of condensation, 27.5 parts by volume of 2 *N* ammonia solution is added and heating is continued for 2½–3 hours at 35°–40°. The alkalinity is reduced to pH 7.5 by addition of a little hydrochloric acid, and the dyestuff is precipitated with sodium chloride and dried under water-jet vacuum at 55°–60°. The resulting dyestuff produces brilliant blue, wash-fast shades on cotton.

(2) Dyestuff of formula (CCXCIII)¹⁸⁷

With trichloropyrimidine as reactive component.

The tetrasulfonyl chloride paste obtained from 57.6 g of copper phthalocyanine is stirred into 500 ml of water and 300 g of ice, 15 g of *m*-aminoacetanilide is added, the pH is adjusted to 8 with ammonia, and heating is continued for 1 hour at 60°–65°, the pH being maintained at 8 by adding more ammonia. On completion of condensation, 250 ml of 35% hydrochloric acid is added, and the suspension is stirred for 3 hours at 85°–90°. The reaction product is then isolated and washed with 1000 ml of 1% hydrochloric acid.

The paste obtained as described is stirred into 1000 ml of water and neutralized by addition of dilute caustic soda solution. It is then heated to 65°–70° and 18.5 g of 2,4,6-trichloropyrimidine is added. The hydrochloric acid liberated during condensation is neutralized by addition of dilute caustic soda. On completion of condensation, the dyestuff is isolated and vacuum-dried at 60°–70°. The resulting blue powder produces turquoise blue shades on cotton and regenerated cellulose.

(3) Dyestuff of formula (CCXCVI)¹⁸⁷

With 2,4,6-trichloropyrimidine as reactive component.

1,4-Diaminobenzene-2-sulfonic acid, 37.6 g, is dissolved in 500 ml of water adjusted with caustic soda to pH 7, and 36.7 g of 2,4,6-trichloropyrimidine is added. The hydrochloric acid liberated during condensation is neutralized by addition of caustic soda. The reaction is complete in 3 hours. To this solution is added the paste of the tetrasulfonyl chloride obtained from 57.6 g of copper phthalocyanine, the reaction mixture is adjusted to pH 7 with caustic soda, then 100 g of sodium acetate and 14 ml of 25% ammonia are added, and stirring is continued for 18 hours. The mixture is then heated to 65°–70°, and after 2 hours the dyestuff is precipitated by addition of sodium chloride, isolated, and vacuum-dried at 60°–70°.

(4) Dyestuff of formula (CCC)¹⁹³

With β -sulfatoethyl sulfone as reactive residue.

β -Hydroxyethyl-(4-amino)phenyl sulfone, 80.4 parts by weight, is converted by heating with 64.8 parts by weight of 60% sulfuric acid into the acid sulfoester, then stirred with 600 parts by weight of water, and after addition of 36.7 parts by weight of caustic soda 33°Bé at 8°–10°, the solution is neutralized to about pH 6 with 12 parts by weight of sodium bicarbonate. To this solution is added 100 parts by weight of copper phthalocyanine-(3)-tetrasulfonyl chloride, 100%, as a moist paste, and

condensation is carried out with stirring at 20°–25° and pH 6–6.5 by the addition of caustic soda and a little pyridine. After completion of condensation, the solution is adjusted with caustic soda 33°Bé to pH 12 and the dyestuff is then salted out by addition of potassium chloride, suctioned off, and dried. The resulting blue powder gives a blue solution in water.

Bright turquoise blue shades are obtained on natural and regenerated cellulosic fibers from salt-containing dye liquors with the aid of alkalies.

(5) Dyestuff of formula (CCCVI)¹⁹⁶

With 6-aminoquinoxaline-2,3-disulfonic acid as reactive component.

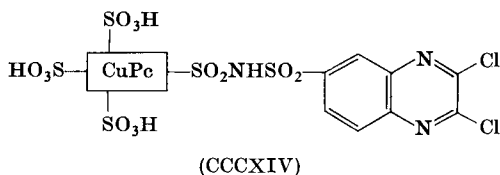
A mixture of 5.8 parts of copper phthalocyanine and 27 parts of chlorosulfonic acid is stirred for 3 hours at 135°–140° and then cooled to 80°. Five parts of thionyl chloride are added and the resulting mixture is stirred for 3 hours at 85°, then cooled to 5° and poured onto ice. The precipitated copper phthalocyanine-3-sulfonic acid tri(3-sulfonyl chloride) is filtered off and washed with water at 1°. The solid sulfonyl chloride is stirred with 150 parts of water, and the pH raised to 7 by the addition of potassium hydroxide. A solution of 10 parts of the dipotassium salt of 6-aminoquinoxaline-2,3-disulfonic acid in 200 parts of water is added and the resulting mixture is stirred for 4 hours at 30°–40°, the pH being maintained between 7 and 8 by the addition of a 10% aqueous solution of potassium carbonate. This mixture is stirred for 16 hours at 20° and ethanol is then added to precipitate the dyestuff, which is subsequently filtered off, washed with a 30% aqueous solution of potassium chloride, and dried.

(6) Dyestuff of formula (CCCXIV)¹⁹⁷

With 2,3-dichloroquinoxaline-6-sulfonyl chloride as reactive component.

An aqueous neutral paste of copper phthalocyanine tetrasulfonyl chloride obtained from 25 g of copper phthalocyanine is stirred with a little water, 14 g of 2,3-dichloroquinoxaline-6-sulfonamide is added, and the mixture is diluted to 225 g by a further addition of water. The temperature is then adjusted to 50° while stirring vigorously, and the pH is increased simultaneously to 9 by the gradual addition of a 10% caustic soda solution and maintained during the reaction between 8.5 and 9.0. After 13 hours the dyestuff is dissolved, using 125 ml of 10% caustic soda solution. The dyestuff solution is separated by filtration from 2 g of unused dichloroquinoxalinesulfonamide, neutralized by gradual addition of a little acetic acid, and precipitated by stirring in 100 g of common salt

and 120 g of potassium chloride. After drying at 50°, 60 g of salt-containing dyestuff are obtained, which as free acid corresponds to the formula



(7) Dyestuff of formula (CCCXI)²⁰¹

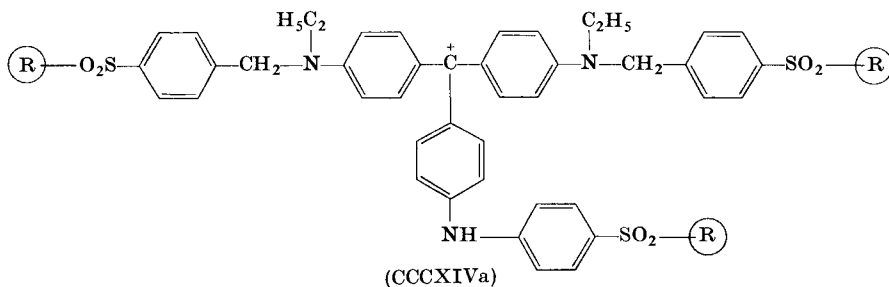
With 6-amino-2-chlorobenzothiazole as reactive component.

A solution of 50 parts of copper tetraphenylphthalocyanine in 400 parts of chlorosulfonic acid is heated gradually to 130°–135° and maintained at that temperature for 5 hours. The cooled solution is then stirred into a mixture of 2500 parts of ice with 1500 parts of water, and the precipitate is filtered off and washed with ice water. The moist filtrate is pasted up with 300 parts of ice and 200 parts of water, and a solution of 21 parts of 2-chloro-6-aminobenzothiazole in 350 parts of acetone and a solution of 5 parts of pyridine in 50 parts of water are then added with vigorous stirring. The reaction is kept neutral for about 50 hours by the addition of a 10% aqueous sodium hydrogen carbonate solution. The dyestuff is salted out with 200 parts of potassium chloride, filtered, and dried at 45°–50° under reduced pressure.

V. Other Reactive Dyes

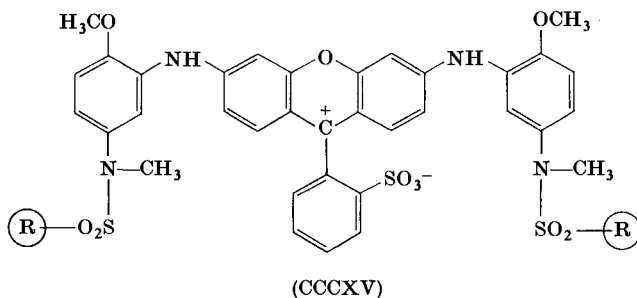
In comparison with the vast fields of azo, anthraquinone, and phthalocyanine reactive dyestuffs, up to the present other chromophore systems have attained very little importance. Without discussing the specific properties of the following dyestuffs, a few compounds mentioned as reactive dyes in the patent literature are listed here.

In the field of triphenylmethane dyestuffs the following blue reactive dye is reported.²⁰⁷:

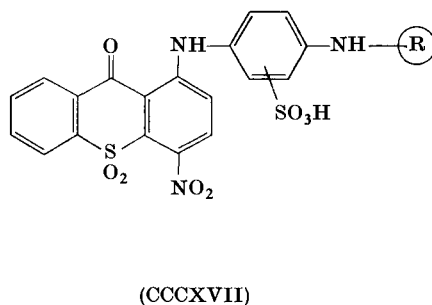
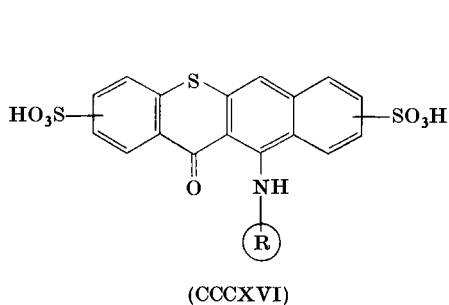


²⁰⁷ FBy, DAS 1,170,898 (15.7.1957).

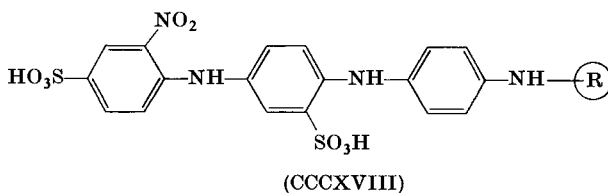
From the field of xanthene dyestuffs the following violet dye is selected.²⁰⁸



The following thioxanthone derivatives are also members of this group.²⁰⁹



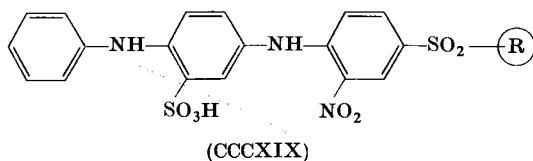
They give khaki or gray-violet shades. Brown shades are obtained with derivatives of *o*-nitrodiarylamine, the linkage between dyestuff and reactive residue being achieved both through amino groups and also through sulfonyl functions.²¹⁰



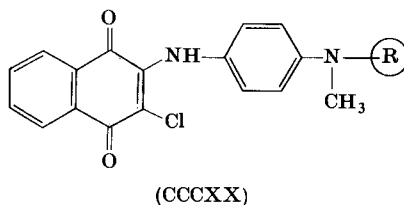
²⁰⁸ FH, *BeP* 614,415 (24.2.1961).

²⁰⁹ FH, *FP* 1,412,793 (28.10.1963); 1,448,600 (30.9.1964).

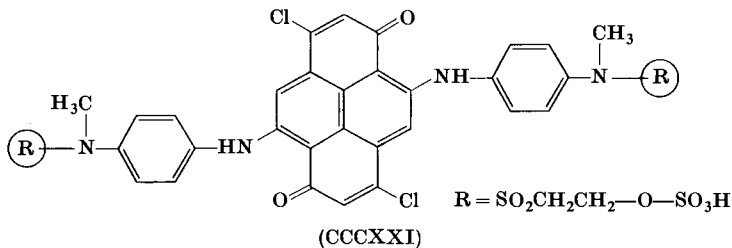
²¹⁰ FB_y, *DOS* 1,544,505 (24.12.1964); FH, *DBP* 965,902 (18.7.1949).



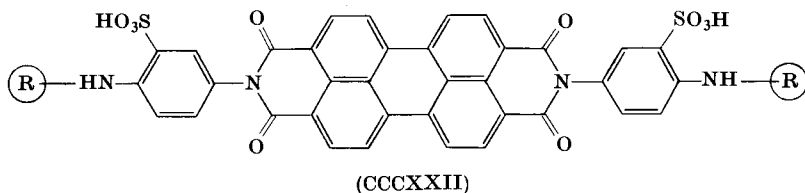
The reactive dyestuff (CCCXX) is described as a derivative of 1,4-naphthoquinone.²⁰⁸



It gives a brown-red shade, while derivatives of diaminopyrenequinone can be used to produce green reactive dyes.²⁰⁸



Derivatives of perylenetetracarbinide give reddish blue reactive dyes.²¹¹



²¹¹ FH, *FP* 87,615/1,412,793 (28.2.1964).

CHAPTER III

REACTIVE DYES: APPLICATION AND PROPERTIES

D. Hildebrand

DYESTUFF APPLICATION DEPARTMENT, FARBENFABRIKEN BAYER, A.G.,
LEVERKUSEN, GERMANY

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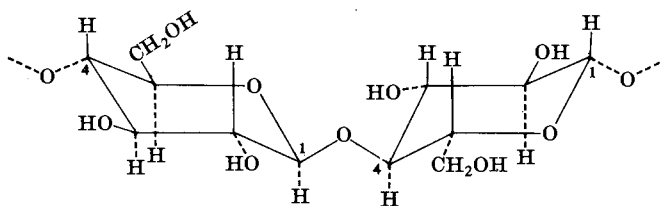
I. Establishment of the Dye-Fiber Linkage

A. BASIC REQUIREMENTS FOR THE FIBER

1. *Cellulosic Fibers*

A covalent bond between a dye molecule and a fiber can only be established if the fiber which is to be dyed contains suitable groups which can be substituted. These groups must not only be present in sufficient quantity to enable deep dyeings, but they must also react under conditions which can be realized from the dyeing point of view. Among the suitable groups are $-\text{OH}$, $-\text{SH}$, and $-\text{NH}_2$. Such groups are present mainly in cellulosic and protein fibers, which are formed from natural polymers.

Although the first successful attempts to obtain the reactive fixation of dyes were made on wool, it has been found that the cellulosic fibers are more suitable as reaction partners for the development of the reactive dyes, since in the case of cotton and viscose staple the fibers which form part of a batch are chemically and physically more homogeneous. As a matter of fact, uniform performance of fibers which have to be dyed is



(VI)

Cellulose conformation

The three hydroxyl groups per anhydroglucose unit correspond to a theoretical substitution capacity of 18.5 moles/kg of fiber. But in most cases the amount of substitution which has actually taken place is far below the theoretical value. It is expressed by the degree of substitution (DS) in percent of the maximum substitution capacity. Only the amorphous fiber spaces are accessible to the bulky dyestuff molecules.^{1,2} Hence the number of OH groups of the cellulose which are effectively accessible to a reactive dye as reaction partners is much smaller than the theoretical value. Hunt *et al.*³ found that the total accessible area in the amorphous range was 71 m²/g in the case of cotton linters. They also found that the size of the pores was 16 Å in the water-swollen state and 20 Å in the caustic-swollen state.

Porter and Schreiber⁴ found that the micellar surface of cotton was 15 m²/g (adsorption of nitrogen from a nitrogen/helium mixture), while correspondingly lower values were found for chemically modified cotton. The pore size was found to be 50 Å.

It is probable that the fiber area which is accessible for the dyeing reaction is identical with the intermicellar surface which can be calculated by means of iodine sorption,⁵⁻⁸ measurement of gas adsorption,⁹ infrared-spectroscopic determination of adsorbents,¹⁰ and from X-ray

¹ H. R. McCleary, *Textile Res. J.* **23**, 673 (1953).

² K. Nishida, *Kolloid-Z. Z. Polymere* **215**, 167 (1967).

³ C. M. Hunt, R. L. Blaine, and J. W. Rowen, *J. Res. Natl. Bur. Std.* **43**, 547 (1949).

⁴ B. R. Porter and S. P. Schreiber, *Textile Res. J.* **37**, 999 (1967).

⁵ K. Schwertassek, *Melliand Textilber.* **32**, 460 (1951).

⁶ G. Nitschke, *Faserforsch. Textiltech.* **3**, 257 (1952).

⁷ B. Gohlke and C. Müller-Genz, *Faserforsch. Textiltech.* **11**, 31 (1960).

⁸ K. S. Bhujang and C. Nanjundayya, *Textile Res. J.* **27**, 79 (1957).

⁹ J. Ruzicka and L. Kudlacek, *Faserforsch. Textiltech.* **18**, 469 (1967).

¹⁰ J. Dechant, *Faserforsch. Textiltech.* **18**, 239 (1967).

data. The accessible or amorphous region occupies 5–14% of the fiber. Speaking in terms of fiber topology, the area which is accessible to the reactive dye will correspond to the reactive area of resin finishing agents,¹¹ so that we can describe and investigate the chemical modification of the cellulose fiber in a uniform manner. But the dyeing reaction has not yet been localized by electron microscope examination in fiber histology. (See also Dolmetsch¹²) in this connection. Swelling of the fiber will also influence the topology of the reaction: swelling processes increase the reactivity of the cellulose,^{13–15} which decreases by thermal treatment, since the intermicellar fiber spaces become smaller if they are exposed to heat.^{16–18} For example, according to Minhas and Robertson,¹⁹ 14% of the hydroxyl groups of a water-swollen fiber are accessible to a chemical reaction, while in a severely (shock-) dried fiber the proportion of accessible hydroxyl groups is only 0.9%. These authors used the thallium ethylate method for their evaluations.

Even before the reactive dyes had been developed, it was a well-known fact that cellulose can, in principle, react in the same way in a heterogeneous medium as an aliphatic alcohol can react in the formation of ethers and esters. General surveys on the chemical modification of cellulose have been given by Rath,^{20, 21} Frieser,^{22, 23} Einsele,²⁴ Stamm,^{25, 26} and Zollinger.²⁶ Alkylation and acylation reactions with water-insoluble alkylating and acylating agents were limited to organic solvents, such as acetone, benzene, dioxane, or xylene, or systems with a low water content. The interaction of cellulose with cyanuric chloride, which is fast and straightforward under these conditions and which led to the first cotton reactive dye, has been described in detail by

¹¹ R. R. Benerito, *Textile Res. J.* **38**, 279 (1968).

¹² Hans and Hilde Dolmetsch, *Melliand Textilber.* **48**, 1449 (1967).

¹³ C. F. Goldthwait, *Am. Dyestuff Repr.* **51**, 928 (1962).

¹⁴ D. D. Gagliardi and A. Wehner, *Textile Res. J.* **37**, 118 (1967).

¹⁵ K. Kh. Razikov, *Vysokomolekul. Soedin.* **9**, 393 (1967).

¹⁶ A. Schaeffer, *Textil-Praxis* **5**, 3 (1950).

¹⁷ I. Yoshino, *J. Chem. Soc. Japan, Ind. Chem. Sect.* **61**, 116 (1958).

¹⁸ B. Philipp, J. Baudisch, and A. Gaudig, *Faserforsch. Textiltech.* **18**, 9 and 461 (1967).

¹⁹ P. S. Minhas and A. A. Robertson, *Textile Res. J.* **37**, 400 (1967).

²⁰ H. Rath, *Rayon Zellwolle Chemiefasern* **9**, 85 (1959).

²¹ H. Rath and U. Einsele, *Melliand Textilber.* **40**, 526 (1959).

²² E. P. Frieser, *SVF Fachorgan Textilveredlung* **14**, 734 (1959).

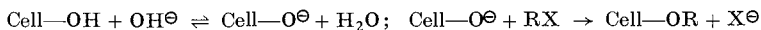
²³ E. P. Frieser, *Textil-Praxis* **21**, 104 (1966).

²⁴ U. Einsele, *Melliand Textilber.* **41**, 721 (1960).

²⁵ O. A. Stamm, *Textil-Rundschau* **19**, 245 (1964).

²⁶ W. Saur, O. A. Stamm, and H. Zollinger, *Textilveredlung* **1**, 4 (1966).

Haller and Hackendorn,²⁷⁻³⁵ as well as by Reid and others.³⁶ In the same manner as the alkylation or esterification of aliphatic hydroxyls, such reactions take place with activated halogen derivatives or sulfuric acid esters in an aqueous alkaline medium at relatively low temperatures. However, a reaction can also take place under conditions of steaming and dry heat fixation.³⁷ The strength of the alkali required for the reaction generally depends on the reactivity of the reactive system used, the reaction taking place in the manner of a Schotten-Baumann reaction as a bimolecular nucleophilic substitution via the cellulose anion, which can be formulated as Cell-O^\ominus .³⁸ In the following equation, R stands for the substituting group and X for the leaving group which has been exchanged for the cellulose anion:



The degree of substitution determines the extent to which the fine structure of the fiber is changed by such a substitution reaction. In every case there is primarily a substitution in the amorphous area.^{39, 40}

Depending on the reagent, the bonds which are formed with cellulose are more of the ether or ester type. The substitution capacity of the three possible hydroxyl groups of the anhydroglucose unit is also different.⁴¹ Extensive research on the distribution of the substituents in reactions with cellulose have shown that the C-2 hydroxyl group is preferred in etherifications, while the C-6 hydroxyl group is given preference in esterification reactions. The reactivity of the primary and secondary hydroxyl groups of regenerated cellulose in heterogeneous and homogeneous acetylations, which has been determined with the help of the

²⁷ CIBA, *DRP* 554,781 (11.4.1929).

²⁸ CIBA, *SP* 124,175 (1930).

²⁹ CIBA, *SP* 144,228 (1931).

³⁰ CIBA, *SP* 145,054 (1931).

³¹ CIBA, *DRP* 583,398 (4.3.1932).

³² CIBA, *USP* 1,896,892 (7.2.1933).

³³ CIBA, *USP* 2,025,660 (1935).

³⁴ CIBA, *BP* 342,167 (1931).

³⁵ CIBA, *BP* 393,914; *FP* 687,301 (21.2.1930).

³⁶ J. Warren, J. D. Reid, and C. Hamalainen, *Textile Res. J.* **22**, 584 (1952).

³⁷ CIBA, *DAS* 1,148,222 (9.4.1959); *BP* 880,624 (10.4.1959).

³⁸ R. H. Wade and C. M. Welch, *Textile Res. J.* **35**, 930 (1965).

³⁹ B. R. Manjunath and C. Nanjundayya, *Textile Res. J.* **35**, 1020 (1965).

⁴⁰ B. R. Manjunath and C. Nanjundayya, *Textile Res. J.* **35**, 377 (1965).

⁴¹ S. P. Rowland, A. L. Bullock, V. O. Cirino, E. J. Roberts, D. E. Hoiness, C. P. Wade, M. A. F. Brannan, H. J. Janssen, and P. F. Pittman, *Textile Res. J.* **37**, 1020 (1967).

triphenylmethane method,^{42, 43} showed that in homogeneous acetylation there is a preferred substitution of the primary hydroxyl groups. In heterogeneous acetylation, the primary OH groups are not clearly preferred in the initial stage, but this preference becomes more pronounced the further the reaction proceeds. Generally the 2-position is the one which is most capable of reacting.⁴⁴ That is why aliphatic reactive groups will substitute cellulose preferably in the 2-position.⁴⁵ In extensive reactive systems where the point of attack is sterically obstructed in the 2-position, the reaction takes place mainly in the 6-position. These are at the same time the reactive systems which form esterlike bonds. Wegmann⁴⁶ reports that triazine derivatives react only in the 6-position. The first fundamental investigations on the reaction of reactive dyes with primary and secondary aliphatic OH groups were made by Dawson *et al.*⁴⁷ These authors compared the rate of reaction of a number of di- and monochlorotriazinyl dyestuffs with primary and secondary alcohols in an aqueous alkaline solution. According to these investigations, the ratio of the reaction rate of primary to secondary hydroxyl groups was between 3.7 and 7.2 for dichlorotriazine dyes or between 13.4 and 15.2 for monochlorotriazine dyes. Since the dichlorotriazine dyestuffs are much more reactive than the monochlorotriazine dyestuffs (see Section I,B,1), the substitution of the secondary hydroxyl group will increase with increasing reactivity of the reactive group.

It was quite difficult to detect the substitution position by isolating corresponding fragments of dyed cellulose due to the resplitting of the glucose-dyestuff bond to substituted glucose during hydrolysis. These difficulties could only be overcome by the use of special reactive systems. For this reason we shall deal with these questions when we deal with the exact evidence for the covalent dyestuff-fiber bond (see Section III).

In order to determine the reaction of reactive dyes with carbohydrates independent of the special conditions of the dyestuff-fiber reaction, various authors⁴⁷⁻⁵⁰ conducted model reactions with soluble polyalco-

⁴² E. Heuser, *Textile Res. J.* **20**, 828 (1950).

⁴³ H. Krässig and E. Schrott, *Makromol. Chem.* **28**, 114 (1958).

⁴⁴ O. A. Stamm, Habilitationsschrift ETH Zürich (1963).

⁴⁵ O. A. Stamm, *Helv. Chim. Acta* **46**, 3019 (1963); H. Zollinger, *Palette* **28**, 32 (1968).

⁴⁶ J. Wegmann, *Melliand Textilber.* **39**, 1106 (1958); *Textil-Praxis* **13**, 938 (1958); *SVF Fachorgan Textilveredlung* **14**, 185 (1959).

⁴⁷ T. L. Dawson, A. S. Fern, and C. Preston, *J. Soc. Dyers Colourists* **76**, 210 (1960).

⁴⁸ E. Bohnert, *Melliand Textilber.* **42**, 1156 (1961).

⁴⁹ W. Beckmann, D. Hildebrand, and H. Pesenecker, *Melliand Textilber.* **43**, 1304 (1962).

⁵⁰ O. A. Stamm, H. Zollinger, H. Zähler, and E. Gäumann, *Helv. Chim. Acta* **44**, 1123 (1961).

hols, sugars, and starch. The model compounds used were mostly sorbitol, mannitol, and glycosides which have primary and secondary OH groups comparable in number with the primary and secondary OH groups of cellulose. D-Glucose and cellobiose each contain an additional free glucosidic OH group which is not present in cellulose as a reaction partner or, if at all, only in negligible amounts as end group [(III), (IV)]. Baumgarte⁵¹ has therefore examined, as suitable models, α -methyl-glucoside, which has only one primary and three secondary OH groups, and α -methyl-D-isorhamnoside, in which the 6-position is also not present. Gluconic acid and saccharic acid have also been used in such investigations. The results of chromatographic analysis of the products of the reaction of chlorotriazine and acrylamide dyes with all the investigated saccharides showed that both the primary and secondary OH groups of carbohydrates are possible reaction partners for a reactive dye. The only compound where no indication of a reaction was found was saccharic acid. There is generally also no reaction with sodium alginate (see also Ulrich⁵²). As already stated, this fact has been interpreted as an indication that there is no reaction of the secondary hydroxyl groups.⁴⁶ The inertness of the sodium alginates to reactive dyes is very important in practical work, because it means that sodium alginates can be used as thickening agents in printing and in padding methods. An explanation which has been offered is that the negative charge carried by the carboxylate anions prevents adsorption of the dye anions.⁵³

In agreement with this idea, a reaction has been established for the undissociated calcium alginate fiber.^{52,56} Other polymers which contain hydroxyl groups, such as polyvinyl alcohol, are likely reaction partners for reactive dyes.^{54,55} This means that reactive dyes can react in an alkaline medium with a wide variety of aliphatic hydroxy compounds. This fact is important not only to understand the chemistry of cellulose as a dyeable substrate, but also to assess side reactions which occur when reactive dyes are applied in the presence of thickening agents based on starch, as well as finishes, low molecular weight cellulose decomposition products, and diluents in combination dyestuffs, as well as auxiliaries which contain alcoholic groups.

The most important prerequisite for a practically useful cotton dyeing method based on a chemical modification of the cellulosic fiber is the

⁵¹ U. Baumgarte, *Melliand Textilber.* **43**, 182 (1962).

⁵² H. M. Ulrich, *Melliand Textilber.* **42**, 81 and 205 (1961).

⁵³ H. Zollinger, *Angew. Chem.* **73**, 125 (1961).

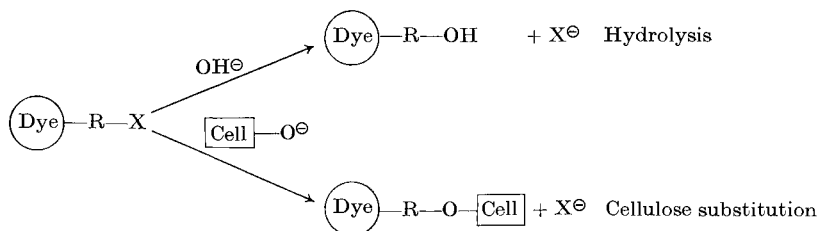
⁵⁴ T. Vickerstaff, *Melliand Textilber.* **39**, 907 (1958).

⁵⁵ U. Einsele, *Melliand Textilber.* **43**, 497 (1962).

⁵⁶ E. E. Tallis, *J. Textile Inst., Trans.* **41**, 151 (1950).

possibility of working in an aqueous medium. The realization of this condition was contrary to the general ideas on the reactive performance of highly reactive systems with cellulose in an aqueous alkaline medium. Even after the work carried out by Rattee,⁵⁷ Bohnert and Weingarten,⁵⁸ Wegmann,⁴⁶ and Vickerstaff⁵⁹ had shown that it is in principle possible to dye cellulosic fibers in an aqueous alkaline medium with water-soluble reactive dyestuffs in deep shades with satisfactory fastness to washing, there was no uniform interpretation of the fact that the major part of the reactive dye does not react with the water, but with the cellulose.

Four hypotheses have been discussed to explain the phenomenon of the preference given to cellulose substitution over the process of hydrolysis:



It was at first assumed that the pH in the fiber is much higher than in the remaining liquor, which would mean that the cellulose substitution is preferred since the speed of reaction increases steeply at an elevated pH level. This hypothesis, however, was abandoned after Sumner⁶⁰ had published his paper on the mechanism of the alkali sorption of cellulose. The preference given to the cellulose substitution was then interpreted as a result of a higher concentration of $\text{Cell}-\text{O}^\ominus$ than of OH^\ominus in the fiber, which involved the postulation of a higher dissociation coefficient for cellulose than for water.⁶¹⁻⁶³ According to Zollinger⁶⁴⁻⁶⁶ the dye particle bound by the fiber must have a decreased tendency to hydrolysis for steric reasons. Bohnert and Weingarten⁵⁸ as well as Beckmann,

⁵⁷ I. D. Rattee, *Endeavour* **20**, 154 (1961).

⁵⁸ E. Bohnert and R. Weingarten, *Melliand Textilber.* **40**, 1036 (1959).

⁵⁹ T. Vickerstaff, *J. Soc. Dyers Colourists* **73**, 237 (1957).

⁶⁰ H. H. Sumner, *J. Soc. Dyers Colourists* **76**, 672 (1960).

⁶¹ H. H. Sumner and T. Vickerstaff, *Melliand Textilber.* **42**, 1161 (1961).

⁶² C. Preston and A. S. Fern, *Chimia (Aarau)* **15**, 177 (1961).

⁶³ W. Ingamells, H. H. Sumner, and G. Williams, *J. Soc. Dyers Colourists* **78**, 274 (1962).

⁶⁴ H. Zollinger, "Chemie der Azofarbstoffe," p. 280. Birkhäuser, Basel, 1958.

⁶⁵ H. Zollinger, *Am. Dyestuff Reprtr.* **49**, 142 (1960); *Angew. Chem.* **73**, 125 (1961).

⁶⁶ H. Zollinger, *Chimia (Aarau)* **15**, 186 (1961).

Hildebrand, and Pesenecker^{49, 67} explained the preference given to the fiber-dye reaction by the higher nucleophilicity of an aliphatic hydroxyl compared with water. This idea has been confirmed by the trials carried out by Dawson, Fern, and Preston, as well as by other authors, with model substances in an aqueous alkaline medium (Fig. 1).

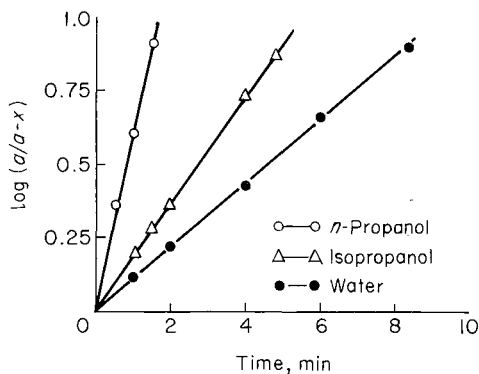


FIG 1. Comparison of the rate of reaction of Procion Red M-GS with *n*-propanol, isopropanol, and water.⁴⁷

The factor of preference given to alcoholysis instead of hydrolysis was 12.7 in the case of methanol and 7.4 in the case of ethanol. Similar

TABLE I

RATE CONSTANTS (k) OF THE REACTION OF OH COMPOUNDS WITH LEVAFIX BRILLIANT RED E-2B IN ALKALINE SOLUTION^a

	Conc. of alcohol (mole/liter)	Alkali consumed 0.1 N NaOH	Time (min)	k'_{alcohol} k_{water}	k_{alcohol} k_{water}	k_{alcohol} (min^{-1}) mole^{-1}
Water	—	13.2	60	—	—	1.5×10^{-3}
Methanol	1	46.4	60	3.3	178	2.7×10^{-1}
Ethanol	1	28.0	60	1.1	59	8.9×10^{-2}
Propanol	1	27	60	1	53	8×10^{-2}
Butanol	1	24	60	0.8	41	6.1×10^{-2}
Sorbitol	1	69.4	15	20	910	1.4
Starch	0.1	—	—	13.3	600	9×10^{-1}

^a k' represents the rate constant of the reaction found for the chosen concentration, k the absolute rate constant of the reaction which is independent of the concentration.

⁶⁷ D. Hildebrand, *Bayer Farben Rev.* No. 9, p. 29 (1964).

results were obtained by Ackermann and Dussy.⁶⁸ The ratio of the rates of reaction with alcohol and water is different for different dyes (Table I). In every case, however, alcoholysis was very distinctly preferred to hydrolysis. Figure 2 shows the analysis of such a reaction between Levafix Brilliant Red E-2B and sorbitol.

We can sum up by explaining the preference for cellulose substitution instead of hydrolysis by the following mechanism: If a reactive dye is brought together with cellulose in an alkaline aqueous medium, both the OH groups of the water and the R—OH groups of the cellulose are available as reaction partners for the dye. These groups enter into the reaction equation in their dissociated form as OH^\ominus and Cell-O^\ominus .⁵⁷⁻⁶¹ In the dyeing reaction, the leaving group of the reactive system, e.g., Cl^\ominus , is exchanged either by Cell-O^\ominus or OH^\ominus , or Cell-O^\ominus and OH^\ominus are added to an activated vinyl compound.⁶⁹ Under the condition that the reactive dyestuff molecule enters into the sphere of a reactive Cell-O^\ominus group, this group reacts with the electrophilic group of the dyestuff 100 times

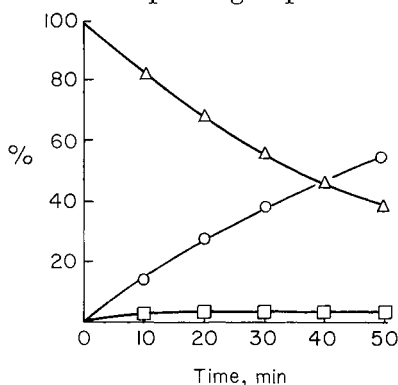


FIG. 2. Reaction of Levafix Brilliant Red E-2B with Sorbitol. Δ , Original dye; \square , first product of hydrolysis; \circ , reaction product with Sorbitol.⁷⁰

faster than OH^\ominus .⁷⁰ Hence the substitution of cellulose in an aqueous medium is a kinetically controlled reaction which is based on the greater nucleophilicity (compared with OH^\ominus) of the aliphatic-substituted R-O^\ominus . The most important fundamental condition for the reactive dyeing of cellulose fiber is the higher reactivity of Cell-O^\ominus in comparison with water.

However, the reaction from an aqueous solution of a reactive dye with a cellulose fiber is only possible if a sufficiently high equilibrium concentration is adjusted on the fiber in such a manner that the particles which

⁶⁸ H. Ackermann and P. Dussy, *Melliand Textilber.* **42**, 1167 (1961).

⁶⁹ E. Bohnert, *Melliand Textilchem.* No. 2, p. 51 (1965).

⁷⁰ D. Hildebrand and W. Beckmann, *Melliand Textilber.* **45**, 1138 (1964).

react with the fiber are replaced from the bath with sufficient speed. This means that the fiber must have a satisfactory adsorption capacity for the dye. This property, which is known as *substantivity*,^{71, 72} is therefore the second fundamental condition which must be fulfilled before a dye-fiber reaction can take place. But the fiber should not only take up the dye from the liquor under pH and temperature conditions which are most favorable for the reaction, but it must also give the dye particle a fair chance to diffuse in the intermicellar range. The most favorable conditions offered by the cellulose as reactive partner are therefore based not only on its great number of substitution sites and their higher nucleophilicity in comparison with water, but also on its substantivity and its accessibility at low temperatures. But the reactivity is not solely dependent on a particularly favorable swelling and adsorption process at low temperatures. Nonsubstantive dye particles can also be applied to the fiber by a padding method, and the reaction is then started by a curing or steaming process which has been specially adjusted to suit the reactivity. Under these conditions, which are particularly important in practice, cellulose can also be made to react with less reactive systems. The reactivity of the cellulose is increased by compounds which have groups which will break hydrogen bonds and which improve the accessibility of the intermicellar region.⁷³ The reactivity is also improved by increasing the Cell-O⁻ concentration in the fiber. Mercerized or caustic-treated cotton will therefore react more easily with reactive dyes than cotton which has not been pretreated. Hence an alkaline pretreatment is often necessary to create favorable conditions for an optimum dye-fiber reaction. If detergents, wetting agents, and emulsifying agents are used at the same time, a degreased and more easily wettable and hence more easily swollen fiber is obtained which enables easier penetration of the reactive dye particle into the cellulose. The basic conditions for an optimum dye-fiber reaction are not fulfilled if the cellulose has lost the substituting OH groups completely or partly due to chemical pretreatment (Table II), for example, by a chemical reaction with crease-proofing agents.⁷⁴ Furthermore, a fiber which has been dyed with a reactive dye and then stripped may have been modified in its reactivity to such an extent that it becomes difficult or even impossible to dye it once again with a reactive dye. The dye-fiber reaction is also adversely affected in the case of cellulose which contains

⁷¹ H. H. Sumner and T. Vickerstaff, *Melliand Textilber.* **42**, 787 (1961).

⁷² W. Beckmann, "Deutscher Färberkalender," p. 131. Franz Eder Verlag, Munich, 1965.

⁷³ S. M. Betrabet, E. H. Daruwalla, and H. T. Lokhande, *Textile Res. J.* **36**, 684 (1966).

⁷⁴ D. Hildebrand, *Melliand Textilber.* **49**, 936 (1968).

low molecular weight glycosidic components, e.g., sizes or finishes containing cotton seed husks or hydroxy groups. Because of the easier accessibility of such OH groups, the dye which is brought onto the fiber will react more easily with these substances, so that the amount of dye which is bonded to the fiber becomes proportionately less. An oxidizing pretreatment or bleaching to an extent which is usually practiced has

TABLE II

SATURATION VALUES OF ANTICREASE-FINISHED COTTON CELLULOSE AGAINST CI REACTIVE RED 41 WHEN DYEING FROM A LONG LIQUOR^a

Type of compound	Catalyst	Fixation	Saturation values		
			In % of untreated fiber	Moles/100 g fiber	g pure dyestuff/100 g fiber
Dimethylol dihydroxy-ethylene urea	200 ml/liter HCl 10 g/liter NH ₄ Cl	Acid wet cross-linking	73	0.0046	3.5
Dimethylol ethylene urea	200 ml/liter HCl 10 g/liter NH ₄ Cl	Acid wet cross-linking	110	0.0069	5.3
Dimethylol dihydroxy-propylene urea	200 ml/liter HCl 10 g/liter NH ₄ Cl	Acid wet cross-linking	105	0.0066	5.1
Epichlorohydrin	15% NaOH padding	Alkaline wet cross-linking	380	0.0240	18.2
Dimethylol propylene urea	15 g/liter ZnCl ₂	5 min 150°	70	0.0044	3.3
Trimethylol melamine	10 g/liter (NH ₄) ₂ SO ₄	5 min 150°	47	0.0029	2.2
Carbamide resin	10 g/liter (NH ₄) ₂ SO ₄	5 min 150°	93	0.0058	4.4
Untreated	—	—	100	0.0063	4.8

^a 2% dyestuff; 20 g/liter soda ash; 50 g/liter Na₂SO₄; 40°; time: 2 hours for every stage.

been found to be less unfavorable. But a more severe oxidizing treatment will modify the fixing properties of reactive dyes in a characteristic manner. For example, Stonehill⁷⁵ found that the yield of fixation would decrease depending on the degree of oxidation when printing was done with di- and monochloro reactive dyes. The influence of the pretreatment became the more noticeable the less reactive the dye was. It was con-

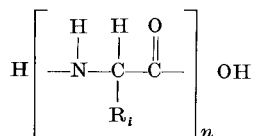
⁷⁵ H. I. Stonehill, *J. Soc. Dyers Colourists* **74**, 584 (1958).

cluded from these observations that the dichloro reactive dye can also react with the secondary OH groups, since its chances to react were hardly affected by blocking the 6-position during oxidation.

Pronounced interference with the dye-fiber reaction can be seen in fibers containing alkaline earth or heavy metal ions which precipitate the reactive dye. It appears that the kinetics of the reaction are obstructed by the formation of insoluble aggregates.

2. Protein and Polyamide Fibers

The protein fibers include wool and other animal hairs (mohair), the regenerated protein fibers, and natural silk. Since they are mixed condensates of different amino acids, they consist of a number of different monomers,⁷⁶⁻⁷⁹ in contrast to the synthetic polyamides, and hence they also contain different groups of varying reactivity toward reactive systems (Table III). All fiber proteins have the following principal chain in common, which has an NH₂ and a COOH end group.



On account of the high molecular weight of the chain and the available NH, OH, and SH groups in the side chains (R_i), the end groups are unimportant, because they will not play any role in the reaction, in contrast to the synthetic polyamides. The side chains can be subdivided into seven groups, as shown in Table IV. Of these, the following groups are basically suitable as reactive partners for reactive dyes: the hydroxyl group of serine and threonine, the SH group of cysteine, the phenolic OH group of tyrosine, the NH₂ group of lysine, the guanidino group of arginine, and the NH group of histidine (see also Zahn *et al.*⁸⁰⁻⁸³). One hundred kilograms of wool will therefore contain as reactive partners 108 equivalents of alcoholic OH, 3 equivalents of SH, 26 equivalents of phenolic OH, 16.3 equivalents of NH₂, and 5.3 equivalents of NH. Due to the closely packed crystalline structure of the native

⁷⁶ K. Ziegler, *Ullmann* **15**, 584 (1964).

⁷⁷ D. H. Simmonds, *1st Intern. Wool Textile Res. Conf., Australia, 1955* Cp. 65 (1956).

⁷⁸ D. H. Simmonds, *Textile Res. J.* **28**, 314 (1958).

⁷⁹ N. J. Hipp, J. J. Basch, and W. Gordon, *Arch. Biochem. Biophys.* **94**, 35 (1961).

⁸⁰ H. Zahn and A. Würz, *Biochem. Z.* **322**, 327 (1952).

⁸¹ P. Alexander, *Kolloid-Z.* **122**, 8 (1951).

⁸² H. Zahn and W. Gerstner, *Biochem. Z.* **327**, 209 (1955).

⁸³ H. Zahn, *Fachzeitschrift das Leder* **6**, 1 (1968).

TABLE III
AMINO ACID COMPOSITION OF NATURAL POLYAMIDE FIBERS (g AMINO
ACID/100 g FIBER)

	<i>Fibroin of natural silk</i>	<i>Keratin of Merino wool</i>	<i>Mohair</i>	<i>Casein</i>
Glycine	39.9	5.2	4.9	2.1
Alanine	31.6	3.7	4.0	3.4
Valine	2.6	5.0	7.8	5.7
Leucine	0.7	7.6	7.3	8.0
Iso-leucine	—	3.1	3.6	6.0
Proline	0.6	7.3	6.4	8.7
Phenylalanine	1.1	3.4	3.9	4.8
Aspartic acid	2.6	6.7	7.2	7.0
Glutamic acid	1.9	15.0	15.5	21.0
Lysine	0.7	2.8	3.2	8.2
Arginine	0.9	10.5	8.6	4.0
Histidine	0.3	0.9	1.1	3.0
Serine	12.8	9.0	7.8	6.3
Threonine	1.1	6.6	5.8	4.5
Tyrosine	10.9	6.4	3.5	7.3
Cystine	0.1	11.3	9.7	0.4
Cysteine	—	0.35	0.37	—
Methionine	2.59	0.6	—	2.6
Tryptophan	0.4	2.1	—	2.0

TABLE IV
NUMBER OF SIDE CHAINS
(MOLES FOR 10⁵ g WOOL)

Acid	65
Basic	82
Phenolic	26
Alcoholic	152
Amide type	81
With sulfur content	104
Hydrocarbon	351

protein fibers, only the amorphous regions of the fiber are accessible for a reaction without changing the fiber properties. This is also true of the cellulosic fibers. But the amorphous regions of the protein fibers are those segments in which the major part of the reactive amino acids is located.

The helical structure of wool⁸⁴ and the structure of silk, which resembles that of plane gratings,⁸⁵ are responsible for an accumulation of these often large-spaced side chains in the amorphous region (see Fig. 3). The amorphous region not only contains a larger proportion of reactive groups, but also chemically bound water which is essential as reaction and diffusion medium. It goes without saying that a satisfactory accessibility of the reactive fiber regions under reactive dyeing conditions is the second demand which must be made on the substrate to be dyed, besides a fundamental ability to react. While silk offers little resistance to penetration of the dye, the penetration of dye molecules in wool is

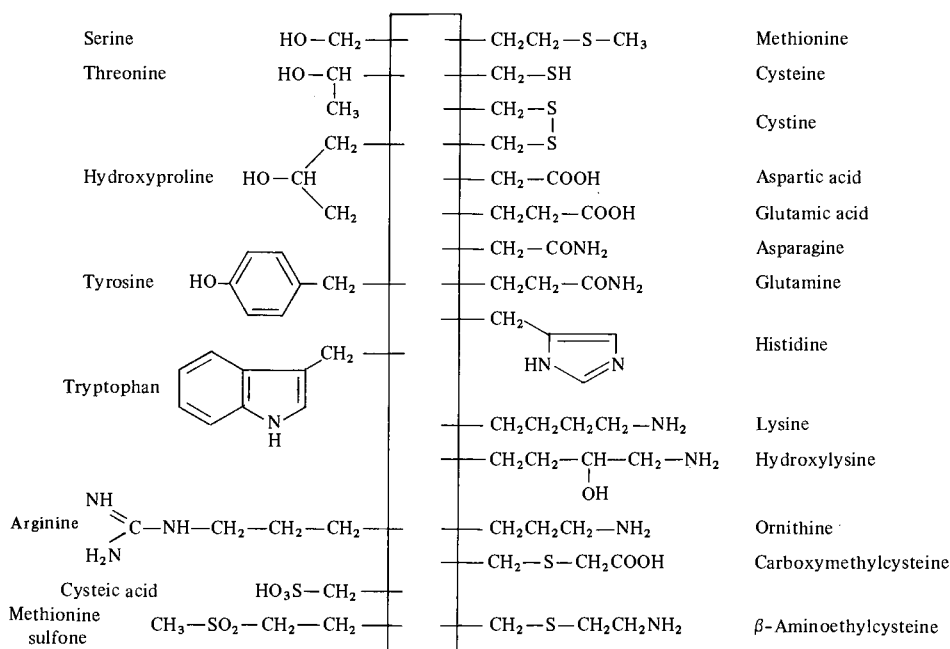


FIG. 3. Functional side chains in proteins.

obstructed by a resistant layer which envelops the fiber and which is known morphologically as cuticle.⁸⁶ Since the cuticle is also decisive for the felting properties of the fiber, its removal in oxidizing nonfelting finishing will, of course, increase the accessibility of the fiber.

⁸⁴ L. Pauling, R. B. Corey, and H. R. Branson, *Proc. Natl. Acad. Sci. U.S.A.* **37**, 205 (1951).

⁸⁵ K. H. Meyer and H. Mark, *Ber. Deut. Chem. Ges.* **61**, 1932 (1928).

⁸⁶ H. Zahn, *Melliand Textilber.* **32**, 419 (1951).

A reaction between dyestuff and fiber can only take place in connection with an adsorption process which, contrary to the substantivity of cellulose, involves a dyeing mechanism dependent upon pH. Hence the adsorption equilibrium of a dyestuff particle which contains sulfo groups must be in the acid range to enable a reaction which will give a reasonable yield. On the other hand, $-O^{\ominus}$, the formation of which is essential for the substitution of OH groups, requires a pH level of 8–9. Under these conditions the ability of the anionic dyestuff to go onto the negatively charged fiber is extremely low. Moreover, the alkaline dye liquors, especially at temperatures above 45° , will lead to a breakdown of the cystine bridges of the wool, so that the fiber is severely tendered.^{87, 88} But a reaction which had started in the acid range by an adsorption process can be completed by increasing the pH, for example, by a mild aftertreatment using ammonia. Cysteine bridges are not present as structural units in silk. Besides, the amino group content of silk is much lower than that of wool, since it is only 4.1 equivalents of NH_2 per 100 kg of fiber. The OH groups of serine, which is present in abundance, will therefore offer sufficient reactive possibilities in the weakly alkaline range (75 equivalents/ 10^5 g fiber). The nucleophilic properties of the NH and NH_2 group, which are higher than those of the OH group, will, however, enable the occurrence of the reaction in the weakly acid range (acetic or formic acid) for a number of reactive groups. The quantity of free NH and NH_2 groups bound in the state of equilibrium will be sufficient to bring about a complete reaction even if the reaction time is short. Highly reactive dyestuffs can even produce a reaction in a sulfuric acid medium in the acid pH range. The SH group can also be effective as a reactive partner on account of its high nucleophilicity.⁸⁹ The reactive performance of reactive dyes in relation to other protein bodies, such as collagen,^{90, 91} gelatine,^{92, 93} histological material,⁹⁴ or living protein, is based on the same functional groups.

Model reactions with amino acids and suitable amino acid derivatives

⁸⁷ D. Hildebrand and H. Zahn, *SVF Fachorgan Textilveredlung* **13**, 376 (1958).

⁸⁸ D. Hildebrand, *SVF Fachorgan Textilveredlung* **14**, 34 (1959).

⁸⁹ J. Shore, *J. Soc. Dyers Colourists* **84**, 408 (1968).

⁹⁰ G. Reinert, Dissertation, Rheinisch Westfälische Technische Hochschule, Aachen (1967).

⁹¹ H. Zahn and G. Reinert, *Kolloid-Z. Z.f. Polymere* **226**, 1 (1968).

⁹² B. Seidel, *Phot. Sci. Eng.* **8**, 76 (1964).

⁹³ H. R. Hadfield and D. R. Lemin, *J. Textile Inst., Trans.* **51**, 1351 (1960).

⁹⁴ V. B. Ivanov, *Dokl. Akad. Nauk SSSR* **137**, No. 2, 419 (1961).

have been conducted by different authors⁹⁵⁻¹⁰¹ to investigate the basic conditions for a reaction between reactive dyes and proteins. The investigations were mainly made with dichloro- and monochlorotriazine dyestuffs, as well as with chloroacetyl, acrylamide, and vinyl sulfone dyestuffs. Using chromatographic methods, these authors tried to find out whether reactions between the dyestuffs and the dissolved model compounds took place under certain conditions. Very recently, Shore¹⁰² conducted a comprehensive kinetic investigation of the entire problem. Investigations on the performance of fiber proteins in dyeing with reactive dyes have been published by Wegmann,¹⁰⁰ Casty,¹⁰¹ Rattee,¹⁰³ Osterloh,¹⁰⁴ von Hornuff and Flath,⁹⁸ Hille,¹⁰⁵ Mella,¹⁰⁶ Baumgarte,⁹⁹ Hine and McPhee,¹⁰⁷ Derbyshire and Tristram,¹⁰⁸ Graham,¹⁰⁹ and Zahn.¹¹⁰ These authors carried out end group determinations and total amino acid analyses of the dyed fiber material. The basis for all such experiments is supplied by the dinitrophenylation¹¹¹ of wool, silk, and polyamide fibers which was developed subsequent to the first trials by Middlebrook¹¹² and Blackburn,¹¹³ by Zahn and co-workers.¹¹⁴⁻¹¹⁶

⁹⁵ J. Vsiansky, *Textil-Praha* **14**, 430 (1959).

⁹⁶ A. D. Wirnik and M. A. Tschekalin, *Technol. Textile Ind. USSR (English Transl.)* **19**, 109 (1960); **20**, 95 (1961).

⁹⁷ B. M. Bogoslovskii, A. D. Wirnik, and M. A. Tschekalin, *Izr. Vysshikh Uchebn. Zavedenii, Tekhnol. Legkoi Prom.* p. 80 (1960).

⁹⁸ G. von Hornuff and H. J. Flath, *Faserforsch. Textiltech.* **12**, 559 (1961).

⁹⁹ U. Baumgarte, *Melliand Textilber.* **43**, 1297 (1962).

¹⁰⁰ J. Wegmann, *SVF Fachorgan Textilveredlung* **14**, 185 (1959).

¹⁰¹ R. Casty, *SVF Fachorgan Textilveredlung* **13**, 586 (1958); CIBA, *SVF Fachorgan Textilveredlung* **13**, 598 (1958).

¹⁰² J. Shore, *J. Soc. Dyers Colourists* **84**, 413 (1968).

¹⁰³ D. M. Lewis, I. D. Rattee, and C. B. Stevens, *3rd Congr. Intern. Rech. Textile Lan., Paris, 1965* p. 213 (1966).

¹⁰⁴ F. Osterloh, *Melliand Textilber.* **41**, 1533 (1960).

¹⁰⁵ E. Hille, *Textil-Praxis* **17**, 171 (1962).

¹⁰⁶ K. Mella, Dissertation, T. H. Aachen (1964).

¹⁰⁷ R. J. Hine and J. R. McPhee, *J. Soc. Dyers Colourists* **81**, 268 (1965).

¹⁰⁸ A. N. Derbyshire and G. R. Tristram, *J. Soc. Dyers Colourists* **81**, 584 (1965).

¹⁰⁹ J. G. Graham, *Deut. Textiltech.* **16**, 178 (1966).

¹¹⁰ G. Reinert, K. Mella, P. F. Rouette, and H. Zahn, *Melliand Textilber.* **49**, 1313 (1968).

¹¹¹ F. Sanger, *Biochem. J.* **39**, 507 (1945).

¹¹² W. R. Middlebrook, *Nature* **164**, 321 (1949).

¹¹³ S. Blackburn and A. G. Lowther, *Biochem. J.* **48**, 126 (1951).

¹¹⁴ E. R. Fritze and H. Zahn, *Biochem. Z.* **327**, 126 (1955).

¹¹⁵ H. Zahn and W. Gerstner, *Forschungsber. Landes Nordrhein-Westfalen* **498** (1957).

¹¹⁶ H. Zahn and A. Würz, *Melliand Textilber.* **36**, 123 (1955).

The first method of determination of the lysine amino groups of wool with the help of the reaction with 1-fluoro-2,4-dinitrobenzene has been described by Speakman.¹¹⁷

The aim of these investigations was, on the one hand, to prove the existence of a covalent bond between reactive dye and protein fiber (see Section III,B) and, on the other hand, to identify the actually substituted groups in the fiber. The results have shown that the percentage share of the individual substituting groups of the fiber is a function both of the structure and reactivity of the reactive groups and of the reaction conditions. Linking reactions have been determined for bifunctional dyes based on dichlorotriazine,¹¹⁸ of the kind earlier described by Zahn,^{119, 120} Alexander,¹²¹ and Rath¹²² for the reaction of wool with bifunctional and polyfunctional reactive systems. Primary and secondary amino groups, e.g., in glycine and *N*-acetylhistidine, reacted in a weakly acid medium, while aliphatic OH groups, e.g., in *N*-benzoylserine, reacted only at pH levels above 10. According to Wegmann,¹⁰⁰ the reaction of the amino groups took place more easily in the acid range the stronger the basicity of the amino group. More dyestuff could be fixed at pH 4 on wool which had been given a reductive treatment, while on oxidized wool less dyestuff could be fixed than on untreated wool at the same pH level. In relation to acrylamide dyestuffs,⁹⁹ it was concluded from this that the SH groups are accessible at pH 4, while the amino groups are accessible above a pH of 5. However, with more highly activated reactive dyes, reactions of the amino group were also found below pH 5.¹²³ A reaction with reactive dyes was also found for the phenol groups of tyrosine. Based on model reactions, it was possible to identify SH, phenolic-OH, and NH groups as probable reaction partners under dyeing conditions. No noticeable reaction of the serine hydroxyls was found in the course of these investigations. Osterloh¹⁰⁴ found with the help of a 10% dyeing of Remalan Brilliant Blue R on wool that the terminal amino acid alanine, aspartic acid, glutamic acid, glycine, serine, and threonine with their amino groups and the internal amino acids cysteine, lysine, and tyrosine had reacted with their functional side chains.

In contrast to this, von Hornuff and Flath⁹⁸ found in trials with

¹¹⁷ J. B. Speakman, *Melliand Textilber.* **33**, 823 (1952).

¹¹⁸ F. Manchester, *J. Soc. Dyers Colourists* **74**, 421 (1958).

¹¹⁹ H. Zahn, *Melliand Textilber.* **31**, 762 (1950).

¹²⁰ H. Zahn, *Kolloid-Z.* **121**, 39 (1951).

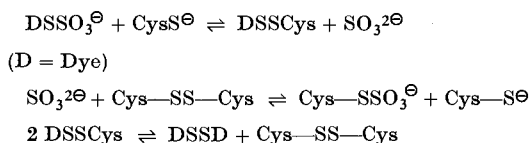
¹²¹ P. Alexander, *Melliand Textilber.* **35**, 3 (1954).

¹²² H. Rath, *Melliand Textilber.* **38**, 78, 181, 321, 656, 794, 927, 1290, and 1406 (1957).

¹²³ D. Hildebrand, and G. Meier *Bayer Farben Revue* No. 20, p. 12 (1971).

triazine dyestuffs that another terminal amino acid, valine, had also reacted, while they did not observe any reaction of aspartic acid and glutamic acid. They found a side-chain reaction with arginine and histidine, but not with lysine. Hille¹⁰⁵ reported as reactive sites the side chains of histidine, serine, cysteine, lysine, and tyrosine, while Derbyshire and Tristram,¹⁰⁸ who investigated acrylamide dyestuffs, were only able to identify the free amino group of the bonded lysine as reaction partner. They could not definitely exclude a reaction of cysteine because of the low cysteine content of wool. The possible reaction with the imidazol group of histidine was not investigated because there was no suitable model substance, but analysis according to Moore and Stein did not give any indication. A possible reaction of the terminal amino groups was not examined because they are present in such low numbers that they could not exercise any appreciable influence on the dyeing result. Contrary to the findings which had been obtained with acrylamide dyestuffs in wool which had been dyed with a metal-free chloroacetyl dyestuff, a reaction of the cysteine and in the imidazol nucleus was found. In a recent paper by Zahn and Rouette¹²⁴ on the performance of untreated, partially reduced and oxidized wool dyed with vinyl sulfone and acrylamide dyestuffs, it has been pointed out that in untreated wool the ϵ -amino groups of lysine will react almost exclusively, apart from the thiol groups which are only present in small numbers. A very striking reaction in partially reduced wool was observed for the SH groups of cysteine in an acid medium and at relatively low temperatures.

Dyes with thiosulfate reactive groups are bonded to the wool at least temporarily via the cysteine groups. In this case cysteine acts as a catalyst. When the reaction is complete, the dye is no longer bonded to the wool, but is present in the fiber as an insoluble pigment:^{125, 126}



The number of substituted groups in the fiber is changed by chemical modification. This changes the reactivity of the fiber and its dyeing performance in relation to reactive dyes. Important changes take place in wool before shearing as the result of exposure to light and to weather.

¹²⁴ H. Zahn and P. F. Rouette, *Textilveredlung* **3**, 241 (1968).

¹²⁵ B. Milligan and J. M. Swan, *Textile Res. J.* **31**, 18 (1961).

¹²⁶ F. Osterloh, *Melliand Textilber.* **44**, 57 (1963).

These affect the chemical properties of the tips of the wool as compared with the remaining fiber, so that a wool fiber can be divided into zones of different reactivity.¹²⁷ Other chemical influences which are important for the performance of wool in relation to reactive dyes, or which can become important, are alkaline scouring, steaming, carbonization, oxidative and reductive bleaching, the stripping of faulty dyeings, chlorination, deamination, and, finally, substitution with acylating and alkylating agents. Such pretreatments can increase or lower the number of reaction sites in the fiber which are essential for the reactive dyeing process. If wool of different origin and different case history, as far as pretreatment is concerned, is mixed, there are bound to be characteristic difficulties if we try to produce level and reproducible dyeings with reactive dyestuffs.

The same conditions which apply for protein fibers are also valid for the reaction between reactive dyes and synthetic fibers. The amino group can be considered as the most important partner in the reaction. This amino group can be present as a terminal group, as is the case with polycaprolactam or hexamethylene adipamide, or it can be present as a side chain as in Meraklon (basic modified polypropylene). But the dye-binding capacity is limited, because the amino group content is much lower than that of natural fibers. (In the case of nylon the amino group content is only 3.7 equiv./10⁵ g fiber). This means that slight differences in the terminal group content can easily lead to uneven dyeings. The mechanism of adsorption is that of an ion exchange in the case of dyestuffs which contain sulfo groups, while in the case of reactive disperse dyes (Procinyl dyestuffs of ICI) this mechanism is represented by a dissolution process. Since there are no bonds which are susceptible to alkali, the pH of the reaction can be in the alkaline range. Alkaline aftertreatment is also permissible.

B. BASIC REQUIREMENTS FOR THE DYE

1. *Reactivity*

a. Assessment and Definition. The most characteristic property of a reactive dye is its reactivity toward a fiber; but to obtain a numerical definition of this term, the rate of hydrolysis under defined pH and

¹²⁷ D. Hildebrand, *Z. Ges. Textil-Ind.* **61**, 180 (1959).

temperature conditions is accepted as a measure of the reactivity.¹²⁸⁻¹⁵¹ The hydrolysis constant k_w (W stands for water), which has been determined at a constant temperature and a constant pH, is used as a measure for this reaction of pseudo-unimolecular order. This measure of reactivity is of course only valid for dyes which react under alkaline conditions with the Cell-O[⊖] group of the cellulose. There is no generally valid relationship between the reactivity towards amino groups of wool in an acid medium and the hydrolysis constant k_w which has been determined in an alkaline medium. So far it has not been possible to introduce a simple and general measure of reactivity for wool-reactive groups. A relative comparison of reactivity is, however, possible by comparing the rate of reaction with a suitable model compound, for example, an amino acid. The derivation and determination of the hydrolysis constant k_w as a measure of the reactivity of a reactive dyestuff in an aqueous alkaline medium are based on the equation for bimolecular reactions which can be assumed as valid for most reactive systems. According to this equation, the decrease with time ($-d[R]$) of

- ¹²⁸ T. Vickerstaff, *J. Soc. Dyers Colourists* **73**, 237 (1957); *Hexagon Digest* **27**, 3 (1958).
¹²⁹ E. Bohnert, *J. Soc. Dyers Colourists* **75**, 581 (1959); *Melliand Textilber.* **40**, 1036 (1959).
¹³⁰ I. D. Rattee, in "Procion Dyestuffs in Textile Dyeing," p. 24. I.C.I., Manchester, 1962.
¹³¹ T. L. Dawson, A. S. Fern, and C. Preston, *J. Soc. Dyers Colourists* **76**, 210 (1960).
¹³² T. Vickerstaff, *Dyer* **76**, 166 (1961).
¹³³ H. H. Sumner and T. Vickerstaff, *Melliand Textilber.* **42**, 1161 (1961).
¹³⁴ J. R. Aspland, A. Johnson, and R. H. Peters, *J. Soc. Dyers Colourists* **78**, 453 (1962).
¹³⁵ H. Ackermann and P. Dussy, *Melliand Textilber.* **42**, 1167 (1961).
¹³⁶ C. Preston and A. S. Fern, *Chimia (Aarau)* **15**, 177 (1961).
¹³⁷ H. Ackermann and P. Dussy, *Helv. Chim. Acta* **45**, 1683 (1962).
¹³⁸ W. Beckmann, D. Hildebrand, and H. Pesenecker, *Melliand Textilber.* **43**, 1304 (1962).
¹³⁹ U. Baumgarte and F. Feichtmayr, *Melliand Textilber.* **44**, 163 and 267 (1963).
¹⁴⁰ D. Hildebrand and W. Beckmann, *Melliand Textilber.* **45**, 1138 (1964).
¹⁴¹ A. A. Charcharov and S. I. Gurtovenko, *Izv. Vysshikh Vchebn. Zavedenii, Tekhnol. Tekstil'n. Prom.* p. 95 (1964).
¹⁴² T. L. Dawson, *J. Soc. Dyers Colourists* **80**, 134 (1964).
¹⁴³ D. Hildebrand, *SVF Fachorgan Textilveredlung* **20**, 644 (1965).
¹⁴⁴ D. Hildebrand, *Bayer Farben Rev.* No. 9, p. 29 (1964).
¹⁴⁵ A. Datyner, P. Rys, and H. Zollinger, *Helv. Chim. Acta* **49**, 755 (1966).
¹⁴⁶ P. Rys and H. Zollinger, *Helv. Chim. Acta* **49**, 749 and 761 (1966).
¹⁴⁷ P. Rys, *Textilveredlung* **2**, 95 (1967).
¹⁴⁸ D. Hildebrand, *Bayer Farben Rev.* No. 13, p. 1 (1967).
¹⁴⁹ D. Hildebrand, *Melliand Textilchem.* p. 102 (1965).
¹⁵⁰ W. Ingamells, H. H. Sumner, and G. Williams, *J. Soc. Dyers Colourists* **78**, 274 (1962).
¹⁵¹ J. R. Aspland and A. Johnson, *J. Soc. Dyers Colourists* **81**, 477 (1965).

the reactive dyestuff concentration $[R]$ of a dyestuff solution is proportional to the dyestuff concentration and the base concentration $[OH^\ominus]$:

$$-\left(\frac{d[R]}{dt}\right)_T = k_{wbi}[R][OH^\ominus] \quad (1)$$

If the reaction takes place at a constant pH, $[OH^\ominus]$ can be included in the constant k_{wbi} , so that a general expression is obtained for the determination of the quantity $[R]$:

$$-\left(\frac{d[R]}{dt}\right)_{T, pH} = k_w[R] \quad (2)$$

The value of k_w is obtained from (2) by integration, or, expressed in logarithmic terms where x represents the dyestuff which has reacted during the time t :

$$-\int \frac{d[R]}{[R]} = k_w \int dT \quad (3)$$

$$[R] = [R]_0 \exp k_w t \quad (4)$$

$$k_w = \frac{2.3}{t} \log \frac{[R]_0}{[R]_0 - x} \quad (5)$$

In these equations, $[R]_0$ is the quantity of reactive dyestuff at the time $t = 0$ ($[R]_0 = 100\%$). According to (5), k_w is easy to calculate if $[R]_0$ and x can be determined by analysis.

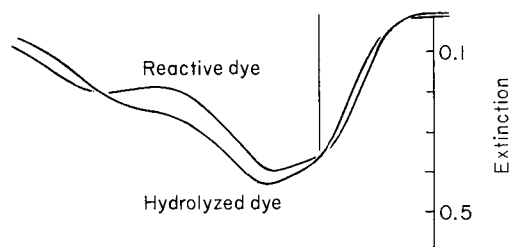


FIG. 4. Determination of the isosbestic point of Procion Brilliant Orange M-GS.

A method of determination which is generally applicable is the chromatographic separation of the initial product and the product of hydrolysis, and the spectrophotometric evaluation of the separated zones.^{131, 139} The photometric determination of the separated zones is done at the isosbestic point (see Fig. 4) either with the eluates of the extracted zones or by direct photometric evaluation on paper or a thin-layer plate (Figs. 5, 6). Accurate and reproducible k_w values can be

obtained in this manner if several measurements are made at different times. It is most important to ensure that the pH and temperature conditions are strictly maintained. In some cases the reduction in the quantity of the original dyestuff as a function of time, as well as the formation of a hydrolysis product, can be followed directly by photo-

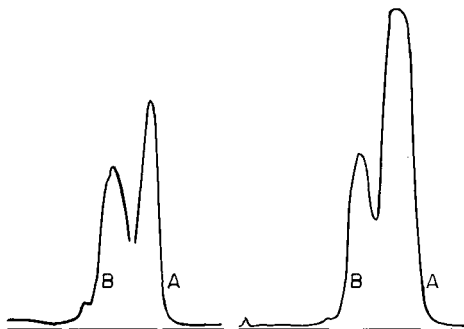


FIG. 5. Photometric determination of the chromatographically separated components of a partial hydrolysate using the Chromoscan (Joyce Loebel Ltd.). A, Starting product; B, hydrolysate.

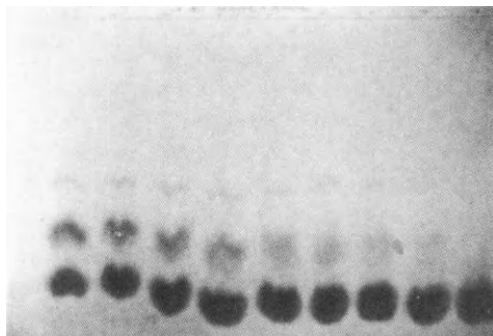


FIG. 6. Chromatographic representation of a partial hydrolysis of Levafix Brilliant Red E-2B.

metric determination. For triazine dyestuffs, use was made of the reaction with pyridine and of the photometric determination of the reaction product to determine the reactive content of a dyestuff solution and therefore to find out how it would change in the course of time under alkaline conditions.¹³¹ A direct method is based on the potentiometric determination of the ionic chlorine of a hydrolysis trial solution with 0.1 *N* silver nitrate solution.¹³⁷

The change of reactive dye content can also be determined by means of titration of the alkali consumption of a dyestuff solution of known molar concentration at a constant pH, or by dyeing. Titration can only be done if the total reactive dye concentration in the reaction mixture is known. This is, however, often difficult to determine, since there are many side reactions in total hydrolysis so that it is very difficult to

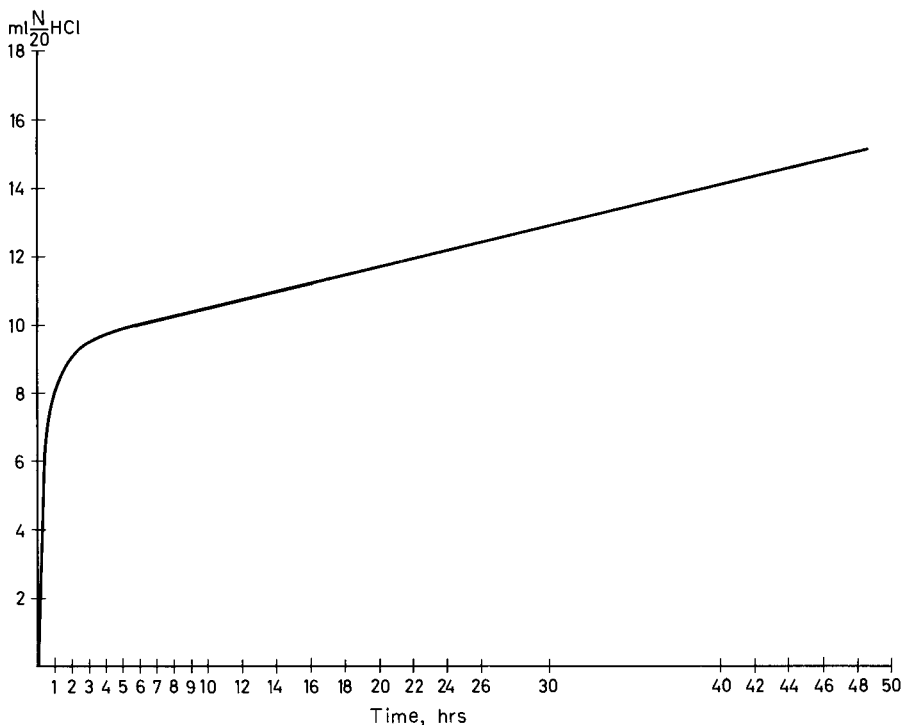
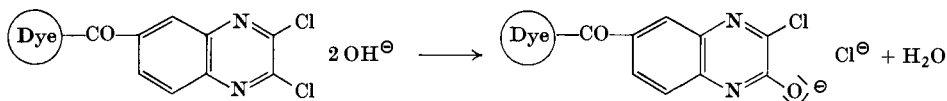


FIG. 7. Hydrolysis curve of Levafix Brilliant Red E-2B in alkaline medium; 0.5 mmole reactive dye; pH = 11.0; 40°C. Titration of the HCl formed as a function of time: 10 ml 0.05 N HCl = 100%. Reactive dye: The steep part of the curve represents the hydrolysis of the first chlorine atom, while the flat part of the curve represents the hydrolysis of the second chlorine atom.

estimate the total amount of alkali consumed. Moreover, if several reactive or leaving groups are present, the separation of the first leaving group may be superimposed on that of the second. The rate of reaction of the individual systems can nevertheless be determined in a few cases by extrapolation of the hydrolysis curves (see Fig. 7).¹⁴⁸ When assessing the

titration results, it should be borne in mind that the quantity of consumed OH^\ominus equivalents is twice the number of hydrolyzed leaving groups, since one equivalent is consumed by the reactive group. For example:

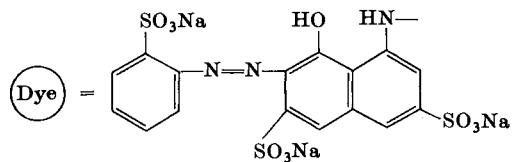


The dyeing method is the most inaccurate of all the methods mentioned above. This method usually consists of allowing a dyestuff solution with a buffered pH value to stand for different lengths of time and then padding this solution onto a cotton fabric, followed by dyeing according to the cold pad-batch process (see Section I,D,3) or by a pad-cure method. In this manner, the progress of hydrolysis with time can be determined, and this can be used as a relative measure of the rate of reaction. This method also serves as the basis for determining the stability of pad liquors. The reactivity can be expressed by the time in which there is a 5% drop in color depth in a given pad liquor (e.g., soda-alkaline). It is difficult to obtain values with this method which are generally comparable, first, because different initial pH values are obtained with the same initial weights of different dyestuffs, and second, because the reproducibility of a dyeing method is not good enough to permit the introduction of a general constant.

Table V gives a survey of the reactivity of different reactive groups with the same chromophoric system at constant pH and temperature. This survey is based on chromatographic determination of the reactivity.

b. Dependence of Reactivity on pH and Temperature. It follows from the derivation of the reactivity as a hydrolysis constant of a bimolecular reaction with the OH^\ominus of the water at a constant pH that, if this relationship is strictly valid, the rate of reaction of the reactive dyestuff will change by the factor 10 for every pH unit. In fact, for a number of dyestuffs in the pH range 8–12 a linear proportionality has been established between the pH and the rate of hydrolysis (Fig. 8). But there are some dyestuffs which behave differently. This is particularly noticeable if the pseudo-monomolecular reaction constants are transformed into the bimolecular constants by means of division through the OH^\ominus concentration. Figure 9 shows that the bimolecular reaction constant of different dyestuffs will drop in a certain pH range. It is obvious that this indicates

TABLE V

REACTION RATE CONSTANTS (MIN^{-1}) OF DIFFERENT REACTIVE GROUPS^a

	0.33
	0.035
	0.017
	0.06
	0.0095
	0.00047
	0.00035

^a pH 10.0, 140°F.

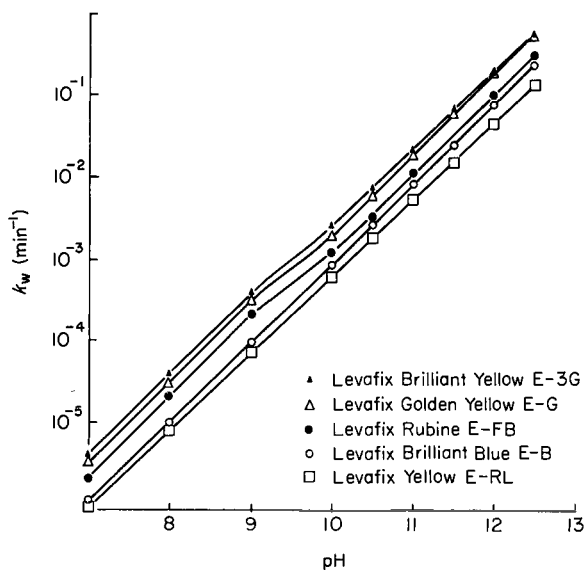


FIG. 8. Pseudomonomolecular reaction constants k_w of Levafix E dyes as a function of pH.

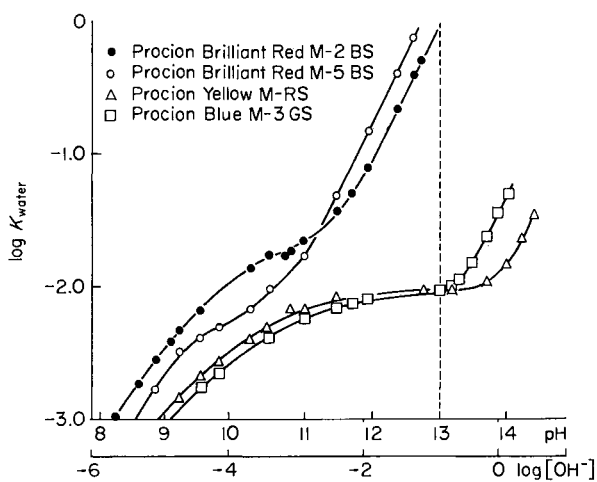


FIG. 9. Pseudomonomolecular reaction constants k_w of Procion dyes as a function of pH.¹³¹

a change of the chemical reactivity. Attention was first drawn to the change of reactivity with changing pH value by Ackermann and Dussy,¹³⁵ and later by Ingamells, Sumner, and Williams,¹⁵⁰ Rys,^{145, 146} and others,¹⁵² and this phenomenon was explained by the dissociation of the secondary amide which links the chromophoric system with the reactive group. However, the reactivity is influenced by dissociation processes even in the case of such dyestuff types which do not contain an amide bridge which is capable of dissociation. It follows from the

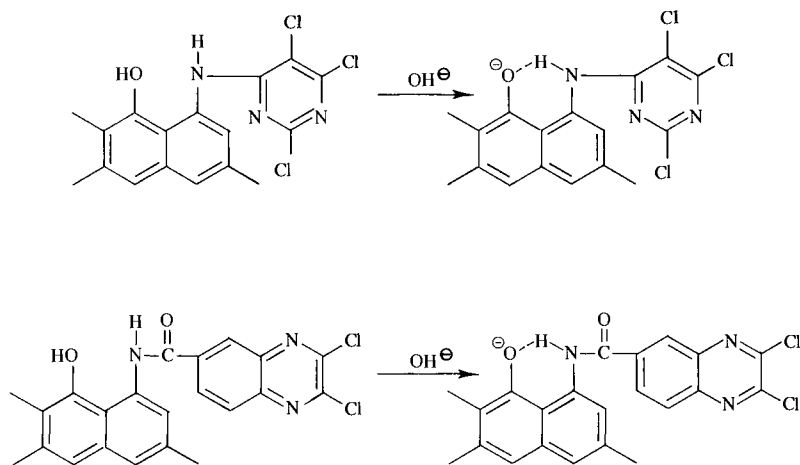


FIG. 10. Formation of hydrogen bonds at the amino bridge of reactive dyes by dissociation of an angular phenol.

chemical structure and from titration values that in this case the drop in reactivity is linked with the occurrence of an anionic charge in the chromophoric system. The effect of the dissociation on the reactivity is due to the positive character of the C atom to which the exchangeable group is attached. This positive character is reduced by the electron pressure of the negative charge. Phenol groups are among the most important groups in the dye molecule which are capable of dissociation (Fig. 10).¹⁴⁰

Like all chemical reactions, the rate of reaction of reactive dyes depends strongly on the temperature. A temperature increase of 10° produces an acceleration of the reaction by a factor of about 3.3. This

¹⁵² K. G. Kleb, K. Sasse, and E. Siegel, *Angew. Chem.* **76**, 423 (1964).

corresponds to an activation energy of approx. 24 kcal/mole.¹⁵³ The exact values are 18.8 kcal/mole in the case of vinyl sulfone dyestuffs, and 24.6 kcal/mole for dichloroquinoxaline dyestuffs.¹⁴⁴ The differences in respect to the change with changing temperature are only slight within one and the same range of dyestuffs, and there are also no significant differences if we compare different reactive systems based on chloro heterocycles, since an activation energy of this kind is generally found in such systems. There is a characteristic difference between the activation energy of the hydrolysis and of the cellulose substitution. Bohnert

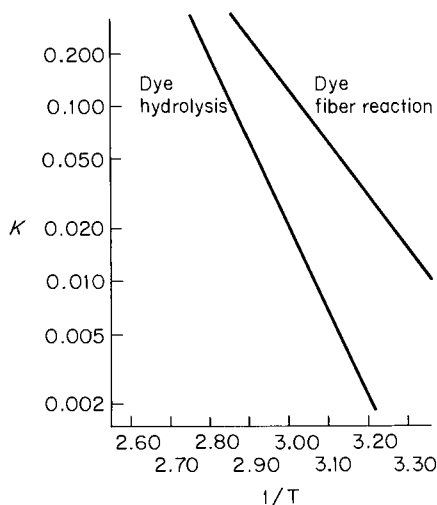


FIG. 11. Dependence of rates of reaction upon temperature.

and Weingarten^{129, 153} were the first authors to draw attention to this characteristic difference (Fig. 11).

c. Reactivity and Chemical Structure. If we compare the different reactive systems which are known today, on the basis of representative hydrolysis constants as a measure of reactivity, we will find that there are not only great differences between different commercial ranges of reactive dyestuffs due to the presence of different reactive groups (see Table V), but that dyestuffs of very different reactivity can be present in a commercial range of reactive dyestuffs, all of which are based on one and the same reactive principle.^{133, 143} We can plot the range of variation of the different members of a commercial range of reactive dyestuffs on

¹⁵³ R. Weingarten, *Textilveredlung* **3**, 151 (1968).

a bar chart with a relative scale to show at a glance the relation between different commercial ranges of reactive dyestuffs on the basis of their reactivity Fowler and Marshall (Fig. 12)^{154, 155} described. This means that the reactivity of a reactive dyestuff is determined by two factors: (1) the chemical structure and arrangement of the supporting group and the leaving group, which jointly form the reactive group, and (2) the influence of the chromophoric system on the reactivity of the reactive system. Investigations on the influence of the chromophoric system on the reactivity of the reactive system have only been made in a few cases, e.g., by Koopman¹⁵⁶ on the influence of substituents on the mobility of chlorine in 4,6-dichloro-1,3,5-triazines, by Ackermann and Dussy¹³⁷ on the chemical structure and reactivity of trichloropyrimidyl amino compounds, and by Kleb, Sasse, and Siegel¹⁵² on the reactivity of different substituted 2,3-dichloroquinoxaline-6-carboxylic acid amides. But these papers are mainly confined to model compounds. The interactions between the chromophoric system and the supporting group can be based on mesomerism or on inductive effects or both. We can neglect the influence exercised on the leaving group. Important factors are therefore the distance between the resonance system of the chromophoric group and the supporting group, as well as the basicity of the nitrogen bridge. The influence of the chromophoric system is particularly noticeable in variations of the dependence of hydrolysis on the pH level compared with the pH dependence of hydrolysis in the bimolecular reaction.

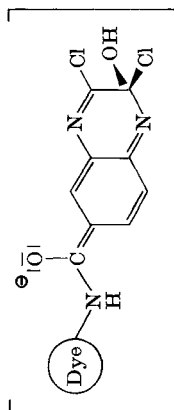
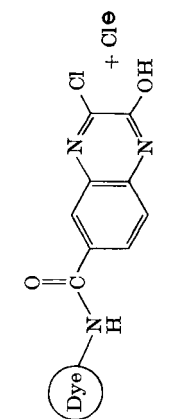
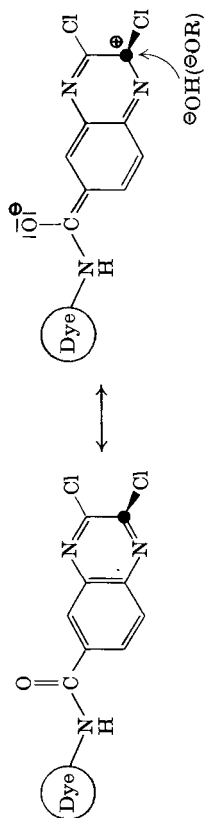
The reactive systems which are known today can mainly be classified into two groups: reactive systems which give nucleophilic substitution reactions, and reactive systems which give nucleophilic additive reactions. The importance of mesomerism for nucleophilic aromatic substitution is shown in the following example, which is based on 2,3-dichloroquinoxaline-6-carboxylic acid amide. In this example, the reaction is triggered by the attack on the positively polarized C atom of the system by a particle with a free pair of electrons, leading to the formation of an intermediate compound of the Meisenheimer type. This compound is transformed, by the elimination of Cl^\ominus as leaving group, into the substitution product. The reaction takes place as a bimolecular second-order reaction in which the formation of the intermediate is the slowest step:

¹⁵⁴ J. A. Fowler and W. J. Marshall, *J. Soc. Dyers Colourists* **80**, 358 (1964).

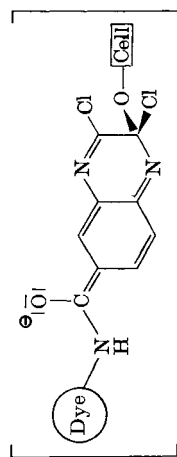
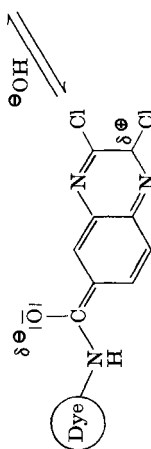
¹⁵⁵ J. A. Fowler and W. J. Marshall, *SVF Fachorgan Textilveredlung* **20**, 243 (1965).

¹⁵⁶ H. Koopman, *Rec. Trav. Chim.* **81**, 465 (1962).

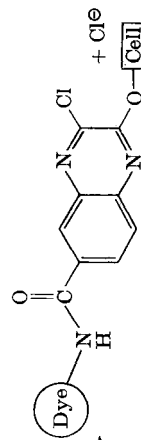
Hydrolysis



Fixation



Meisenheimer complex
intermediate



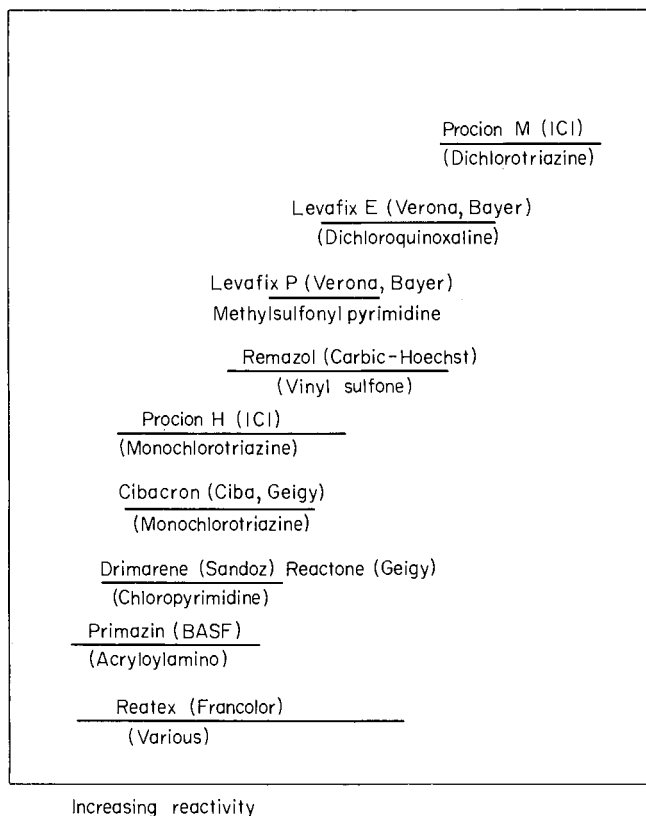
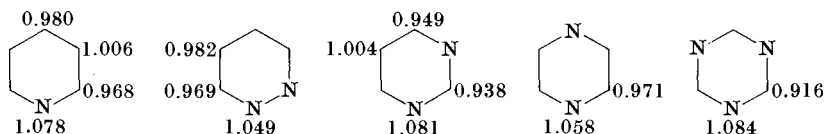


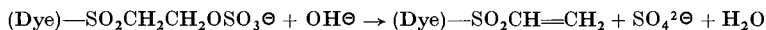
FIG. 12. Relative reactivity of commercial dyes with different reactive systems. The arbitrary scale is based on the conditions required for fixation of the dyes on cellulosic fibers (pH, temperature, time). From Fowler and Marshall, *JSDC*, **80**, 358 (1964).

The inductive effect of the electronegative nitrogen in heterocyclic ring systems can be seen clearly from the following diagram of the charge distribution in five heterocyclic molecules as calculated by Peacock.¹⁵⁷

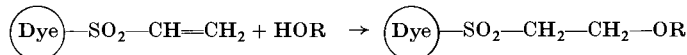
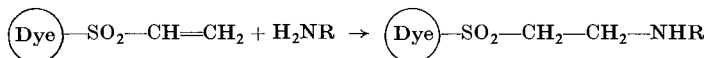


¹⁵⁷ T. E. Peacock, "Electronic Properties of Aromatic and Heterocyclic Molecules," p. 103. Academic Press, New York, 1965.

Among the dyes which react on the basis of an addition mechanism we should underline particularly the Remazol dyestuffs.¹⁵⁸ The reactive group of these commercially available dyestuffs is a sulfatoethyl sulfone: (Dye)—SO₂CH₂CH₂OSO₃Na, which is easily transformed into the reactive vinyl sulfone when alkali is added^{129, 144, 159, 160}:



This reaction is extremely rapid even under mild conditions, e.g., at room temperature, so that there is no significant increase of the pH when NaOH or Na₂CO₃ solutions are added dropwise to concentrated dyestuff solutions until the amount of alkali added agrees with the amount which is required by the equation given above. The vinyl sulfone dyestuffs which are formed in this manner have a high additive capacity for OH[⊖] and [⊖]O—R, as well as H₂N—R:



Rys and Stamm¹⁶¹ were able to show by synthesis that the symmetric bis-arylsulfonylethyl ether can also be formed as a by-product.

d. Influence of Electrolytes and Concentration on Reactivity. Since reactive dyes have only low substantivity, salt is required for dyeing in a long liquor and as a component of alkali pad baths in the two-bath padding method salt increases the dye uptake of the cellulose and prevents separation of the dyestuff from the fiber by the pad liquor. The electrolyte screens the forces of repulsion between the negatively charged cellulose and the dyestuff anions. But we can expect on the basis of the reaction mechanism that the salt will also exercise a positive effect on the rate of reaction of the dye itself, since generally speaking polar media will facilitate the formation of the transition state or intermediate of the Meisenheimer complex type. The dependence of the rate of reaction on the ion concentration of the reactive medium is known as primary salt effect.^{161a, 162} In fact, a positive primary salt effect

¹⁵⁸ H. U. von der Eltz, *Melliand Textilber.* **40**, 69 (1959); **46**, 286 (1965).

¹⁵⁹ *DRP* 842,198 (8.1.1942)

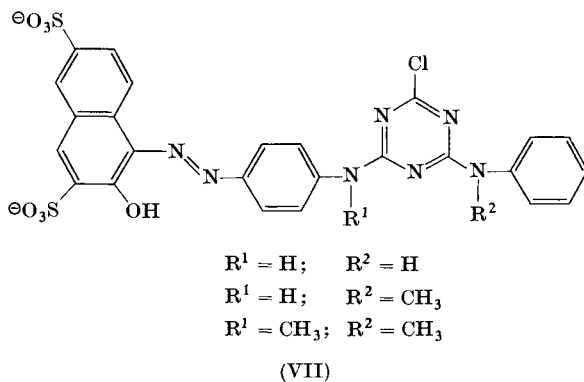
¹⁶⁰ L. A. Kowshin and A. A. Charcharov, *Technol. Textile Ind. USSR (English Transl.)* **39**, 100 (1964).

¹⁶¹ P. Rys and O. A. Stamm, *Helv. Chim. Acta* **49**, 2287 (1966).

^{161a} J. N. Brönsted, *Z. Physik. Chem.* **102**, 169 (1922); **115** 337 (1925).

¹⁶² A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed., p. 151. Wiley, New York, 1961.

can be shown both for the hydrolysis and for the substitution of reactive chlorine, using soluble model compounds for this purpose.¹⁴³ It is also possible to exercise a positive influence on the cellulose substitution with the help of salt even if the process of going on the fiber (which depends on the amount of electrolyte present) has already been completed. This positive influence of salt on the cellulose substitution can be promoted, for example, by spraying the fixing solution onto the fiber without leading to the formation of a liquid phase in the fabric. In addition, the salt effect will increase the internal pH value.¹⁶³ If there are precipitations due to excessive electrolyte content, the rate of reaction will drop. Corresponding observations have been made in highly concentrated solutions of reactive dyestuffs and in the case of dyestuffs which tend to form aggregates. According to investigations carried out by Datyner *et al.*¹⁴⁵ as well as by Rys¹⁴⁶ on the hydrolysis of reactive monochloro dyestuffs, the influence of preceding association equilibria can be derived from the kinetics of hydrolysis of the dyestuffs. According to these authors, a dyestuff having the structure (VII) will produce aggregates if the dyestuff concentration is 6×10^{-4} mole/liter, but there will be no aggregates if the concentration is 6×10^{-6} mole/liter.

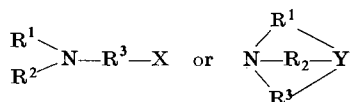


Similar results have been obtained in the extensive theoretical work of Rys¹⁴⁷ on the reactive behavior of reactive dyes. In this case, too, kinetic anomalies are explained, partly by tautomerism equilibria (see Section I,D,1), and partly by association equilibria which depend on the presence of electrolytes and on the concentration. This means that hydrolysis also depends on the buffer system.

e. The Effect of Catalysts on Reactivity. The search for means to increase the reactivity of the relatively inert monochlorotriazine and

¹⁶³ H. H. Sumner, *J. Soc. Dyers Colourists* **76**, 672 (1960).

chloropyrimidine dyes led to the result that it is possible to increase the rate of reaction of reactive dyes which have at least one mobile chlorine atom linked to a diazine or triazine ring system, by a factor of 4–8 with the help of certain tertiary amines, hydrazines, tetrazenes, and hydrazones.^{164–173} Such products are commercially available, e.g., under the names Cibacron Catalyst CCB or CCI.^{174–180} This possibility appeared to be particularly interesting for the application of monochlorotriazine dyestuffs by the exhaustion method,¹⁷⁹ and the cold pad-batch method,¹⁸⁰ as well as for cutting down the steaming times required in textile printing^{174, 176, 177} and in continuous dyeing methods.^{178, 180} Another possibility offered by the use of such products is that one and the same range of reactive dyes can be used under different conditions of application, and that the reactivity can be adjusted to suit the requirements of the dyeing or printing process in each case. In this method, compounds of the following formulas (or water-soluble salts of such compounds) are used as tertiary amines in a quantity of 0.1–10% of the dye employed.



¹⁶⁴ ICI, *BeP* 595,299 (22.9.1960); *BP* 927,772 (24.9.1959).

¹⁶⁵ CIBA, P. Ulrich, H. P. Schaub, H. H. Bosshard, and E. J. Koller, *SP* 393,249 (17.8.1961); *SZAS* 962,561, 10687/61 (14.9.1961); *BeP* 621,442 (16.8.1962); 622,423 (13.9.1962); *AustP* 238,132; *USP* 3,211,513; *BP* 981,258; *FP* 1,336,406; *DAS* 1,213,820 (16.8.1962); CIBA, *FP* 1,417,574 (14.12.1964).

¹⁶⁶ H. P. Schaub and P. Ulrich, *Textil-Rundschau* **16**, 815 (1961).

¹⁶⁷ P. Ulrich, *Textil-Rundschau* **16**, 411 (1962); *SVF Fachorgan Textilveredlung* **17**, 162 (1962).

¹⁶⁸ P. Ulrich and W. Baek, *Textil-Rundschau* **17**, 362 (1962).

¹⁶⁹ ICI, *BeP* 628,381 (13.12.1963); 628,855 (25.2.1963).

¹⁷⁰ ICI, *FP* 1,370,185 (15.5.1963); *BP* 973,906 (6.2.1963); 999,233 (18.2.1963).

¹⁷¹ S, *FP* 1,385, 660 (12.12.1963).

¹⁷² S, A. Barthold, and W. Wehrli, *BeP* 635,896; 635,897 (6.8.1963).

¹⁷³ S, M. Capponi, and R. Entschel, 635,252; 638,513 (10.10.1963).

¹⁷⁴ H. Werdenberg, *SVF Fachorgan Textilveredlung* **16**, 751 (1961).

¹⁷⁵ M. Haelters, *Ciba Rundschau* p. 43 (1962).

¹⁷⁶ W. Badertscher, *Am. Dyestuff Repr.* **52**, 38 (1963).

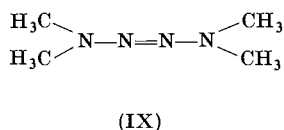
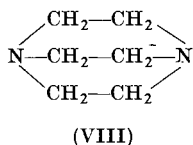
¹⁷⁷ W. Badertscher, *SVF Fachorgan Textilveredlung* **18**, 229 (1963).

¹⁷⁸ M. Haelters, *SVF Fachorgan Textilveredlung* **18**, 287 (1963).

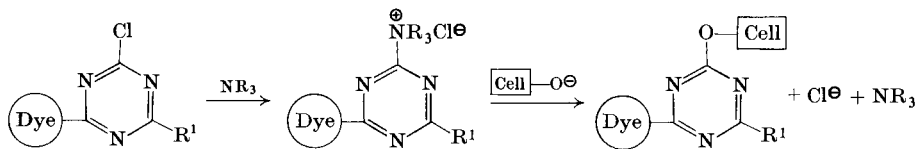
¹⁷⁹ M. Peter, *Ciba Rundschau* p. 43 (1963); *SVF Fachorgan Textilveredlung* **18**, 426 (1963).

¹⁸⁰ M. Haelters and P. Perrin, *Ciba Rundschau* p. 43 (1964).

In these structural formulas, R^1 and R^2 represent alkyl or alkylene groups with 1-4 carbon atoms, R^3 an alkylene group with 1-10 carbon atoms, $X = H$ or OH , and $Y = N$ or CH . A typical example which deserves to be mentioned is 1,4-diazabicyclo[2.2.2]octane (VIII). Charcharov and Gurtovenko¹⁸¹ and Zacharova¹⁸² have shown that it is also possible to use amines (such as triethanolamine) containing hydroxy groups. *N,N*-Dimethylhydrazine is a suitable hydrazine derivative. Among the tetrazene compounds which are suitable, special attention was given to tetramethyltetrazene (IX).



A suitable hydrazone is acetone dimethylhydrazone.¹⁷² The reactivity of the halogen N-heterocycles is governed both by the electron-attracting effect of the heterocycle and by the ability of the linkage between the heterocycle and the leaving group. The reactivity of chloroheterocycles can be modified by the following mechanism¹⁸³ (see also Stamm¹⁸⁴):



Hence the catalytic process is a quaternization of the amine by the electrophilic C atom of triazine, where the transition complex which has been formed in this manner will react much more easily with the cellulose anion than the monochlorotriazine itself. The catalytic effect increases with increasing basicity of the tertiary amine and with increasing electronegativity of the substituent R^1 . This means that the effect exercised by a catalyst on the acceleration of the rate of reaction is different for different dyes. We learn from the dependence upon temperature that the activation energy of the catalyzed hydrolysis

¹⁸¹ A. A. Charcharov and S. I. Gurtovenko, *Izv. Vysshikh Uchebn. Zavedenii, Tekhnol. Textil'n. Prom.* p. 98 (1965).

¹⁸² T. D. Zacharova, *Izv. Vysshikh Uchebn. Zavedenii, Tekhnol. Textil'n. Prom.* p. 107 (1967).

¹⁸³ T. L. Dawson, *J. Soc. Dyers Colourists* **80**, 134 (1964).

¹⁸⁴ O. A. Stamm, *J. Soc. Dyers Colourists* **80**, 416 (1964).

is reduced by 5 kcal/mole. According to investigations by Dawson¹⁸³ on the kinetics of reaction of monochlorotriazine dyes in the presence of tertiary amines as catalyst (see Table VI), the yield of fixation on the fiber is greatly dependent on the hydrolysis, which is accelerated more than fixation. The catalyst thus reduces the cellulose selectivity of the monochlorotriazine dyes and it also reduces the stability of the pad

TABLE VI

FIXATION OF PROCIION BRILLIANT RED H-3B ON PAPER CELLULOSE BY MEANS OF *N,N*-DIMETHYLHYDRAZINE^{a, b}

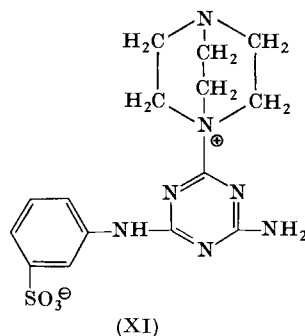
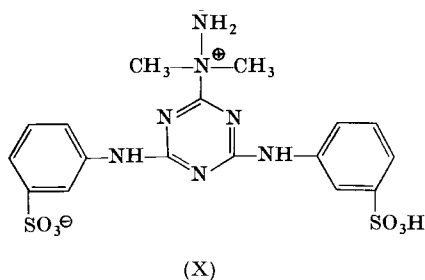
<i>Batching time (hr)</i>	<i>Catalyst conc. (g/liter)</i>	<i>Fixation (x) %</i>	<i>Monochloro dye</i>	<i>Unfixed species Quaternized dye</i>	<i>Hydrolyzed dye (y)</i>	<i>Ratio (x:y)</i>
0.25	0.25	12.7	77.5	4.7	5.1	2.5
	0.54	28.6	46.2	17.5	7.7	3.7
0.5	0.25	21.8	65.6	2.8	9.8	2.2
	0.54	48.0	33.5	4.8	13.7	3.5
1	0.25	36.0	50.6	0	13.4	2.7
	0.54	63.3	16.7	2.2	17.8	3.5
2	0.25	54.1	32.6	0	14.3	3.8
	0.54	74.3	4.9	0	20.8	3.6
3	0.25	60.3	21.0	0	15.7	3.8
	0.54	75.0	3.8	0	21.2	3.5
5	0.25	65.0	19.9	0	16.1	4.0
	0.54	75.6	2.9	0	21.5	3.5
24	0.25	79.5	0	0	20.5	3.9
	0.54	79.0	0	0	21.0	3.7

^a Dawson.¹⁸³

^b Temp. 18°; pH of soln. 11.05; dye conc. 15 g/liter.

liquors. Since the acceleration effect is (in first approximation) proportional to the concentration of catalyst, it will be possible to adjust the reactivity to the most favorable value for each process. Besides the tertiary bases and their salts which have already been mentioned, patents have also been applied for quaternary ammonium compounds (X) and (XI), which do not have dyestuff character and which are added to the padding solution of monochlorotriazine dyes. These compounds will also increase the rate of reaction.¹⁸⁵

¹⁸⁵ G. Hölzle, P. Ulrich, and H. P. Schaub, CIBA, *BeP* 625,803 (7.12.1962).



2. Diffusion and Substantivity

Before a reactive dye can react with a cellulose fiber, it must go on the fiber from the aqueous dye solution, and it must be able to migrate to the sites in the fiber which are capable of reaction. Since only that dye is fixed which has gone on the fiber, while the portion of the dye which has remained in the liquor can only hydrolyze under the conditions of the reaction, we can establish a quantitative relationship between the constant for the rate of reaction, the diffusion constant, and the quantity of dye which has gone on the fiber. Hence the three fundamental data which describe the dyeing performance of a reactive dye are its diffusion property, substantivity, and reactivity.^{186, 187} According to Sumner,¹⁸⁸ Danckwerts has given an equation (6) which describes the relation between the rate of reaction dye-cellulose (K_{Cell}), the amount of dye which has gone substantively on the fiber (C_F), and the diffusion constant (D). We have already drawn attention to this equation when we discussed the question of preferential cellulose substitution.

$$Q_F = C_F \left(t + \frac{1}{2K_{\text{Cell}}} \right) (D \cdot K_{\text{Cell}})^{1/2} \quad (6)$$

where Q_F is the amount of dyestuff which reacts with the fiber during the time t ; C_F , the dyestuff concentration in the substrate; K_{Cell} , the rate of reaction constant for the dyestuff-fiber reaction; D , the diffusion constant, and t , the time. By differentiating this equation with respect to t we get the speed dQ_F/dt from which we can calculate according to Rattee¹⁸⁹ the efficiency P , assuming that both the cellulose substitution

¹⁸⁶ H. H. Sumner and T. Vickerstaff, *Melliand Textilber.* **42**, 1161 (1961).

¹⁸⁷ W. Beckmann, "Deutscher Färberkalender," p. 131, Franz Eder Verlag, Munich, 1965.

¹⁸⁸ H. H. Sumner, *J. Soc. Dyers Colourists* **76**, 672 (1960).

¹⁸⁹ I. D. Rattee, *Melliand Textilber.* **45**, 782 (1964).

and the hydrolysis are equally dependent on the temperature and take place at the same rate:

$$P = ZS \left(\frac{D}{K_w} \right)^{1/2} \quad S = \frac{C_F}{C_w} \quad (7)$$

In Eq. (7), Z is a constant which is characteristic for every dye $[(K_{\text{Cell}}/K_w)^{1/2}]$, while S stands for the substantivity. The decrease of the yield P with increasing temperature is therefore due to the decrease in substantivity S and the increase of K_{Cell} . If dyeing is done in a long liquor, the yield is directly proportional to the substantivity, while the ratio rate of diffusion/reactivity appears in this equation only in the form of its root value.

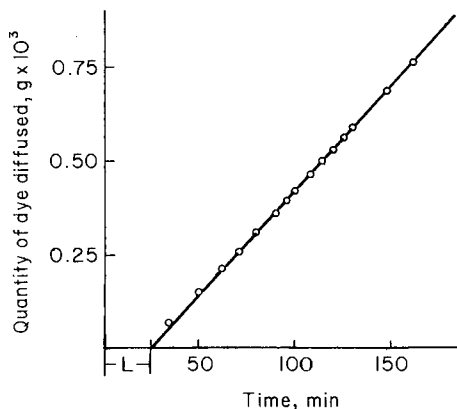


FIG. 13. Rate of diffusion of Procion Rubine M-B into viscose film at 20° ($[\text{NaCl}] = 0.5 \text{ N}$; neutral buffer concentration = 0.2 N).¹⁷⁰

It is difficult to measure the diffusion constant D directly under reactive dyeing conditions, since the dye will react in an alkaline medium either with the cellulose or with the water, and only indirect conclusions can be drawn from measurements carried out in the neutral range, due to the dependence of the dye-dye and dye-fiber interaction upon pH. Sumner and Taylor¹⁹⁰ have therefore evaluated integral diffusion coefficients of suitable inactivated dyes where the reactive chlorine was replaced by ammonia. Viscose film was used as diffusion medium. The determination was made in accordance with Fig. 13 using Eq. (8).

$$D = \frac{dQ_d}{dt} \frac{x}{AC_F} \quad (8)$$

¹⁹⁰ H. H. Sumner and B. Taylor, *J. Soc. Dyers Colourists* **83**, 445 (1967).

In Eq. (8), Q_d represents the amount of dye which diffuses in the time t through the effective area A having a layer thickness x , while C_F stands for the dye concentration at the surface of the viscose film. According to the results obtained by Sumner and Taylor, the differences in the diffusion capacity of the individual dyes are considerable, even if the reactive group is the same. Besides, in some dyes the rate of diffusion increases with increasing pH, while in others the rate of diffusion decreases. Table VII shows data obtained for Procion Brilliant Red M-2BS, Procion Yellow M-RS and Procion Rubine M-BS for different dye concentrations of the solution (D_s). The rate of diffusion governs not only the fixation process, but also the rate at which the unfixed portion of the dye is washed off.¹⁹¹

The influence of the diffusion is particularly noticeable in textile printing and in continuous padding processes. Since the rate of reaction is strongly dependent on the temperature, it is the diffusion process which governs the rate of reaction.¹⁹² Dry heat fixation of phthalocyanine dyes¹⁹³ is therefore a great problem when reactive dyes are used, especially on regenerated cellulose, because its enveloping layer will severely obstruct diffusion.

The substantivity $S = C_F/C_W$ is calculated according to Zollinger¹⁹⁴ by determining the absorption value in the state of equilibrium in percent (E), taking the liquor ratio L into consideration:

$$S = \frac{LE}{100 - E} \quad (9)$$

For reasons which are easy to understand, the diffusion property and the substantivity must operate in opposing directions (Fig. 14). In other words, high substantivity means low rate of diffusion, and vice versa. Capponi and Senn¹⁹⁵ plotted the roots of the relative diffusion coefficients against the percentage of bath exhaustion. Dyes of similar constitution were located in narrow bands running from the top left-hand corner to the bottom right-hand corner. The term "similar constitution," means both the chromophoric system and the reactive group. The influence of different chromophoric systems is shown schematically in Fig. 15 and Fig. 16 and in Table VIII, respectively. These figures show that the 1:2 metal complex dyes and the phthalocyanines diffuse at a parti-

¹⁹¹ F. I. Sadov and T. D. Balasova, *Tekstil'n. Prom.* **24**, 61 (1964).

¹⁹² D. Hildebrand, *Melliand Textilber.* **49**, 67 (1968).

¹⁹³ M. Haelters, *SVF Fachorgan Textilveredlung* **18**, 287 (1963).

¹⁹⁴ H. Zollinger, *Textil-Rundschau* **15**, 75 (1960).

¹⁹⁵ M. Capponi and R. C. Senn, *J. Soc. Dyers Colourists* **82**, 8 (1966).

TABLE VII
EXTRAPOLATED VALUES OF THE DIFFUSION COEFFICIENT ($\text{cm}^2/\text{min} \times 10^8$) FOR A GIVEN D_S IN ALKALINE SOLUTION^{a,b}

Procion Brilliant Red M-2BS				Procion Yellow M-RS				Procion Rubine M-BS			
pH	$D_S 4 \times 10^{-5}$	$D_S 8 \times 10^{-5}$	$D_S 1.6 \times 10^{-4}$	$D_S 4 \times 10^{-5}$	$D_S 8 \times 10^{-5}$	$D_S 1.6 \times 10^{-4}$	$D_S 3 \times 10^{-5}$	$D_S 6 \times 10^{-5}$	$D_S 1.2 \times 10^{-4}$		
6.4	210	240	270	5.9	7.2	8.7	36	40	46		
8.0	210	240	270	6.6	8.1	9.8	32	36	43		
9.1	210	240	270	7.0	8.6	10	27	30	35		
9.7	220	240	280	7.2	8.9	11	21	23	28		
11.0	260	300	340	8.2	10	12	10	11	13		
11.5	310	350	400	8.8	11	13	8.9	10	12		
11.9	400	450	510	9.5	12	14	9.3	10	12		
12.4	620	690	790	11	14	17	12	13	15		
12.7	1200	1300	1500	13	17	20	16	18	21		

^a Sumner and Taylor.¹⁹⁰

^b Viscose film; temp. 20°; 0.5 N NaCl; buffer conc. 0.2 N; D_S = dye concentration in g moles/liter.

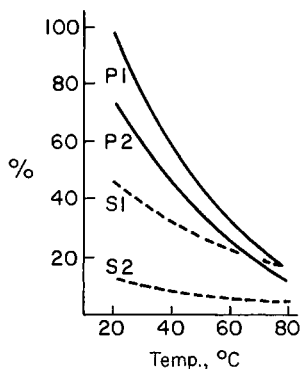


FIG. 14. Dependence of substantivity (S) and yield (P) upon temperature. (1) Remazol Brilliant Red BB; (2) Remazol Brilliant Orange RR.

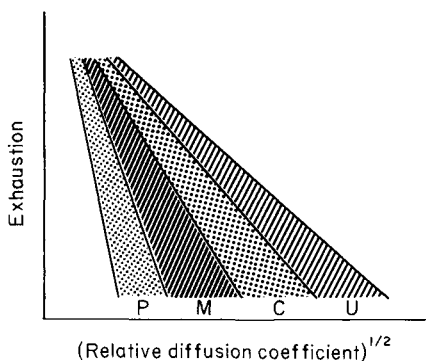


FIG. 15. Influence of chemical constitution of reactive dyes on substantivity and diffusion properties: U, Unmetallized dyes; C, 1:1 metal-complex dyes; M, 1:2 metal-complex dyes; P, phthalocyanine dyes.

cularly slow rate. We can therefore subdivide the reactive dyes into two groups according to their substantivity and their diffusion properties: (1) dyes which can be dyed in a long liquor, and (2) dyes which can only be applied by padding and in textile printing (Fig. 16).¹⁹⁶

The higher the reactivity, the lower is the minimum substantivity required for dyeing in a long liquor. Plotting the yield against the substantivity of the Remazol dyes, the curve shown in Fig. 17 was obtained.¹⁹⁷ The change of substantivity with temperature is inverse to

¹⁹⁶ M. Capponi and A. Barthold, *Textil-Praxis* **17**, 155 and 255 (1962).

¹⁹⁷ R. Weingarten, *Textilveredlung* **3**, 151 (1968).

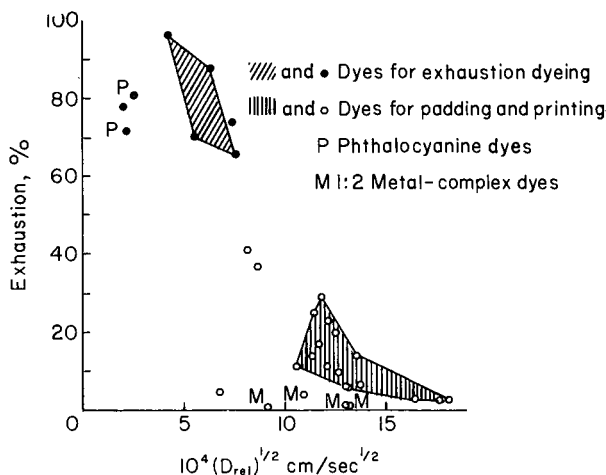


FIG. 16. Diffusion and substantivity of trichloropyrimidyl dyes. Crosses and filled circles represent exhaustion dyeing; diagonals and open circles represent padding and printing; P, phthalocyanine dyes; M, 1:2 metal-complex dyes.

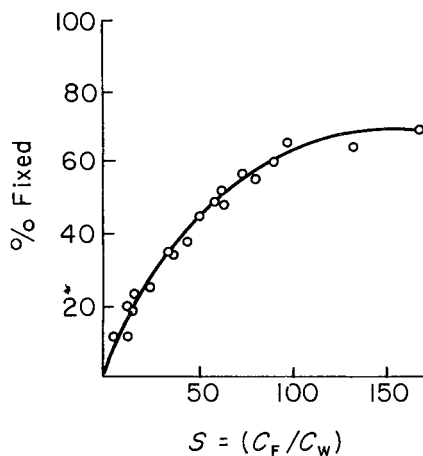
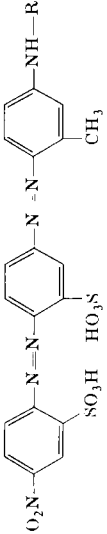

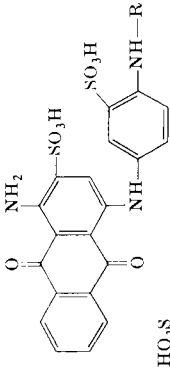

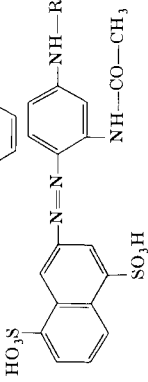
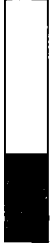
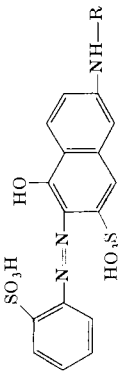

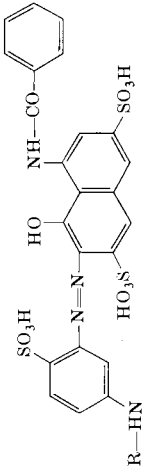



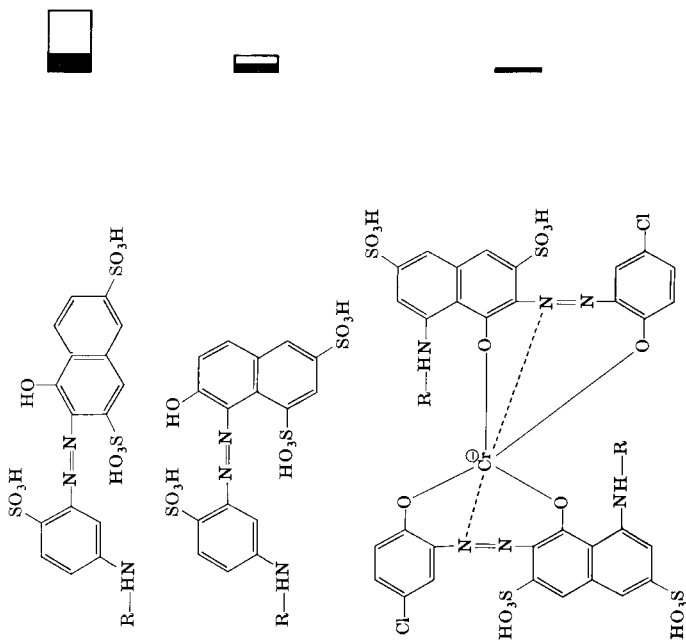
FIG. 17. Yield of fixation and substantivity of Remazol dyes.¹⁹⁷

the change of reactivity and diffusion with temperature. Figure 14 shows that the amount of dyestuff which has been absorbed substantively by the fiber, and hence the yield, decreases with increasing temperature. The dependence of the substantivity on the electrolyte concentration is therefore very important. The loss in substantivity which occurs as a result of an increase in temperature can be partially compensated by

TABLE VIII

EXHAUSTION CAPACITY (MERC. COTTON, LIQUOR 30:1) AND CHEMICAL STRUCTURE OF THE CHROMOPHORE SYSTEM^{a, b}

Exhaustion 90°	
	
	
	
	
	



^a Capponi and Barthold.¹⁹⁶

^b R = 2,4,5,6-tetrachloropyrimidine. Glauber's salt calc. open bar, 80 g/liter; solid bar, 20 g/liter.

adding more electrolyte. The amount of substantively bound dye in the state of equilibrium will thus increase with decreasing temperature, decreasing liquor ratio, and increasing salt content. Figure 18 shows how the substantivity S and the yield change with the addition of electrolytes in the case of Remazol Brilliant Red BB and Remazol Brilliant Orange

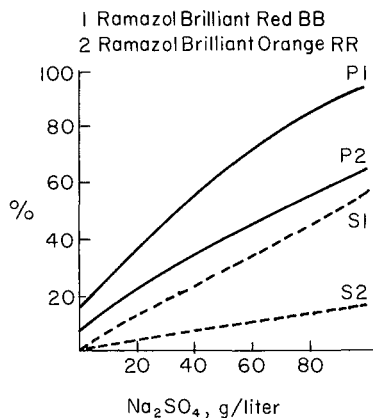


FIG. 18. Dependence of substantivity (S) and yield of fixation (P) of Remazol Brilliant Red BB and Remazol Brilliant Orange RR upon electrolyte addition.¹⁹⁷

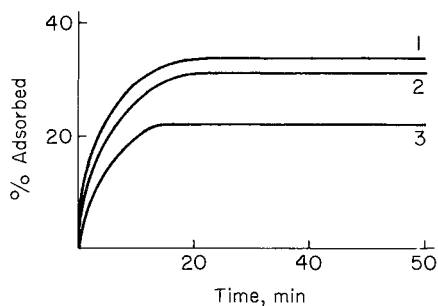


FIG. 19. Substantivity of Remazol Brilliant Blue R: 1, Alone; 2, in combination with Remazol Brilliant Yellow GL; 3, in combination with Remazol Yellow GR.

RR. But substantivity effects are not only due to interactions between dye and salt, but also to interactions between dye and dye in the dyeing of combination shades. Such interactions can be shown, for example, by the difference between a spectrum of a two-color mixture and that of a purely optical mixture which has been produced by placing the cuvettes with the individual components one after the other into the beam of light. If the individual components exercise a strong influence on each

other, the reactive behavior of these individual components is disturbed.^{197, 198} Figure 19 shows the sorption isotherm of 1% Remazol Brilliant Blue R as an individual dyestuff (1) and in combination with Remazol Brilliant Yellow GL (2) and Remazol Yellow GR (3), determined in the absence of alkali. It will be seen that the interaction (Fig. 20) between Remazol Brilliant Blue R and Remazol Yellow GR results in a steep decline of substantivity, while the interaction with Remazol Brilliant Yellow GL is only slight.

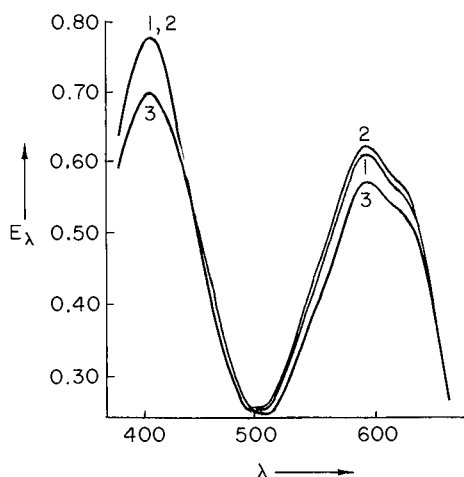


FIG. 20. Absorption spectra of a mixture of Remazol Yellow GR and Remazol Brilliant Blue R. (1) 250 mg/liter Remazol Yellow GR, 500 mg/liter Remazol Brilliant Blue R in separate cuvettes (of 0.1 cm each), optical mixture; (2) 250 mg/liter Remazol Yellow GR in 0.1 cm and 250 mg/liter Remazol Brilliant Blue R in 0.2-cm cuvettes; (3) 125 mg/liter Remazol Brilliant Blue R in a cuvette (0.2 cm) distilled water in 0.1-cm cuvette, genuine mixture.

According to Konkova and Belenkij,¹⁹⁹ the mutual influence produced by the components of the mixture will be the greater, the higher their affinity. This interaction does not take place in the liquor, but during the sorption process on the fiber.

3. The Reactive Performance of Polyfunctional Reactive Dyestuffs

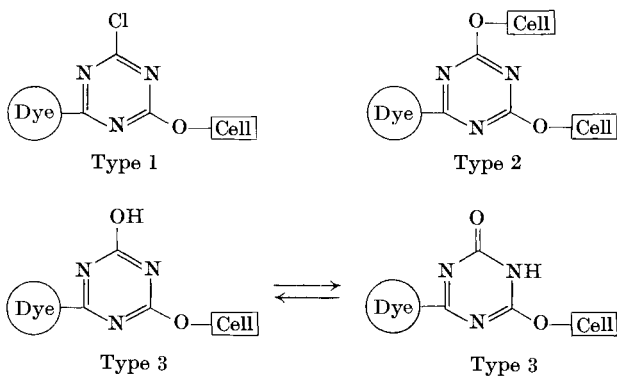
Dyestuffs with only one reactive group are generally considered to be monofunctional although the dichlorotriazine²⁰⁰ and the dichloro-

¹⁹⁸ T. A. Konkova and L. I. Belenkij, *Tekstil'n. Prom.* **27**, 66 (1967).

¹⁹⁹ T. A. Konkova and L. I. Belenkij, *Jsv. Vysshikh Uchebn. Zavedenii, Tekhnol. Tekstil'n. Prom.* p. 102 (1967).

²⁰⁰ S. Horrobin, *J. Chem Soc. (London)* p. 4130 (1963).

quinoxaline²⁰¹ reactive systems also contain two chlorine atoms which can be substituted at different rates of reaction. Ackermann and Dussy^{202, 203} were able to prove even for the dyestuffs based on tetrachloropyrimidine that under drastic reaction conditions more than one chlorine atom is exchanged for the cellulose radical. But polyfunctional reactive dyestuffs in the real sense are usually such dyestuffs which contain more than one supporting group with corresponding leaving groups which are exchangeable under the same reaction conditions. For example, in the case of 2,3-dichloroquinoxaline dyestuffs the reactivity of the second chlorine atom is slower by a factor of 50 than the substitution of the first chlorine atom.²⁰⁴ This is because there is no activation for the 2-position by the carboxylic acid amide group in the 6-position. Although there is also a noticeable difference in the reactivity of the first and second chlorine atom in the dichlorotriazine dyestuffs, the reactive level of the entire system is so high that the second chlorine atom is also likely to react with cellulose, since the monochlorotriazine itself still meets the conditions of a useful reactive group. According to investigations by Rattee,^{205, 206} Fern and Preston,²⁰⁷ Dawson,²⁰⁸ as well as Vickerstaff,²⁰⁹ the second chlorine atom of the dichlorotriazine dyes contributes substantially to the total yield, so that we can distinguish between three types of dye-fiber linkages, the third type being present in the tautomeric keto form:



²⁰¹ K. G. Kleb, E. Siegel, and K. Sasse, *Angew. Chem.* **76**, 423 (1964).

²⁰² H. Ackermann and P. Dussy, *Melliand Textilber.* **42**, 1167 (1961).

²⁰³ H. Ackermann and P. Dussy, *Helv. Chim. Acta* **45**, 1683 (1962).

²⁰⁴ D. Hildebrand, *Melliand Textilchem.* No. 1, p. 102 (1965).

²⁰⁵ I. D. Rattee, *Endeavour* **20**, 154 (1961).

²⁰⁶ I. D. Rattee, *Chimia (Aarau)* **18**, 293 (1964).

²⁰⁷ C. Preston and A. S. Fern, *Chimia (Aarau)* **15**, 177 (1961).

²⁰⁸ T. L. Dawson, A. S. Fern, and C. Preston, *J. Soc. Dyers Colourists* **76**, 210 (1960).

²⁰⁹ T. Vickerstaff, *Hexagon Digest* No. 27 (1958); *Textil-Rundschau* **13**, 267 (1958).

The cross-linkage of cellulose chains which is caused by type 2, can be confirmed by means of solubility tests.²⁰⁹

According to investigations carried out by Mehta, Ravikrishnan, Parmar, and Chitale,^{210, 211} the viscosity of the reactive-dyed cellulose in cuprammonium solution increases with increasing color depth even if no cross-linkage is possible. This anomalous viscosimetric behavior was explained by the formation of dye-copper complexes.

Polyfunctional reactive dyes in this sense with more than one supporting group and more than one leaving group of the same mobility have intrinsically better chances to react, since every reactive group can cover another area of the fiber with the same probability. Hence dyes with more than one reactive system are characterized by yields between 80 and 98% of the dye used. This will considerably reduce the washing-off problem.²¹² But the rate of reaction with the fiber is not increased by introducing another reactive group of the same reactivity. Since as a rule the additional yield obtained in this manner is not more than 20% of the dye used, the introduction of a second reactive group is mainly a question of price. A polyfunctional cellulose substitution can produce a harsh handle and a loss in strength of the fabric. To avoid obstructing the diffusion by an additional weighting of the dye, reactive systems are preferred which are derived from small supporting groups. The Levafix dyes belong to the group of reactive dyes having more than one reactive system. The Procion Supra dyes represent a new development. Dyes with more than one reactive group can also be found among several metal complex dyes, especially dyes based on phthalocyanine, since in such cases it appears to be a paying proposition to have another reactive group, as otherwise the yield is often unsatisfactory.

4. *The Reactive Performance of Dye-Fiber Cross-Linking Agents*

Fixation with high wet-fastness of a dyestuff molecule to high molecular weight fiber substrates of nucleophilic reactivity is possible not only for reactive dyes. A covalent bond between dye and substrate is also possible by linking the dyestuff to the fiber by bifunctional or

²¹⁰ H. U. Mehta, M. R. Ravikrishnan, and A. G. Chitale, *J. Soc. Dyers Colourists* **78**, 552 (1962).

²¹¹ P. C. Mehta, H. U. Mehta, and R. S. Parmar, *J. Soc. Dyers Colourists* **79**, 315 (1963).

²¹² *Intern. Dyer, Textile Printer, Bleacher Finisher* **138**, 122 (1967).

polyfunctional crosslinking agents.²¹³⁻²³⁶ The first practically feasible dyeing and printing method based on this principle was achieved by BASF with their Basazol dyestuffs.²³⁷⁻²⁴⁰ As is the case with the reactive dyes in the stricter sense of the word, these linking reactions are not confined to cellulose. Since the cross-linking reaction is chemically based on the same conditions, all fibers can be used as reaction partners which can also be dyed with reactive dyes. Suitable sites of reaction in the fiber besides the cellulose anion are therefore the amino and mercapto groups of natural polyamides or the hydroxy groups of other substrates such as starch. High molecular weight polyamides like wool and silk will, however, give lower yields, in contrast with their performance when dyed with reactive dyes, probably due to different diffusion and reaction conditions. Dyeing and printing with linking agents are therefore confined to cellulosic fibers. Chemically

²¹³ CIBA, *USP* 3,073,667 (4.9.1957).

²¹⁴ FBy, *FP* 1,218,093 (1.2.1958).

²¹⁵ DuP, *USP* 3,044,843 (13.5.1959).

²¹⁶ CIBA, *BeP* 596,158 (20.10.1959).

²¹⁷ Ashahi, *SP* 371,090 (18.1.1960).

²¹⁸ BASF, *DAS* 1,139,093 (2.11.1960).

²¹⁹ S, *SZAS* 362,051 (5.5.1960).

²²⁰ BASF, *DAS* 1,241,408 (8.11.1961); *FP* 83,056/1,318,627 (8.11.1962); *BP* 967,028.

²²¹ BASF, *DAS* 1,355,847 (10.3.1962).

²²² BASF, *FP* 1,359,935 (28.3.1962).

²²³ CFM, *SP* 388,257 (4.4.1962).

²²⁴ BASF, *BeP* 613,442 (2.8.1962); 624,513 (7.11.1962).

²²⁵ BASF, *DAS* 1,247,260 (19.4.1962); *BeP* 631,237 (18.10.1963); *FP* 1,360,892 (19.4.1963); *BP* 1,032,887 (19.4.1963); *AustP* 241,409 (19.4.1963); *SP* 415,538 (24.1.1963).

²²⁶ BASF, *BeP* 631,585 (Addition to *BeP* 613,442) (28.10.1963).

²²⁷ S, *SP* 404,605 (8.2.1963).

²²⁸ NSK, *JP* 14,638/66 (23.7.63).

²²⁹ BASF, *BeP* 619,906 (7.11.1963).

²³⁰ CFM, *BeP* 656,363 (27.11.1963).

²³¹ Deutsche Akademie der Wissenschaften, *AustP* 246,690 (13.4.1964).

²³² Deutsche Akademie der Wissenschaften, *FP* 1,402,211 (15.6.1964).

²³³ S, *BeP* 650,041 (2.7.1964); *FP* 1,381,885 (6.2.1964).

²³⁴ BASF, *DAS* 1,259 (28.10.1965).

²³⁵ G. Meyer and H. Wirth, *Melliand Textilber.* **44**, 274 (1963); *Tex* **22**, 460 (1963); *Textil-Praxis* **18**, 767 (1963).

²³⁶ B. C. M. Dorset, *Textile Mfr.* **90**, 511 (1964).

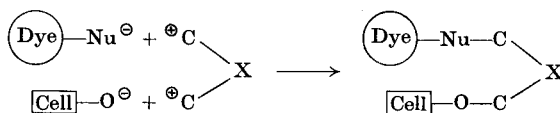
²³⁷ G. Lützel, *Melliand Textilber.* **47**, 129 (1966).

²³⁸ G. Meyer, *Melliand Textilber.* **47**, 1296 (1966).

²³⁹ G. Lützel, *J. Soc. Dyers Colourists* **82**, 217 (1966).

²⁴⁰ H. R. Hensel and G. Lützel, *Angew. Chem.* **77**, 303 (1965).

speaking, the linking reaction is based on the same mechanism as dyeing with reactive dyes.²⁴⁰ The positively polarized C atom, however, does not form part of the dye, but of the bridge group. This means that any losses due to hydrolysis do not have to be borne by the dye, but by the bridge group. Thanks to the possibility of using the components containing the dye and the positively polarized C atoms separately and in different quantities, the following reaction shown can be shifted in the direction of higher yield of the more valuable dyestuff component:



Nu = a nucleophilic group; X = a polyfunctional cross-linking system

If in polyfunctional linking agents one of the functions is eliminated by hydrolysis, a bond can be easily brought about with the help of the other functions. Moreover, hydrolysis of the bridge group produces compounds with radicals having a nucleophilic reaction, which in turn can be included in the reaction. The assumption that new covalent linkages have been formed was verified with the help of methods which have already been used for reactive dyes. Suitable linking agents are compounds which have at least two positively polarized C atoms which can be the site of a nucleophilic attack. In accordance with the behavior of the reactive dyes, the linking agents can be subdivided into three groups: compounds which react by addition to activated double bonds, compounds which act according to a substitution mechanism, and compounds which act by a condensation mechanism. The best results are obtained with cyclic, trifunctional linking agents of the 1,3,5-triacylhexahydro-*s*-triazine type, e.g., triacrylformal, which Wegler and Ballauf²⁴¹ have described as an easily accessible compound. Linking agents which can be catalyzed in an acid and alkaline medium of the kind used, e.g., in anticrease finishing of cellulose textiles, have not been found useful as dyestuff linking agents in this case. Compounds like the disodium salt of tris(β -sulfatoethyl)sulfonium ion will probably react with cellulose, but only to a limited extent with the dye. Besides, compounds which would produce an anticrease effect apart from the dye linking would not be suitable for another reason. They would cause the fiber to become hard in certain areas and to an uncontrollable extent, which would constitute an unacceptable risk because of the overall effect it would have on the handle of the goods. The dyes which are suitable for

²⁴¹ R. Wegler and A. Ballauf, *Chem. Ber.* **81**, 527 (1948).

dyeing with the help of linking agents according to Lützel^{237, 239, 240} contain groups which can react with reactive groups in a manner similar to the reaction of the cellulose anion. Generally good fixation yields are obtained with primary or secondary amino groups, sulfonamide groups, and hydroxy or mercapto groups, as well as active methylene groups or NH groups in heterocyclic ring systems. Apart from the fact that all dyes which are to be used in this process must be capable of diffusion (a condition which applies equally to all reactive dyes), they must contain a group of sufficiently nucleophilic character. The chemical structure of the entire dye molecule is very important to ensure this nucleophilic character, since substitution influences play an even greater part than with the usual reactive dyes. But the dye can also contain, in addition, a reactive group which reacts directly with the fiber. Conversely, considerably improved yields have been obtained in some cases by adding

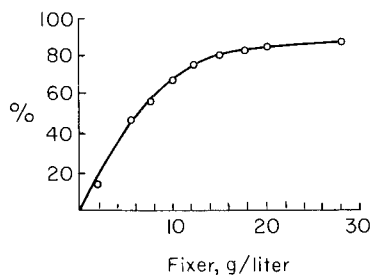
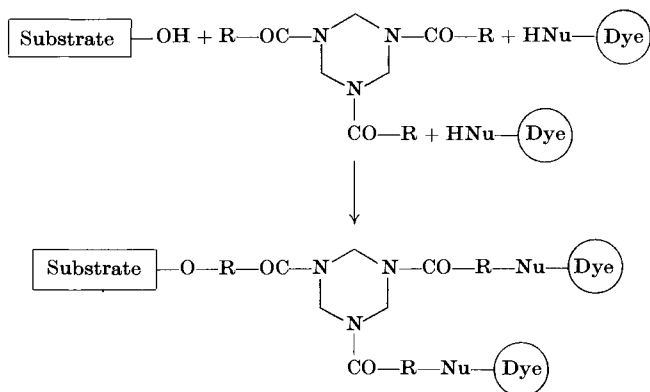


FIG. 21. Influence of the fixer concentration on the fixation yield in percent of dyestuff used.²³⁹

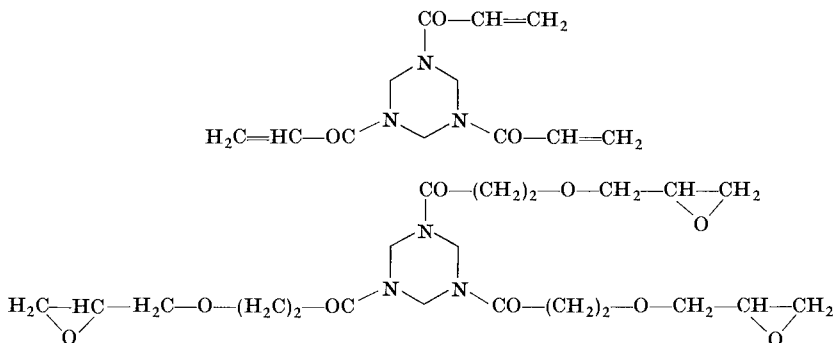
linking agents to print pastes prepared with conventional reactive dyes. The substantivity of the dyes which can be linked in this manner is low. Since the linking agent itself is also not substantive, this fixation method can only be used in textile printing and in padding. On the other hand, the only slight loading of the dye molecule by a reactive group makes it possible to prefer the use of metal complexes as chromophoric systems. If used in reactive dyes which occupy a lot of space metal complexes are more likely to lead to difficulties because of their low rate of diffusion.

For a given dye, the color yield depends on the kind and quantity of linking agent used. With triacrylformal, which is available under the commercial name Fixer P, maximum yield is obtained for the Basazol dyestuffs using a dye/linking agent ratio of 2:1 to 3:2. In practice it is therefore possible to work with a constant dye/linking agent ratio. In dyestuff formulations below 10 g/liter, however, it is advisable not to use less than 6–10 g/liter of Fixer P (see Fig. 21). With soda ash or sodium bicarbonate as alkali, the final yield is obtained by steaming at 102° for

3 minutes, at 110° for 45 seconds, in dry heat at 150° after treating the goods for 3 minutes, and at 190° after treatment for 1 minute.



According to Rexroth,²⁴² soluble dye-fixing agents are obtained by treatment of 1,3,5-triacryloylhexahydro-*s*-triazine with alkaline agents and compounds containing NH or SH groups, using up to two-thirds of an equivalent of these compounds per mole of triazine. Linking reactions between a dye molecule and a fiber also form the basis of processes in which dyeings produced on natural or synthetic polyamides are after-treated with carbodiimide ($\text{R}-\text{N}=\text{C}=\text{N}-\text{R}'$)²⁴³ or water-soluble derivatives of dihalotriazine or dihalopyrimidine.²⁴⁴ The following are examples of polyfunctional derivatives for the fixation of dyes with reactive hydrogen atoms²⁴⁵:

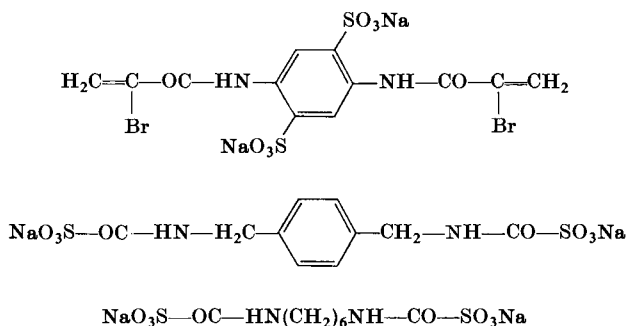


²⁴² BASF, E. Rexroth, *DAS* 1,259,897 (28.10.1965).

²⁴³ P. M. Heertjes and H. C. A. Van Beek, *DAS* 1,230,393 (7.2.1963).

²⁴⁴ ICI, R. L. Denver and H. R. Hadfield, *USP* 2,940,812 (18.11.1957).

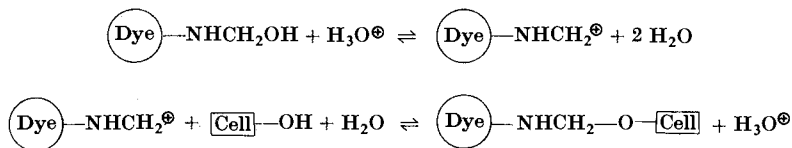
²⁴⁵ J. Wegmann, *Melliand Textilber.* **49**, 687 (1968).



Wegmann²⁴⁵ has reviewed the general principle of dyestuff fixation by cross-linking agents.

5. The Reactive Performance of Reactive Dyestuffs which Can Be Fixed in the Acid Range

The substitution reactions at the cellulose hydroxyl are not limited to reactions which can be catalyzed in the alkaline range. The manifold possibilities of cross-linking of the cellulose chains by means of condensation reactions which can be catalyzed in the acid range are well known. It was therefore reasonable to use this mechanism as the basis for the development of reactive dyes which can be fixed in the acid range. This made it possible to combine reactive dyes—especially when dyeing fabrics made from blended yarns—with other types of dyes which are decomposed by alkali. The first commercial range of reactive dyes which can be fixed at an acid level was released in 1966 by the American Cyanamid Company under the name Calcobond dyestuffs.^{246, 247} The reactive group of these dyes consists of a methylolated nitrogen atom. A reactive carbonium ion intermediate is formed according to the following equation:



In contrast to the alkali-induced nucleophilic substitution, this is, therefore, a genuine catalytic reaction, since the hydroxonium ion, which

²⁴⁶ H. R. McCleary, A. L. Caze, F. Fordemwalt, and F. F. Loffelman, *Am. Dyestuff Repr.* **56**, 46 (1967).

²⁴⁷ A. F. Copeland, *Am. Dyestuff Repr.* **57**, 329 (1968).

has acted as catalyst, is finally set free again. The position of the equilibrium as a function of the pH level, and the reactivity of the carbonium ion formed as a result of this reaction, depend greatly on the chemical structure of the supporting group. The equilibrium has been adjusted in such a manner that the final yield is obtained in a fixation time of 1–3 minutes with ammonium chloride as catalyst and dry heat of 150–160°. The final yield is 80–95% of the amount of dyestuff used. The reactive group which can be fixed in the acid range requires condensation

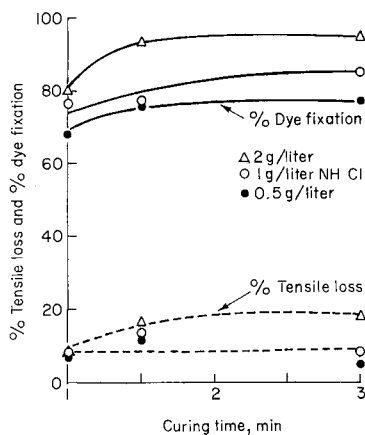


FIG. 22. Dye fixation and tensile loss versus curing time at 176°C, 5 g/liter Calcobond Red 3B.

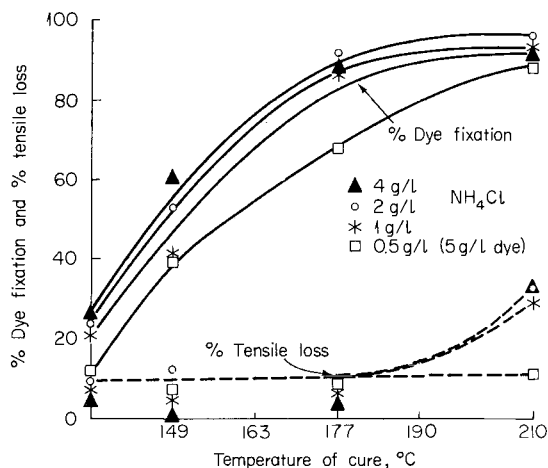


FIG. 23. Dye fixation and tensile loss versus curing temperature. Curing time: 1 minute; 10 g/liter Calcobond Red 3B.

conditions to react, and substantivity is not required. Since urea is involved in this reaction with cellulose, it cannot be used for dissolving the dyestuff and for swelling the fiber. Satisfactory diffusion capacity is therefore very important for the acid-fixable reactive dyes. Cellulose fibers dyed according to this method lose some of their strength, because they are tendered by the action of the acid catalyst and (if polyfunctional reactive groups are used) also by linking reactions. Depending on depth of shade, the loss in strength can be 10–20% (see Figs. 22 and 23). Due to the strong nucleophilicity of nitrogen, reactive systems which will react with cellulose only in the alkaline range can also be made to react in the acid range with fibers containing NH groups, such as wool and polyamide. Correspondingly, reactive dyes can also be fixed on cellulose with halogen heterocycles in combination with resin finishes based on methylol compounds containing NH groups. In this case, therefore, there is an indirect linkage to the fiber. The dye reacts with the NH group of the resin, while the methylol group of the resin reacts with the fiber.

C. THE DYEING PROCESS AS A HETEROGENEOUS REACTION

1. *Rate of Fixation and Yield*

a. Cellulosic Fibers. i. Assessment and Definition. In contrast to hydrolysis and to homogeneous model reactions, the fixation of reactive dyestuffs on the fiber is a heterogeneous chemical reaction in which the physically explainable adsorption processes and the chemical reaction with cellulose and water overlap and influence each other. A reactive dye is therefore characterized, first of all, by the fixation yield which can be obtained under different fixation conditions. Secondly, the rate at which the process of fixation takes place is another important factor. These two factors can be demonstrated using fixation curves which are plotted in the form of yield versus time curves. Such fixation curves are given in the pattern cards released by the dyestuff manufacturers, mostly for exhaustion methods. But cold pad-batch, padding, continuous, and printing methods have also been investigated and described quantitatively in this manner.^{248–255}

²⁴⁸ H. Aekermann and P. Dussy, *Melliand Textilber.* **42**, 1167 (1961).

²⁴⁹ M. Capponi and A. Barthold, *Textil-Praxis* **17**, 255 (1962).

²⁵⁰ O. Thumm and J. Benz, *Angew. Chem.* **74**, 712 (1962).

²⁵¹ I. D. Rattee, T. Vickerstaff, I. Seltzer, I. M. S. Walls, J. A. Fowler, D. K. Lawman, and W. J. Marshall, in "Procion Dyestuffs in Textile Dyeing, pp. 15, 41, 115, 147, 199. I.C.I., Manchester, 1962.

²⁵² M. Capponi, *Melliand Textilber.* **44**, 720 (1963).

²⁵³ H. U. von der Eltz, *Textil-Praxis* **19**, 523 (1966).

²⁵⁴ M. Haelters, *Melliand Textilber.* **48**, 191 (1967).

²⁵⁵ K. Bühler, D. Hildebrand, and R. Schwaebel, *Bayer Farben Rev.* No. 13, p. 1 (1967).

This is illustrated by a few examples in Figs. 24–27. A fixation curve is obtained in exhaustion dyeing by photometric determination of the dye content of the liquor before and after the dyeing process. The unfixed portion of the dye which has gone substantively on the fiber is extracted separately. This means that two curves are obtained as function of time,

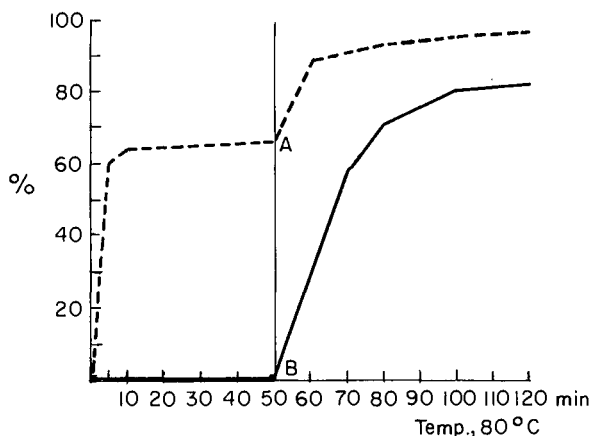


FIG. 24. The effect of time of alkali addition on the exhaustion and fixation curves: Viscose staple fiber, bright, fixed with Na_2CO_3 , using the two-step method: Alkali addition after 30 minutes, dyed with 1% Cibacron Navy Blue RE. A, Exhaustion curve; B, fixation curve.

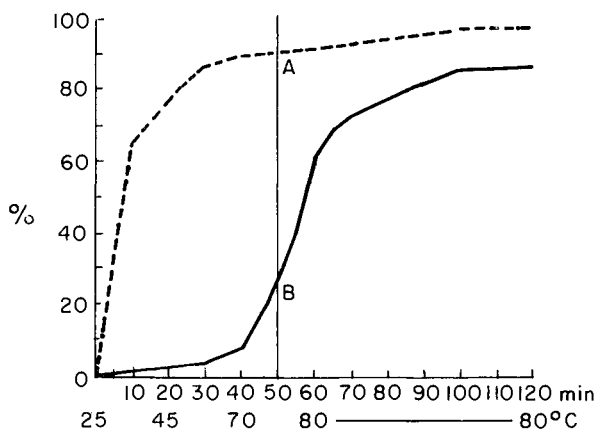


FIG. 25. The effect of time of alkali addition on the exhaustion and fixation curves: Viscose staple fiber, bright, fixed with Na_2CO_3 , using the all-in method. The bath is set up with alkali and dyestuff; dyed with 1% Cibacron Navy Blue RE. A, Exhaustion curve; B, fixation curve.

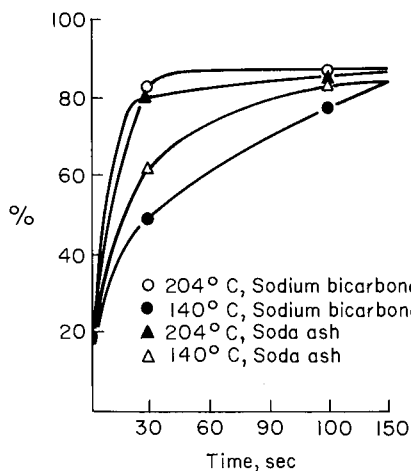


FIG. 26. Effect of temperature and alkali on rate of fixation in pad-thermofixation process. Levafix Brilliant Red P-3B (40 g/liter urea, 10 g/liter sodium bicarbonate (yield in %).

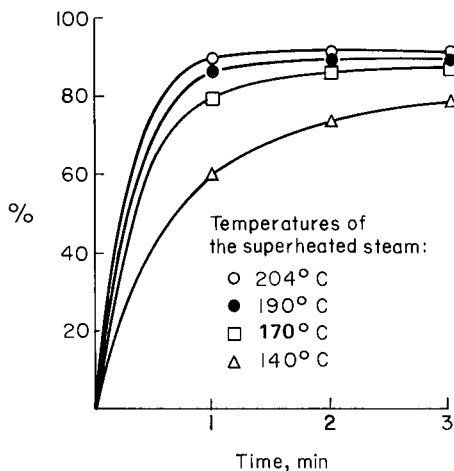


FIG. 27. Yield of fixation of Levafix Brilliant Red P-3B with superheated steam without intermediate drying.

namely, the substantive sorption curve and the fixation curve. Since the absorption spectrum of the dye liquor changes during dyeing because of the formation of hydrolyzed dye, measurements are always carried out at the isosbestic point (see Fig. 4).²⁵⁶ In the quantitative evaluation of

²⁵⁶ W. Beckmann, D. Hildebrand, and H. Pesenecker, *Melliand Textilber.* **43**, 1304 (1962).

padding and printing processes, the amount of dye applied to the fiber is determined by neutralization after padding or printing and extraction of a cut-out swatch of known area. After fixation, a swatch of equal area is extracted. The difference between the amount of dye used and the unfixed portion of the dye in percent of dye used gives the percentage yield of fixation. If the swatch which is to be investigated becomes available only after fixation, the amount of dye used and the fixed portion can be determined by dissolving swatches of equal weight or area, before and after rinsing, in cold 70% sulfuric acid.^{257, 258} The yield of fixed dye is then obtained from the extinction of the solution of the washed-off swatch in percent of the extinction of the swatch which has not been washed off, measured at the same wavelength. The unfixed portion of the dye can consist of hydrolyzed dye and of dye which is still capable of reacting. A fixation process is considered complete when the fixation curve runs parallel to the time axis. While the parallel run of the fixation curve in relation to the time axis indicates that the reactive dye has reacted completely if the goods were dyed in a long liquor, it can happen in rapid continuous processes that the fixation phase is passed without complete reaction either by hydrolysis or fixation. This applies in particular to thermofixation (curing) processes,²⁵⁹ since in such cases the diffusion into the inside of the fiber and hence the reaction can be obstructed by overdrying of the cellulose to such an extent that any further reaction is blocked. However, in very deep dyeings and if the amount of dye used is high, the fixation process can come more or less to a standstill, even in exhaustion methods, before the total quantity of reactive dye has been completely used up.²⁶⁰

To keep a close watch on the change of the reactive dye in the course of the entire fixation process, the fixation and sorption curves are supplemented by curves showing the active content and the hydrolysis.²⁰⁴ The active content curve describes the percentage content of the system in respect to reactive dye (i.e., dye which is capable of reaction), while the hydrolysis curve shows the percentage content of the system in respect to hydrolyzed dye. The amounts of fixed, reactive (capable of reaction), and hydrolyzed dye will always add up to 100%. Figures 28–30 are examples for the representation of such total balances, showing dyeing processes of dichlorotriazine and dichloroquinoxaline dyes. If the reaction balance shows that the dye has not completely reacted during a fixation process, the dye–fiber reaction is obstructed or slowed down.

²⁵⁷ A. G. H. Michie and R. Thornton, *J. Soc. Dyers Colourists* **69**, 629 (1953).

²⁵⁸ T. L. Dawson, A. S. Fern, and C. Preston, *J. Soc. Dyers Colourists* **76**, 210 (1960).

²⁵⁹ D. Hildebrand, *Melliand Textilber.* **49**, 67 (1968).

²⁶⁰ E. Valk, M.-L. Kehren and E. Loers, *Textilveredlung* **4**, 46 (1969).

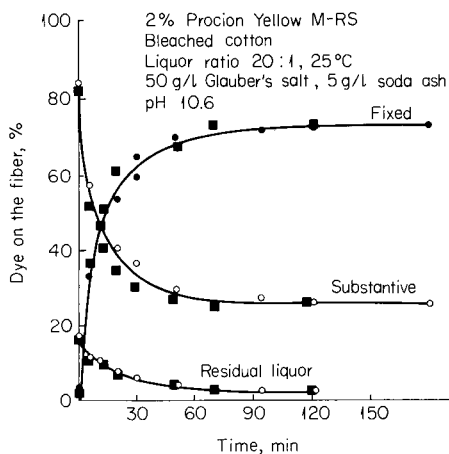


FIG. 28. Dyestuff distribution of a reactive dye adsorbed by the cotton fiber when dyeing from long liquor.²⁵⁶

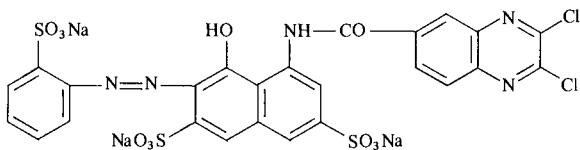
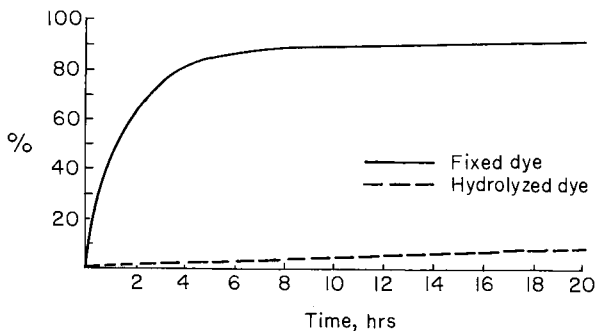


FIG. 29. Progress of the reaction, i.e., of fixation and hydrolysis, of the indicated dye in the cold pad batch process on bleached cotton; 10 g/liter urea.²⁶⁰

This can be due to the following causes: The amount of alkali present was too low, or the goods were too dry, so that the diffusion of the dye was interfered with, or the amount of dye used was higher than the bonding capacity of the fiber under the prevailing reaction conditions. It has been concluded that in the heterogeneous dye-fiber reaction the re-

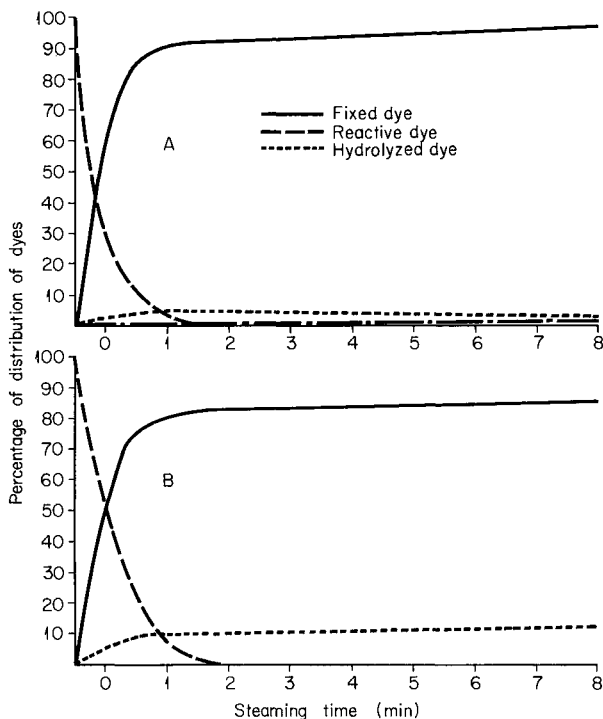


FIG. 30. Reaction balance for printing with 10 g/kg sodium bicarbonate with the dye illustrated in Fig. 29: A, on cotton; B, on viscose staple.²⁶⁰

action conditions change during the fixation process, so that the rules of homogeneous reaction cannot be easily applied to the heterogeneous fixation reaction.^{259, 261} We must therefore differentiate between rate of fixation and rate of reaction. Rate of fixation is the speed at which the fixation process takes place, to be measured by means of a fixation curve, while rate of reaction is the speed at which the dye would react under prevailing pH and temperature conditions if the dye-fiber linkage were determined only by the reactivity of the reactive dye. The rate of reaction, in analogy to the rate of hydrolysis, should be a reaction of pseudo-unimolecular order which can be characterized by a constant k_{Cell} if we assume that there is a satisfactory excess of Cell-OH groups. Hence, *rate of fixation* is the collective term which depends not only on the rate of reaction, but also on the absorption equilibrium²⁶² of the

²⁶¹ U. Baumgarte and F. Feichtmayr, *Melliand Textilber.* **44**, 163 (1963).

²⁶² M. Capponi and R. C. Senn, *Chimia (Aarau)* **19**, 271 (1965).

dyestuff, the rate of diffusion, the accessibility^{263, 264} of the Cell-OH groups, and in continuous processes on the rate of heating of the fabric (Fig. 31). Depending on the application conditions, one or another effect predominates. Generally, the rate of fixation increases with increasing values of reactivity, substantivity, and diffusion.²⁶⁵⁻²⁶⁷ Different methods have been tried to calculate or eliminate such effects with the help of special experimental designs, so that the reaction constant (k_{Cell}) could be derived directly from the rate of fixation. For this purpose, Sumner and Weston²⁶⁸ examined the penetration of the dyestuff into a film and calculated the reaction constant according to the formula given by Danckwerts²⁶⁹ (see Section I,B,2).

This method implies that the diffusion coefficients and substantivity are taken into consideration at high pH values. Bohnert and

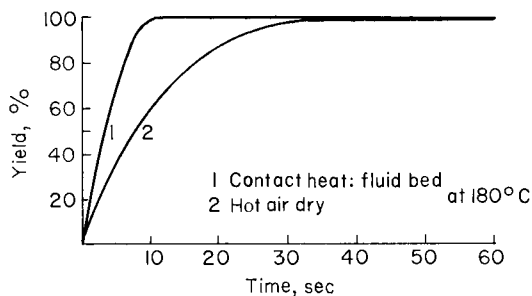


FIG. 31. Rate of fixation plotted against rate of heating.²⁵⁹

Weingarten²⁷⁰ padded the dye without alkali on piece goods and then fixed it in alkaline salt solution. Similar methods were also used by Ackermann and Dussy²⁴⁸ and Hildebrand and Beckmann²⁷¹ in a series of experiments. The diffusion coefficient and the substantivity are not included in the results. However, the distribution of the dye on the fiber is probably different when dyeing in a long liquor. For this reason, the rate of reaction of that portion of the dye which will go substantively on

²⁶³ W. Beckmann, *Can. Textile J.* **35**, 75 (1966).

²⁶⁴ D. Hildebrand, *Melliand Textilber.* **49**, 936 (1968).

²⁶⁵ H. H. Sumner and T. Vickerstaff, *Melliand Textilber.* **42**, 787 (1961).

²⁶⁶ H. H. Sumner and T. Vickerstaff, *Melliand Textilber.* **42**, 1161 (1961).

²⁶⁷ I. D. Rattee, *Chimia (Aarau)* **18**, 293 (1964).

²⁶⁸ H. H. Sumner and C. D. Weston, *Am. Dyestuff Repr.* **52**, 442 (1963).

²⁶⁹ P. V. Danckwerts, *Trans. Faraday Soc.* **46**, 300 (1950).

²⁷⁰ E. Bohnert and R. Weingarten, *Melliand Textilber.* **40**, 1036 (1959).

²⁷¹ D. Hildebrand and W. Beckmann, *Melliand Textilber.* **45**, 1138 (1964).

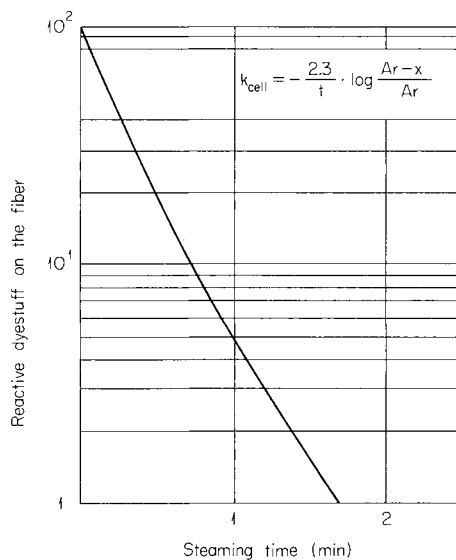
the fiber in absorption processes was determined in another investigation.²⁷² If the substantive adsorption and the diffusion can be eliminated by a padding process, the rates of reaction will be proportional to the yields according to the kinetic formulation for parallel reactions.²⁷¹ We have, therefore,

$$\frac{D_{\text{fixed}}}{D_{\text{hydrolyzed}}} = \frac{k_{\text{cell}}[\text{Cell-OH}]}{k_{\text{w}}[\text{H}_2\text{O}]} \quad (10)$$

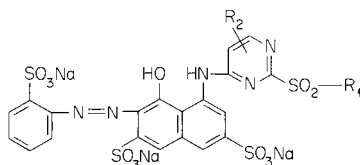
This formula is valid for monomolecular reactions provided $[\text{Cell-OH}]$ and $[\text{H}_2\text{O}]$ do not change during the reaction. Since the hydrolysis takes place in solution at the same rate as on the fiber,²⁵⁶ the independently calculated hydrolysis constants can be inserted for k_{w} . Furthermore, the competing amount of water must also be considered. If we assume that this is identical with the "swelling water," Eq. (9) enables us to derive reaction constants for the cellulose substitution which in turn should mainly depend only on the temperature and on the pH value. In curing processes, the water content of the fiber is removed by drying. Under such conditions the share of hydrolysis as a competing reaction is only of secondary importance. The influence of the factors of the heterogeneous reaction on the rate of fixation is expressed in more or less distinct variations from the reaction of pseudo-unimolecular order.

According to the progress of a reaction example illustrated in Fig. 32, the reaction equation, which can be expected for the saturated steam fixation in the presence of a great excess of cellulose OH groups, has been fulfilled.²⁵⁹ The equation applies for an adsorbed quantity of dye which has diffused into the fiber during drying. This is the state of affairs which we find when we dye according to the pad-steam process. This formula is only valid if the dye particles do not mutually affect each other. This applies only for dyeings of less than 1%. If higher quantities of dye are used, there will be somewhat strong deviations from this simple relationship. They will become all the more noticeable the greater the rate of reaction, the higher the reaction temperature, and the larger the dye molecule. Due to these influences, it is no longer possible to determine a reaction constant for the fixation process. The reaction constant, which can be defined according to Fig. 32, decreases during the fixation process. This means that the fixation time is increased and that the yield decreases, since the ratio rate of fixation/rate of hydrolysis is shifted to the disadvantage of the fixation. According to Beckmann and Hildebrand,²⁷² there is also no reaction constant for dyeing in a long liquor with 2,3-dichloroquinoxaline-6-carbamide dyestuffs. The rate of reaction changes

²⁷² W. Beckmann and D. Hildebrand, *J. Soc. Dyers Colourists* **81**, 11 (1965).



Rate of reaction of



with viscose (100 °C, pH 10.0)

FIG. 32. Reaction curve of the fixation reaction for a 15 g/liter pad dyeing on caustic-treated viscose staple cloth. The amount of fixable dye on the fiber is plotted in logarithmic scale against the steaming time. (The rate constant of the reaction dye-cellulose, k_{cell} , is calculated on the basis of the equation which has been given for reactions of pseudo-unimolecular order from the initial concentration of reactive dye on the fiber (A_i) = 100 and the quantity (x) fixed in the time (t), in percent of the amount of dye used (A_i). The expression for k_{cell} has been formulated with a negative sign to express the negative increase of the reaction curve.

continuously, so that the kinetics found in this study corresponds neither to a reaction of pseudo-unimolecular order nor pseudo-bimolecular order. On the other hand, the rate of reaction found in these experiments was seen to be a function of the total amount of dye present on the fiber.

A comparison with the rate of reaction of the same dye with sorbitol in

a homogeneous medium showed that the heterogeneous dye-fiber reaction takes place at a rate which is 25 times slower than the homogeneous sorbitol substitution. It is therefore not possible to find a reason on the basis of the heterogeneous character of the dyeing reaction for the fact that reactive dyes react with cellulose fibers in an alkaline aqueous medium with considerable yields. The fact that the substrate which is to be dyed is insoluble is not an essential condition for the reaction. In fact, it is rather a hindrance, i.e., the heterogeneous reaction with cellulose is topochemically obstructed.²⁷¹ The extent of this topochemical inhibition has been found to depend not only on the fiber substrate, but also on specific dye properties. The number of Cell-OH groups present in the cellulose fiber is therefore limited and will decrease during the fixation process with increasing dye absorption at a faster rate than would correspond to the degree of substitution. This is due to steric shielding by the large dye molecule. Hence the cellulose fiber has in relation to reactive dyes dye-specific saturation values which are lower, the bulkier and the more substantive the dye molecule.²⁷³ Since the saturation value depends on the accessibility of the fiber, it will also depend on the fixation method.²⁶⁴ It is therefore lower, the less the fiber has swollen during the fixation process. With increasing approach to the saturation value, the fixation reaction slows down, and the yield drops. Although the saturation value is not attained in color depths which occur in practice, the fiber saturation is indicated in advance by a decrease (which is striking if the amount of dye used is high) of the gross rate of fixation and yield.^{274, 275}

ii. *Influence of pH and temperature.* Corresponding to the hydrolysis reaction, the rate of fixation is also dependent on the pH, so that an increase of the pH level of the reaction conditions will lead to a drastic acceleration of the rate of fixation.²⁷⁶⁻²⁷⁹ With increasing pH, therefore, the fixation curves become steeper and will flatten out after shorter fixation times into the straight line which is independent of time. The maximum yields of fixation processes which have been accelerated in this manner are, however, lower than the yields of slow dyeing reactions

²⁷³ D. Hildebrand, *SVF Fachorgan Textilveredlung* **20**, 644 (1965).

²⁷⁴ D. Hildebrand and R. Schwaebel, *Textil-Praxis* **22**, 796 (1967).

²⁷⁵ R. Kuth and D. Hildebrand, *Z. Ges. Textil-Ind.* **69**, 329, 405, and 473 (1967).

²⁷⁶ D. Hildebrand, *Colourage Annu.* p. 71. (1969).

²⁷⁷ D. Hildebrand and R. Kuth, *Textil-Praxis* **22**, 346 (1967).

²⁷⁸ T. Vickerstaff, in "Procion Dyestuffs in Textile Dyeing," p. 34. I.C.I., Manchester, 1962.

²⁷⁹ H. U. von der Eltz, *Melliand Textilber.* **42**, 672 (1961).

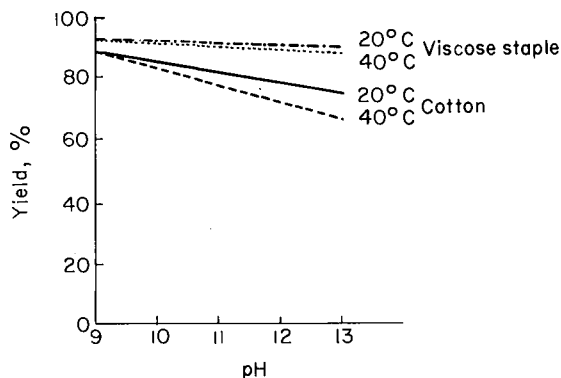


FIG. 33. Yield of fixation of pad batch dyeings at different pH and temperatures. Two-phase wet developing process.²⁷¹

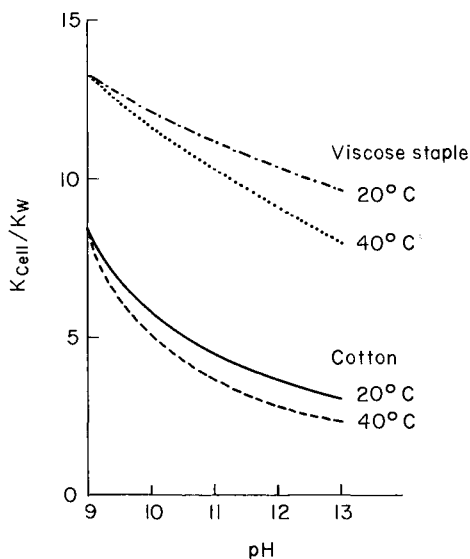
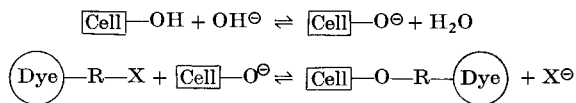


FIG. 34. Dependence of the ratio k_{Cell}/k_w upon pH for Levafix Brilliant Red E-2B at different temperatures.

(Figs. 33 and 34). The following equation represents the pH-dependence of the cellulose substitution²⁸⁰:



²⁸⁰ H. H. Sumner, *J. Soc. Dyers Colourists* **76**, 672 (1960).

According to this equation, for the fixation reaction and for the hydrolysis reaction, the same dependence on the pH is to be expected. In fact, it was found that in pad dyeings the rate of reaction of the cellulose substitution depended on the pH in almost the same manner as had been found for hydrolysis (see Table IX).²⁷¹ However, as already stated in the

TABLE IX
DETERMINATION OF THE RATE OF REACTION OF LEVAFIX
BRILLIANT RED E-2B WITH COTON AS A REACTION OF
PSEUDO-UNIMOLECULAR ORDER FOR 1% DYE USED

<i>pH</i>	<i>Yield</i> <i>in %</i>	$\frac{k'_{cell}}{k_{water}}$	$\frac{k'_{cell}}{k_{water}}$	k_{cell} (<i>min</i> ⁻¹)
20° C				
9	89	8.1	40.5	6.8×10^{-4}
10	86	6.1	30.5	3.8×10^{-3}
10.5	84	5.2	27.5	9.2×10^{-3}
11	82	4.5	23.8	2.2×10^{-2}
11.5	80.5	4.1	22	5.5×10^{-2}
12	79	3.7	20	8.2×10^{-2}
12.5	77	3.3	19	10.5×10^{-2}
40° C				
9	89	8.1	40	8×10^{-3}
10	83.5	5.06	25	3.75×10^{-2}
10.5	81	4.2	21	8.4×10^{-2}
11	78	3.5	17	1.8×10^{-1}
11.5	75.5	3.1	15.5	4.6×10^{-1}
12	72.5	2.6	13	6.4×10^{-1}
12.5	70	2.3	11.5	7.6×10^{-1}
60° C				
9	78.6	3.7	17	4.1×10^{-2}
10	69.3	2.3	11	2.0×10^{-1}
10.5	65.8	1.9	8.8	3.8×10^{-1}
11	63.4	1.7	7.8	1.0

preceding section, the similarity between the pH dependence of the rate of hydrolysis and that of cellulose substitution does not exclusively govern the rate of fixation.^{281,282} In any case substantivity and diffusion effects have to be considered since the substantivity is inversely pro-

portional to the pH.²⁸¹⁻²⁸⁵ pH values below 11.5 will not exercise an appreciable influence on the substantively bound amount of dye, which will, however, begin to drop from an elevated pH value upwards with increasing pH due to the increasing ionization of the cellulose (Fig. 35). Corresponding to the dependence of the hydrolysis on the

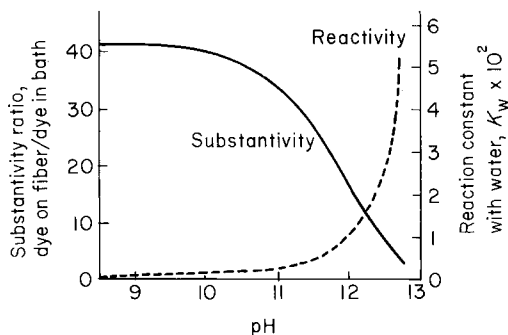


FIG. 35. Influence of pH on substantivity and reactivity of Procion Brilliant Red M-2BS.^{284, 285}

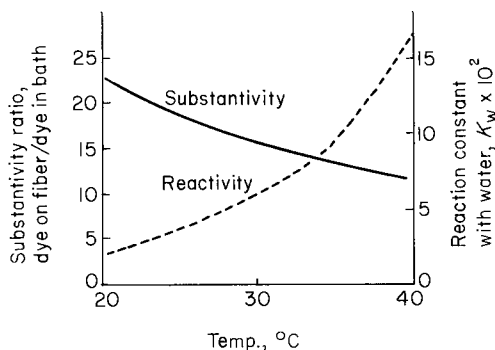


FIG. 36. Influence of temperature on substantivity and reactivity of Procion Brilliant Red M-2BS.

temperature, however, the rate of reaction with the cellulose will increase with increasing temperature.

But the substantivity, which is essential for dyeing in a long liquor, decreases as the temperature goes up (Fig. 36). Table IX shows a few

²⁸¹ T. Vickerstaff, *Hexagon Digest* No. 6, p. 3 (1960) (German Ed.).

²⁸² I. D. Rattee, *Endeavour* **20**, 154 (1961).

²⁸³ W. Beckmann, "Deutscher Färberkalender," p. 131. Franz Eder Verlag, Munich, 1965.

²⁸⁴ J. A. Fowler and W. J. Marshall, *J. Soc. Dyers Colourists* **80**, 358 (1964).

²⁸⁵ J. A. Fowler and W. J. Marshall, *SVF Fachorgan Textilveredlung* **20**, 242 (1965).

rate constants which have been determined for Levafix Brilliant Red by the cold pad-batch method. The activation energies of the dye-fiber reaction follow from the rates of reaction determined at different temperatures. Bohnert and Weingarten were the first to point out that the activation energy of the dye-fiber reaction is smaller than the activation energy of hydrolysis.²⁷⁰

Beckmann²⁶³ has also reported not only on different rates of reaction of hydrolysis and fiber reaction, but also on a different dependence of these constants on the temperature, in agreement with the results obtained by Bohnert and Weingarten²⁷⁰ (see also Rattee²⁸⁶).

For the reaction of Levafix Brilliant Red E-2B with native cellulose, an activation energy of 22.9 kcal/mole was found, while the corresponding values for regenerated cellulose are 21.8 kcal/mole and for the reaction with sorbitol 21.7 kcal/mole.²⁸⁷ On the other hand, the activation energy of the hydrolysis was 24.6 kcal/mole. Similar observations were made by Baumgarte and Feichtmayr²⁸⁸ when they investigated the reaction of dyes of similar constitution, but containing different reactive groups, with α -methylglucoside, *n*-butanol, and α - and β -dextrin. As the temperature increases, the preference observed for the dye-fiber reaction will thus become less and less. Since, on the other hand, the heterogeneous fixation reaction at high temperatures cannot be increased like a homogeneous reaction, the ratio $k_{\text{Cell}}/k_{\text{W}}$, which is important for the yield, will decrease both with increasing pH and with increasing temperature of the fixation conditions.

iii. Influence of fixation auxiliaries. It has been found useful to employ urea as an auxiliary in fixation processes where the dye is applied to the fiber in the form of concentrated liquors or print pastes, particularly if the reaction is carried out after preliminary drying as a curing or steaming process. The action of urea is seen in an increased rate of fixation and yield, often also in a better penetration of the goods (Fig. 37).²⁸⁹⁻²⁹³ In printing on viscose staple, the full yield is often obtained only after pretreatment with a urea solution.²⁹⁴

The quantity of urea required for optimum fixation is different. It

²⁸⁶ I. D. Rattee, *Am. Dyestuff Repr.* **52**, 320 (1963).

²⁸⁷ D. Hildebrand, *Bayer Farben Rev.* No. 9, p. 29 (1964).

²⁸⁸ U. Baumgarte and F. Feichtmayr, *Melliand Textilber.* **45**, 775 (1964).

²⁸⁹ G. Kögel, *SVF Fachorgan Textilveredlung* **14**, 694 (1962).

²⁹⁰ M. R. Fox, W. J. Marshall, and N. D. Stewart *J. Soc. Dyers Colourists* **83**, 493 (1967).

²⁹¹ D. Hildebrand and R. Kuth, *Textil-Praxis* **22**, 346 (1967).

²⁹² B. Weigl, *Deut. Textiltechn.* **17**, 775 (1967).

²⁹³ D. Hildebrand, *Melliand Textilber.* **49**, 67 (1968).

²⁹⁴ H. Rafael, *SVF Fachorgan Textilveredlung* **16**, 754 (1961).

depends on the substantivity and the fixation temperature. According to Capponi²⁹⁵ there is an optimum urea concentration in the thermofixation of Drimaren Z dyestuffs. At high temperatures, the optimum urea concentration will again decrease. In concentrated dye formulations, urea acts as a dye-dissolving agent,²⁹⁶⁻²⁹⁹ while it will act as a fiber-swelling agent on cellulose. It increases the rate of diffusion of the dye in the fiber³⁰⁰ and prevents overdrying of the cellulose during drying and curing.³⁰¹ According to Preston³⁰² the swelling value of the cellulose

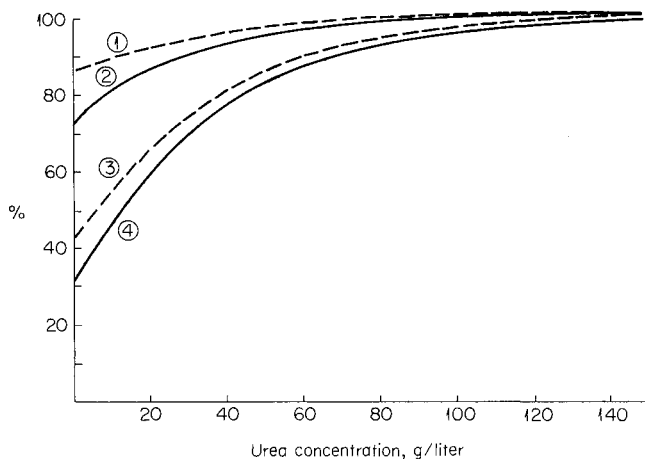


FIG. 37. Influence of urea on the yield of fixation of reactive dyes in high-temperature fixation processes.²⁹⁴ Thermofixed (cured) ③ and steamed ④ at 60 seconds, 150°C. Viscose staple: broken line ①; bleached cotton: solid line ②.

fiber increases by approx. 5% if the urea concentration of the solution is increased by 10%. Hence urea has a double function in the application of reactive dyes from pad liquors and print pastes: it disaggregates the dye in the solution³⁰³ and it improves the accessibility of the fiber. According to Baumgarte,³⁰¹ urea reacts with the fiber in alkaline curing

²⁹⁵ M. Capponi, *SVF Fachorgan Textilveredlung* **16**, 229 (1961).

²⁹⁶ H. Berthold, *Melliand Textilber.* **31**, 575 (1950).

²⁹⁷ H. Rath, J. Rau, and D. Wagner, *Melliand Textilber.* **43**, 718 (1962); **94**, 969 (1963).

²⁹⁸ H. Rath, "Lehrbuch der Textilchemie," 2nd ed., pp. 492 and 686. Springer Verlag, Berlin and New York, 1963.

²⁹⁹ R. Escales and H. Koepke, *J. Prakt. Chem.* [2] **87**, 272 (1913).

³⁰⁰ M. Peter, *SVF Fachorgan Textilveredlung* **16**, 219 (1961).

³⁰¹ U. Baumgarte, *Melliand Textilber.* **46**, 851 (1965).

³⁰² J. M. Preston, J. F. Clark, W. R. Beath, and M. V. Nimkar, *J. Textile Inst., Trans.* **45**, 504 (1954).

³⁰³ P. Ulrich, *SVF Fachorgan Textilveredlung* **16**, 241 (1961).

processes which are usually employed in the fixation of reactive dyes, so that cellulose will bind nitrogen. At temperatures above 150°, urea will decompose with formation of ammonia, ammonium cyanate, biuret, and cyanuric acid, according to Escales and Koepke²⁹⁹ and Werner.³⁰⁴ The acids formed by these decomposition reactions will consume alkali,

TABLE X
FIXATION YIELD OF LEVAFIX P DYESTUFFS
DEPENDING ON THE UREA CONTENT AND ON
ADDITION OF THIOUREA AND DICYANDIAMIDE^{a, b}

<i>Grams/liter of</i>	<i>Yield (%)</i>
50 Urea	72
70 Urea	74
80 Urea	76
90 Urea	80
100 Urea	85
70 Thiourea	56
80 Thiourea	56
90 Thiourea	56
35 Dicyandiamide	65
40 Dicyandiamide	66
45 Dicyandiamide	64
25 Dicyandiamide + 25 urea	73
35 Dicyandiamide + 35 urea	74
25 Dicyandiamide + 25 thiourea	68
35 Dicyandiamide + 35 thiourea	66
50 Dicyandiamide + 50 urea	80

^a Kuth and Hildebrand.²⁷⁵

^b For 40 g/liter Levafix Brilliant Red P-B;
8 g/liter Ludigol; 10 g/liter sodium bicarbonate;
60 sec at 210° therm.; on bleached cotton cloth.

which can exercise an adverse influence on the dye-fiber reaction. It has therefore been suggested that dicyandiamide may be used as fixing agent in curing processes.³⁰⁵⁻³¹² In this sense, caprolactam²⁶⁶ and other

³⁰⁴ E. A. Werner, *J. Chem. Soc. (London)* **103**, 1019 and 2276 (1913).

³⁰⁵ R. Mack, *Z. Ges. Textil-Ind.* **69**, 101 (1967).

³⁰⁶ CIBA, *BeP* 564,836 (14.12.1958).

³⁰⁷ S, *BeP* 597,039 (14.11.1960).

³⁰⁸ G, *DAS* 1,126,840 (21.4.1961).

³⁰⁹ Gy, *BeP* 602,933 (24.4.1961).

³¹⁰ CIBA, *SZAS* 5,059/63 (23.4.1963).

³¹¹ CIBA, *BeP* 642,943 (24.1.1964).

³¹² ICI, F. Dawson, R. W. Tomlinson, and A. Topham, *BP* 1,060,063 (18.1.1963).

amides and urea derivatives can also be used in place of or in mixture with urea. But it has not been possible to get a better yield in this manner than with urea.³¹³ The higher cost of these products is also an obstacle to their widespread use. Apart from a reaction between urea and fiber and a using-up of the alkali content of the fabric by decomposition reactions, direct reactions between dye and urea have been observed at high temperatures for dyes based on vinyl sulfone.^{313, 314} Such dyes cannot therefore be used together with urea at high temperatures.^{315, 316} On the other hand, urea will not affect the rate of hydrolysis of reactive dyes in aqueous solutions.³¹⁷

b. Wool and Polyamide Fibers. The basic criterion for the fast dyeing of wool with reactive dyes is the degree of covalent fixation of the dye on the fiber.³¹⁸ This is determined by the individual properties of each dye and the selected fixation conditions. The most important factors governing the reaction are, as in the cases we discussed previously, the pH value and the temperature of the reaction medium.³¹⁹⁻³²⁷ These factors determine both the rate of adsorption and the rate of fixation. Both processes can be separated and can be described by means of adsorption and fixation curves. The adsorption curve is determined by photometric assessment of the residual liquor in relation to the initial concentration. The rate of fixation can only be determined if we know the total amount of dye which has gone on the fiber for every gram of the fiber. The unfixed portion of the dye on the fiber is found by extrac-

³¹³ E. Kissa, *Textile Res. J.* **39**, 734 (1969).

³¹⁴ H. U. von der Eltz, *Textil-Praxis* **21**, 523 (1966).

³¹⁵ K. Wagner, *Z. Ges. Textil-Ind.* **63**, 278 (1961).

³¹⁶ E. Kissa, *Am. Dyestuff Repr.* **56**, 106 (1967).

³¹⁷ A. Uibel and D. Wagner, *Melliand Textilber.* **49**, 457 (1968).

³¹⁸ V. P. Pobedimskij and P. V. Moryganov, *Izv. Vysikh Uchebn. Zavedenii, Tekhnol. Tekstil'n. Prom.* No. **4**, p. 102 (1966); *Sow. Beitr. Faserforsch. Textiltech.* **3**, 657 (1966).

³¹⁹ J. Wegmann, *SVF Fachorgan Textilveredlung* **14**, 185 (1959).

³²⁰ H. R. Hadfield and D. R. Lemin, *J. Textile Inst., Trans.* **51**, 1351 (1960); *Dyer* **123**, 872 (1960).

³²¹ U. Baumgarte, *Melliand Textilber.* **43**, 1297 (1962).

³²² R. Hahn, *Prakt. Chem.* **16**, 71 (1965).

³²³ R. J. Hine and J. R. McPhee, *J. Soc. Dyers Colourists* **81**, 268 (1965).

³²⁴ A. N. Derbyshire and G. R. Tristram, *J. Soc. Dyers Colourists* **81**, 584 (1965).

³²⁵ J. G. Graham, *Deut. Textiltech.* **16**, 178 (1966).

³²⁶ D. R. Lemin, *Teintex* **31**, 19 (1966).

³²⁷ H. Zahn and P. F. Rouette, *Textilveredlung* **3**, 241 (1968).

tion.³²⁸⁻³³¹ Adsorption and fixation processes are as a rule inversely proportional to the pH value (see Figs. 38-40). Since the dye-fiber reaction will be most favorable in the pH range of minimum swelling of the wool, the heterogeneous reaction of the wool will require higher temperatures than the heterogeneous reaction of cotton, even if highly reactive dyes are used for the wool (see Fig. 41). But in contrast to the dyeing conditions which apply to cotton, hydrolysis plays only a minor part in the reactive dyeing of wool, so that the rival effect of hydrolysis is low, since the amino group has a much higher nucleophilic potency and the dye hydrolysis has a minimum value in the weakly acid pH range.

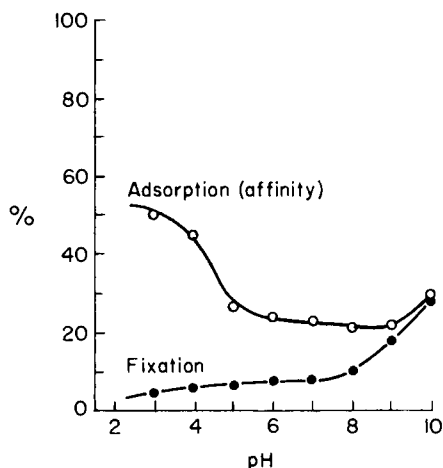


FIG. 38. 10% dyeing of Remazol Brilliant Blue R (vinyl sulfone form) at 50°, 2 hours, with changing pH—on untreated wool.³²⁷

The optimum pH level for a particular class of dyes is found by determining the degree of fixation as a function of the pH. Levelness is the main problem in the use of reactive dyes on wool. In contrast to the reactive dyeing of cellulose fibers, which is distinguished by its reproducibility and which can be easily controlled to get the required levelness the adsorption and fixation process in wool depends very strongly on the

³²⁸ N. G. Klemin, P. V. Moryganov, and A. A. Solo'ev, *Zh. Prikl. Khim.* **21**, 797 (1954).

³²⁹ G. Pusch, *Z. Ges. Textil-Ind.* **60**, 188 (1958); A. N. Derbyshire and J. G. Graham, *Dyer* **130**, 891 (1963); **131**, 31 (1964).

³³⁰ O. I. Eremina, V. R. Bojno-Rodcevic, and S. A. Plencova, *Tekstil'n. Prom.* **26**, No. 7, p. 8 (1966).

³³¹ V. P. Pobedimskij and P. V. Moryganov, *Izv. Vysshikh Uchebn. Zavedenii, Tekhnol. Tekstil'n. Prom.* No. 3, p. 90 (1966).

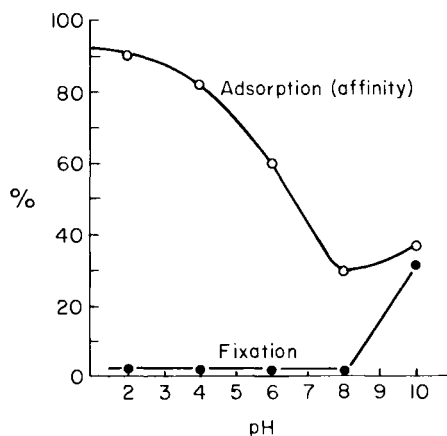


FIG. 39. 10% dyeing of Remazol Brilliant Blue R (vinyl sulfone form) at 50°, 2 hours, with changing pH—on oxidized wool.³²⁷

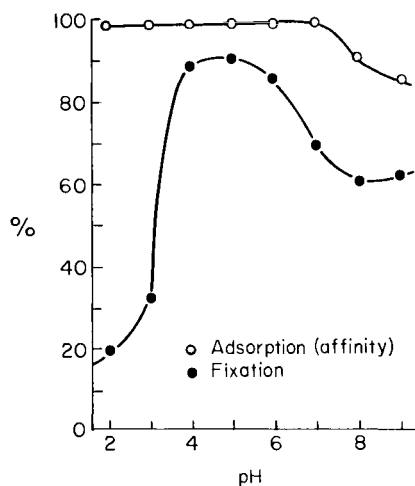


FIG. 40. 10% dyeing of Remazol Brilliant Blue R (vinyl sulfone form) at 50°, 2 hours, with changing pH—on partially reduced wool.³²⁷

properties and performance of the individual dyes and fibers. Although it is possible in principle to describe the dyeing process with the help of the affinity and fixation curves as a function of the individual process variables, which will enable us to select the most favorable conditions, we cannot conclude anything about the compatibility of different dyes simply by comparing the adsorption and fixation curves, since these curves can be regarded as integrals of the individually different properties

of the fibers that make up a lot. The heterogeneous chemical and physical nature of wool is an obstacle to the assessment of a range of wool-reactive dyes with respect to their compatibility on the basis of the adsorption and fixation curves. Since adsorption and fixation depend on the pH in a different manner, they can be separated and can also be controlled and adjusted more or less independently. For example, in the case of dyes which possess reactive groups of the structure $-\text{SO}_2(\text{CH}_2)_2\text{OSO}_3\text{Na}$ it is first of all necessary that a free sulfone is formed as reactive partner.

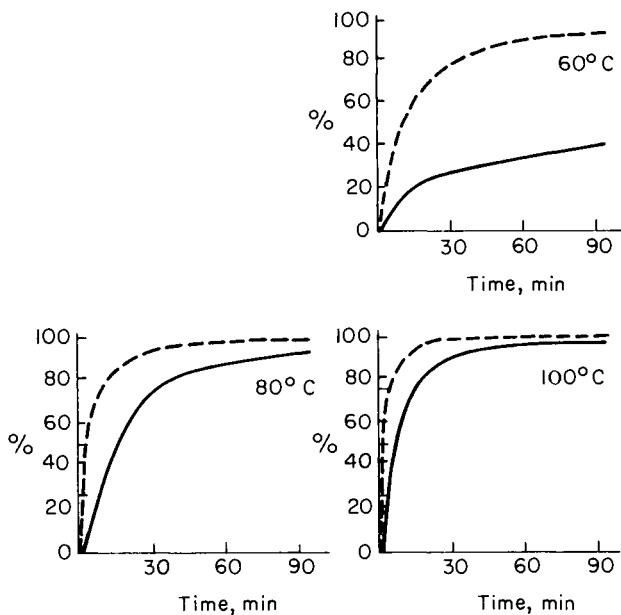


FIG. 41. Isotherms for bath exhaustion and dye fixation of a reactive dye on wool as a function of time.³⁴³ ---, Exhaustion; —, fixation. 2% Lanazol Red B; 2% acetic acid 80%; 5% Glaubers salt anhydrous; 1% Albigal B.

This is only possible at a satisfactory rate using an alkaline medium in which the anionic dye has practically no affinity at all.^{334,335} Besides soluble reactive dyes, dyes which are insoluble in water can also react with wool and regenerated protein fibers.³³⁶ But the application of these

³³² ICI, BP 893,976 (13.11.1959).

³³³ H. U. von der Eltz and W. Hacker, *Z. Ges. Textil-Ind.* **63**, 356 (1961).

³³⁴ W. Hausmann, *Textil-Praxis* **17**, 38 (1962).

³³⁵ N. Kollodzeiski, *Melliand Textilber.* **45**, 51 (1964).

³³⁶ ICI, BP 809,204 (15.6.1956); 874,513 (8.5.1959); 875,105; 875,106; 875,451 (21.3.1960); 877,666; 877,667 (20.9.1961).

dyes is limited to the synthetic polyamides. The Procilan dyes are azo dye-metal complexes containing reactive groups (such as $-\text{NH}-\text{CO}-\text{CH}=\text{CH}_2$). Figure 42 compares the fixation performance of Procion and Procilan dyestuffs.

To make up for the individual differences in the properties of the dyes and fibers, reactive dyeing of wool is linked to the development of

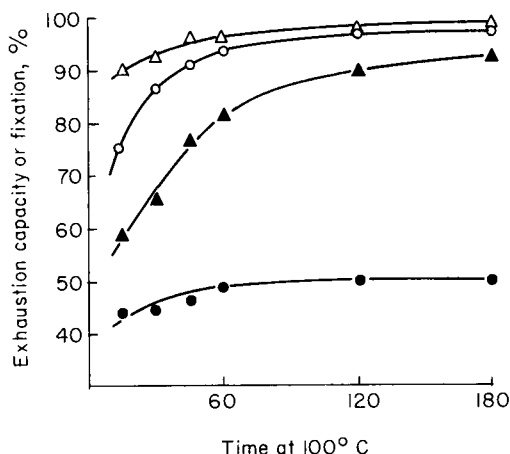


FIG. 42. Comparison of the yield of fixation and bath exhaustion of Procilan and Procion dyes, 325 on wool. ●, Fixation of Procion dyes; ○, bath exhaustion of Procion dyes; ▲, fixation of Procilan dyes; △, exhaustion of Procilan dyes.

suitable auxiliaries whose presence in the dyebath is an essential condition for level dyeing.³³⁷⁻³⁴³ Oxyethylation products which contain nitrogen are particularly suitable, e.g., reaction products of aliphatic amines with 15-30 moles of ethylene oxide,³⁴⁴⁻³⁴⁶ also cetyltrimethyl ammonium bromide^{347, 348} or stearyl aminopropyltrimethyl ammonium bromide.³⁴⁹ Phosphonium compounds have also been patented.³⁴⁷

³³⁷ H. Abel, *Ciba Rundschau* **6**, 50 (1963).

³³⁸ R. Casty, *SVF Fachorgan Textilveredlung* **13**, 586 (1958).

³³⁹ H. Abel, *Ciba Rundschau* **4**, 41 (1961); **1**, 38 (1962).

³⁴⁰ W. Badertscher, *SVF Fachorgan Textilveredlung* **16**, 194 (1961).

³⁴¹ *Ciba Rundschau* No. 5, p. 42 (1962).

³⁴² H. Abel, *Ciba Rundschau*, No. 2, p. 46 (1967).

³⁴³ A. Bühler and R. Casty, *Melliand Textilber.* **48**, 693 (1967).

³⁴⁴ CIBA, *BeP* 576,927 (20.3.1959).

³⁴⁵ CIBA, *FP* 1,260,343 (15.6.1960).

³⁴⁶ Gy, *BeP* 617,998 (23.5.1962).

³⁴⁷ ICI, *BP* 869,150 (8.10.1958); *BeP* 664,880 (6.3.1964).

³⁴⁸ S, *SZAS* 82,320/59 (24.12.1959).

³⁴⁹ S, *BeP* 598,566 (27.12.1960); *FP* 1,277,635 (12.1.1961); *BeP* 608,149 (13.9.1961).

Figure 43, e.g., shows the effect of an auxiliary (Albegal B) on the fixation curve of Lanazol Blue 3R, dependent on Albegal B concentration. Using 1 and 2% Albegal B the dye uptake is increased; but using very high auxiliary concentrations the affinity of the wool is reduced. In general 1–2% of auxiliary is recommended, independent of depth of shade. The use of the surface-active compounds which contain nitrogen can be coupled with the use of anionic compounds, e.g., dinaphthylmethanedisulfonic acid, triisopropyl-naphthalenesulfonic acid, or oleyl

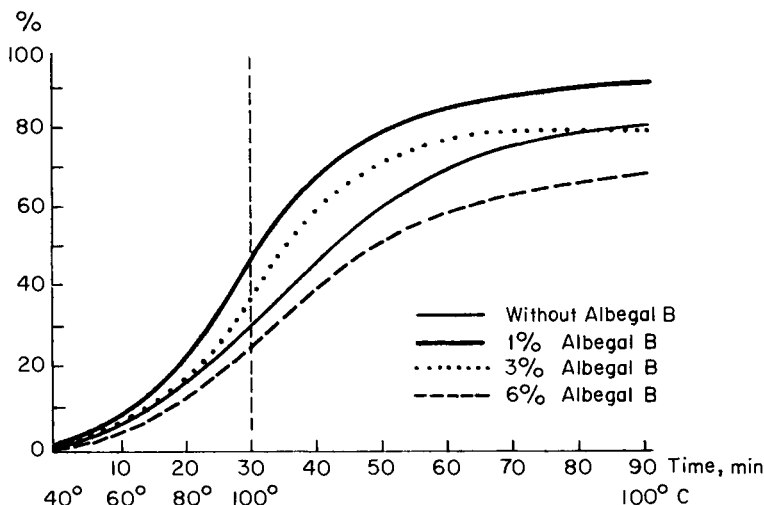


FIG. 43. Adsorption of Lanazol Blue 3R on wool without and with increasing quantities of Albegal B.

sulfate.³⁵⁰ Investigations have shown that the following types of compounds are very suitable: Fatty acid diethanolamides^{351–354} and their ethoxylation products, as well as salts of fatty amines, such as *n*-octadecylamine or 1-amino-2-alkylimidazoline, also alkyl aminotriazole in combination with polyhydroxyethylene or polyhydroxypropylene compounds.³⁵⁵ The levelness of a reactive dyeing on wool can also be improved by pretreating the wool with an auxiliary at low temperature, followed by dyeing at an elevated temperature.³⁵⁶ There

³⁵⁰ ICI, *BeP* 617,445 (9.5.1962).

³⁵¹ Gy, *BeP* 611,779 (20.12.1961); *SP* 371,430 (21.12.1960).

³⁵² Gy, *SZAS* 1,479/61 (8.12.1961).

³⁵³ Gy, *BeP* 618,318 (30.5.1962).

³⁵⁴ Gy, *SZAS* 5,312/62 (3.5.1962).

³⁵⁵ NSK, *JP* 20,635/63 (29.3.1961).

³⁵⁶ Teintureries Laval, *FP* 1,483,892 (25.4.1966).

is no agreement on the mechanism of the action of the auxiliary. Interactions of the auxiliary with both the dye and the fiber have been found. The addition of auxiliaries will usually accelerate the adsorption and fixation processes, and it will also increase the degree of fixation. We can therefore also consider such products as fixation auxiliaries which exercise a direct influence on the heterogeneous reaction. The general idea that the action of leveling agents is due to a retarding mechanism is therefore not correct as far as the reactive dyeing of wool is concerned.

Several methods have been patented which aim at improving the dye bonding capacity of wool by a preliminary reduction treatment. Suitable reducing agents are, for example, thioglycolic acid,³⁵⁷ mercaptobenzoic acid,³⁵⁸ monoethanolamine sulfite,³⁵⁹ and sodium sulfite.³⁶⁰

Another possibility for improving the reactivity of keratin fibers is to pretreat the wool first with peroxide and then to treat it with reducing agents which contain sulfur. This process has been patented by Precision Processes.³⁶¹ It is also possible to dye wool in airtight packages at low temperatures, using at the same time 20 ml/liter of acetic acid or 50 ml/liter of 80% formic acid and 200–300 ml/liter of ethyl alcohol.³⁶² Special auxiliaries have been developed for the continuous dyeing of wool with reactive dyes.³⁶³ The reaction with the fiber is promoted by steaming, and in special cases also by superheated steam.³⁶⁴ Synthetic polyamide fibers can be dyed not only with wool-reactive dyes derived from acid dyes,^{365–369} but also with specially developed, water-insoluble reactive dyes which are used as disperse dyes.^{366, 370–374} Hence the

³⁵⁷ S, SZAS 75,361/59 (1.10.1959); USP 3,097,041 (27.6.1960); SP 367,474 (26.6.1959).

³⁵⁸ S, BeP 592,292 (24.6.1960).

³⁵⁹ S, SZAS, 14,971/62 (20.12.1962).

³⁶⁰ Turner Hall, USP 3,340,000 (14.4.1966).

³⁶¹ Precision Processes Ltd., FP 1,333,995 (17.7.1962).

³⁶² Gillet-Thaon, FP 1,474,863 (25.1.1966).

³⁶³ FBy, BeP 658,675 (22.1.1965); DAS 1,280,808 (22.1.1964).

³⁶⁴ ICI, FP 1,485,342 (1.7.1966); BP 28,134/65 (2.7.1965).

³⁶⁵ J. Chanel, *Rev. Textile Tiba* **57**, 504 (1958).

³⁶⁶ D. F. Scott and T. Vickerstaff, *J. Soc. Dyers Colourists* **76**, 104 (1960).

³⁶⁷ A. Schaub, *Ciba Rundschau* **13**, No. 152, p. 43 (1960).

³⁶⁸ V. N. Ufimcev, *Zh. Vses. Khim. Obshchestva im. D. I. Mendeleeva* **31**, 16 (1966).

³⁶⁹ A. A. Charcharov, I. J. Kalontarov, M. M. Golcman, and Z. I. Artamonova, *Tekstil'n. Prom.* **25**, 63 (1965).

³⁷⁰ CIBA, BeP 563,861 (10.1.1958); FP 1,189,668 (11.1.1957).

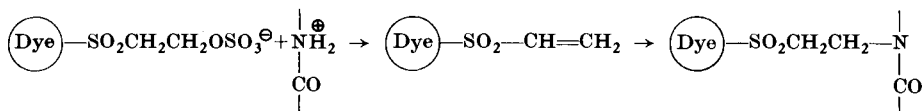
³⁷¹ ICI, DAS 1,239,268 (12.6.1957); BeP 558,533 (15.6.1957); FP 1,179,434 (15.6.1956); USP 3,042,477 (3.6.1962).

³⁷² ICI, DAS 1,098,911 (29.10.1959); BP 895,424 (7.11.1958); BeP 584,370 (5.11.1959).

³⁷³ R. L. Denyer and J. A. Fowler, *Melliand Textilber.* **42**, 535 (1961).

³⁷⁴ FW, EGP 24,479/22a (10.2.1960).

heterogeneous reaction does not take place via a saltlike linkage to the fiber, but rather via a dissolution mechanism. Trials have also been conducted to make acrylic fibers accessible to a reaction with reactive dyes. The acrylic fiber Nitron can be dyed with Remazol dyestuffs by pretreatment with hydroxylamine salts. The maximum yield of the dyestuff, which is linked to the fiber according to the following equation,³⁷⁵ was found to be 18–25%.



The Procynyl dyestuffs are a special range of polyamide dyestuffs based on the dissolution mechanism. If anionic dyestuffs are used, synthetic polyamides can only be dyed in the presence of leveling agents which belong to the same group of compounds. Special investigations on leveling agents in dyeing with wool-reactive dyes have been conducted by Moncrieff,³⁷⁶ as well as Kalontarov and Charcharov.³⁷⁷ The fiber-dye reaction is brought about by steaming^{378,379} or by treatment in a boiling dyebath. The amount of alkali required is higher than in the case of wool. It is also possible to dye in an acid medium and then to fix in an alkaline medium, if necessary at an elevated temperature.³⁸⁰

Shore has measured the relative reactivities of a chlorotriazine dye with simple model compounds for the functional groups in wool and other proteins.³⁸¹ The results were used to predict the reactivities of water-soluble proteins of relatively low molecular weight and the predictions were compared with measured reactivities of the proteins themselves. Shore then dyed chlorinated wool with a monochlorotriazine dye under infinite dyebath conditions. The rate constants for the reaction between the dye and the fiber, obtained by using the Danckwerts equation for diffusion into an infinite cylinder with surface saturation, agreed well with theoretical constants calculated from the reactivities of model compounds and data from amino acid analysis. The relative

³⁷⁵ S. V. Picchadze, S. M. Sosina, and V. F. Androsov, *Izv. Vysshikh Uchebn. Zavedenii, Tekhnol. Tekstil'n. Prom.* p. 94 (1967).

³⁷⁶ R. W. Moncrieff, *Textile Mfr.* **90**, 497 (1964).

³⁷⁷ I. J. Kalontarov and A. A. Charcharov, *Izv. Vysshikh Uchebn. Zavedenii, Tekhnol. Tekstil'n. Prom.* p. 94 (1965).

³⁷⁸ Gy, *BeP* 652,584 (10.9.1964); *SP* 10,371 (7.8.1964).

³⁷⁹ ICI, *EGP* 56,524 (27.7.1966/20.6.1967); *BP* 32,707/65 (30.7.1965).

³⁸⁰ ICI, *FP* 1,243,980 (7.11.1959); *BP* 895,424 (7.11.1958).

³⁸¹ J. Shore, *J. Soc. Dyers Colourists* **84**, 408, 413, and 545 (1968); **85**, 14 (1969).

contributions of the individual types of reactive site to the total reactivity of wool have been discussed.

2. *Removal of the Unfixed Portion of a Dye*

a. From Cellulose Fibers. Since the chemical reaction between a reactive dye and the cellulose fiber will not quantitatively favor the dye-fiber linkage, it will be necessary to remove that portion of the dye which has not been linked chemically to the fiber and which has merely been adsorbed by the fiber, i.e., which is only bound substantively. This removal is effected by washing off and rinsing. As a rule, the unfixed portion of the dye which remains on the fiber after fixation consists of hydrolyzed dye. However, if final fixation has not been achieved, it can also happen that dye which is still capable of reaction is washed off before it has reacted. Dyestuff particles which have not been linked chemically to the fiber and which are attached to the fiber more or less firmly by adsorption will stain the accompanying fabric on exposure to wet treatments. This means that the good wet-fastness properties which are so characteristic of reactive dyeings can only be obtained if the substantively bound portion of the dyestuff is removed as completely as possible. This is particularly true for the production of deep shades in textile printing, where dyed areas are adjacent to undyed areas. The main problem of the washing-off of reactive dyeings and prints concerns the fastness to water, since there is normally no staining of cotton fabric under the conditions which apply to treatment at the boil. However, highly substantive reactive dyes can also go on cotton under washing conditions. If they are still capable of reaction at this stage, this can lead to an irreversible reactive staining of the white fabric areas. If unreacted reactive dye merely migrates in the first rinsing bath from the swollen film into adjacent undyed fabric areas, alkali which may still be present can cause subsequent fixation in these areas before the dye has an opportunity to desorb into the washing bath. This will lead to unsharp outlines and a generally dull appearance of the goods. We can therefore say that the washing-off properties are characterized by the rate at which a given quantity of chemically unfixed dye can be removed from the fiber by hot rinsing. This depends both on the substantivity and on the rate of diffusion. In turn, the substantivity determines the adsorption by the fiber and the readsorption from soiled washing liquors. In practice, however, the relative washing-off property, which depends on the yield, is the really important factor, while the absolute measure of the washing-off capacity, which is independent of the yield of fixation, is relatively unimportant, for the washing-off problem is greater, the greater the quantity of dye which has to be washed off.

The relative washing-off property expresses the comparative washing-off rates of dyestuff formulations which produce dyeings or prints of equal color depth. A number of tests have been suggested for a quantitative comparison of the washing-off properties of reactive dyes. These tests take into consideration both the time required to get a clear rinsing bath, as well as the readsorption and marking off. We define the time required to get a clear rinsing bath as the time during which a dyeing or a print has to be treated with hot water in changing baths until the rinsing liquor is free from dye. A relative washing-off curve is obtained by photometric determination of the dye content of baths placed in series, the dye content being expressed in percent of the total amount of dye to be washed off. This washing-off curve depends on the color depth, the yield, and the thickening agent (mainly sodium alginate), and applies to a certain textile material. The washing-off property of a reactive dye is an important application characteristic. It can be obtained in this manner as a figure on which a comparative assessment of the performance of different dyes can be based.³⁸²⁻³⁸⁴ Meyer³⁸⁵ has published suitable methods for determining staining and marking off.

To make good use of the high working speeds which are necessary in the application of dyes used in padding and printing, we have to give equal importance to the washing-off properties and to the rate of fixation, if we look at the problem from the viewpoint of the speed at which the goods pass through the dyeing or printing plant. Meier-Windhorst and Schraud³⁸⁶ have formulated an expression in which the rinsing process is represented by an equation which applies particularly to reactive dyeings. In this formula, the rate of washing off follows an exponential law which is represented by the curves shown in Fig. 44 where the simplest case has been assumed.³⁸⁴ The curve shown applies to a washing-off process of a nonsubstantive compound in a rinsing liquor which has been diluted to infinity. Formally, the expression is the same as that which is used to represent the rate of reaction of a dye with an infinite excess of OH groups (see Section I,B,1,a). Under prescribed test conditions, the washing-off constant x can also be used to characterize the application properties of a reactive dye. The constant x depends also on the temperature and the quality of the goods. The value of this method is clearly seen by comparing the washing-off curve of a nonsubstantive dye suitable for a continuous process with that of an

³⁸² K. Bühler, D. Hildebrand, and R. Schwaebel, *Bayer Farben Rev.* No. 13, p. 1 (1967).

³⁸³ D. Hildebrand and R. Schwaebel, *Textil-Praxis* **22**, 796 (1967).

³⁸⁴ D. Hildebrand, *Melliand Textilber.* **49**, 67 (1968).

³⁸⁵ G. Meyer, *Melliand Textilber.* **49**, 336 (1968).

³⁸⁶ A. Meier-Windhorst and A. Schraud, *Melliand Textilber.* **45**, 1388 (1964).

exhaustion dye. The curve obtained for Levafix Brilliant Red P-3B corresponds almost exactly with that of a nonsubstantive compound. The factors which govern the washing-off process, such as dyeing equilibrium, diffusion, adsorption, desorption, and heat of dyeing of hydrolyzed reactive dyes have been calculated by Balasova and Sadov³⁸⁷ using Procion Yellow RS and Procion Brilliant Blue RS as examples. These factors have partly been brought in relation to substantive dyes.

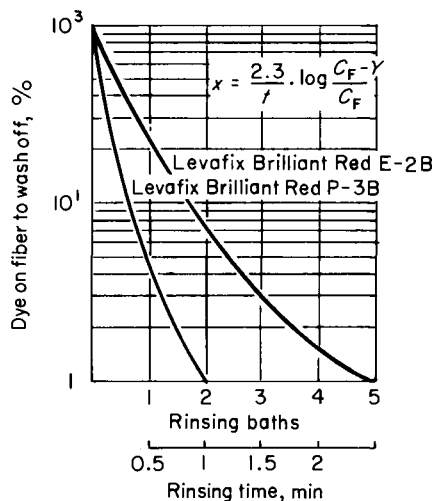


FIG. 44. Graphic demonstration of the washing-off properties of a reactive dye: The logarithm of the dye to be washed off from the cotton fiber is expressed as a function of the washing-off time.³⁸⁴ The washing-off curve corresponds in first approximation to the equation with the washing-off constant x ; C_t is the dye concentration on the fiber which has to be washed off, and y , the portion of dye which must be washed off during the time t .

b. From Wool and Polyamide Fibers. While the substantivity of reactive dyes for cotton is extremely low compared with that of direct dyes, anionic reactive dyes have the affinity of an acid dye when applied on wool and polyamide fibers under dyeing conditions, so that the chemically unfixed portion of the dye cannot be removed from the fiber by simple rinsing or washing off. Moreover, the sensitivity of wool to alkali does not permit alkaline soaping at the boil in the manner often practiced on cotton. The main goal of a reactive dyeing on wool is therefore, apart from levelness, the achievement of a maximum degree of fixation, which will reduce the problem of washing off or which will do

³⁸⁷ T. D. Balasova and F. I. Sadov, *Izv. Vysshikh Uchebn. Zavedenii, Tekhnol. Tekstil'n. Prom.* p. 94 (1963).

away with it completely. In the case of reactive dyes for wool, therefore, we do not characterize the fastness properties by the stability of the bond, but by means of the degree of fixation which can be obtained for the dye in question (see Section I,A,2). The most important fastness properties, which are required to determine the portion of dye which has not been chemically linked to the fiber, are the fastness to acid perspiration and to potting, as well as the fastness to cross-dyeing. The saltlike linkage is stable to the water-fastness test at 40°, in contrast to the substantive type of adsorption.

If the reactive dye has a particularly strong secondary valence linkage with the wool due to the presence of an aromatic chromophoric system, that portion of the dye which has not been linked via the reactive group will behave in a manner which corresponds to the behavior of that class of dye. These considerations led to the development of 2:1 metal complex dyes with reactive groups to improve the fastness to washing.

In the case of the conventional anionic reactive dyes, aftertreatment with ammonia is necessary in deep dyeings, using 2–4% of 25% NH₃ (pH 8–8.5) at 60–80° to remove the unreacted dye from the fiber. The purity of the commercial dyestuff is particularly important. The degree of fixation of the dyeing is reduced by the presence of a portion of non-reactive dye in the amount of dyestuff used, i.e., in the original supply. The maximum fastness level, which could have been attained if the dyestuff had been supplied in a pure quality, is, of course, reduced by such impure components.

D. CONDITIONS OF APPLICATION

1. *Hydrolysis and Rate of Hydrolysis in Dye Formulations*

The fact that reactive dyes react with water is decisive not only for the yield during the dyeing process, but also for the application performance before the actual dyeing and printing process. These application properties are the storage stability of the dyestuffs, the stability of pad liquors and print pastes (pot life), and the changes in reactive dye content caused by hot dissolution of the dyestuff formulations.^{388–391}

Decomposition of the dye by hydrolysis already begins under conditions of synthesis and during drying and grinding of the individual

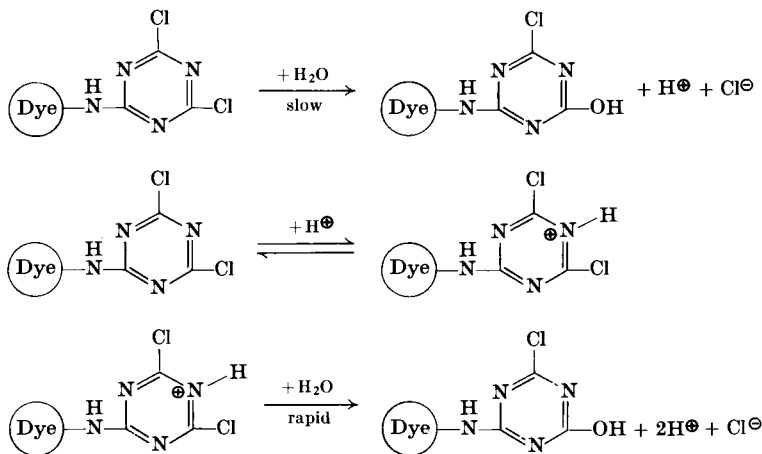
³⁸⁸ W. J. Marshall, in "Procion Dyestuffs in Textile Dyeing," p. 115. I.C.I., Manchester, 1962.

³⁸⁹ J. A. Fowler and W. J. Marshall, *J. Soc. Dyers Colourists* **80**, 358 (1964); *SVF Fachorgan Textilveredlung* **20**, 242 (1965).

³⁹⁰ D. Hildebrand, *Melliand Textilchem.* No. 4, p. 102 (1965).

³⁹¹ K. G. Kleb, E. Siegel, and K. Sasse, *Angew. Chem.* **76**, 423 (1964).

batches. If the proportions of decomposed dye are different from one batch to another, this must be taken into consideration when adjusting the supplies to standard. The stability during drying and storage is governed by the pH level of the solution from which the dye was isolated. Some dyes can be isolated under weakly acid conditions without loss of reactivity by premature hydrolysis. In some highly reactive halogen heterocycles which are easily protonated,³⁹²⁻³⁹⁴ however, isolation and storage can only be done under neutral conditions. Dichlorotriazine dyes, for example, are best isolated in the presence of buffer systems. If such buffer mixtures are incorporated into the commercial product, the stability of a dyestuff formulation is greatly improved, since even traces of separated HCl can be responsible for an autocatalytic reaction which will inactivate even large batches in a very short time.



It follows from this that very different pH values are obtained when dye liquors, pad liquors, and print pastes are prepared with the same quantities of different dyestuffs. On the other hand, if the same quantities of different dyestuffs, even of dyestuffs with the same reactive group, are adjusted to a desired reactive pH, it will be found that the amount of alkali required for this adjustment can vary considerably (Fig. 45). This is due to the content of the individual chromophoric groups with respect to the content of dissociable groups. Hence a neutralization

³⁹² K. Wagner, *Textil-Praxis* **17**, 273 (1962).

³⁹³ I. D. Rattee, *Endeavour* **20**, 154 (1961).

³⁹⁴ E. Siegel, *3rd Intern. Farbensymp., Interlaken, 1967*, *Chimia* 1968 (Suppl.) p. 100.

reaction, in which part of the alkali used is consumed, is at first superimposed on the slow alkali consumption by hydrolysis. This effect is more marked, the lower the quantity of alkali employed. The fixation pH which is produced in dye and pad liquors and in print pastes will therefore depend on (1) the type and concentration of the alkali used; (2) the chemical structure and concentration of the dyestuff; and (3) the kind and quantity of buffer or salt employed (see Tables XI–XIII).

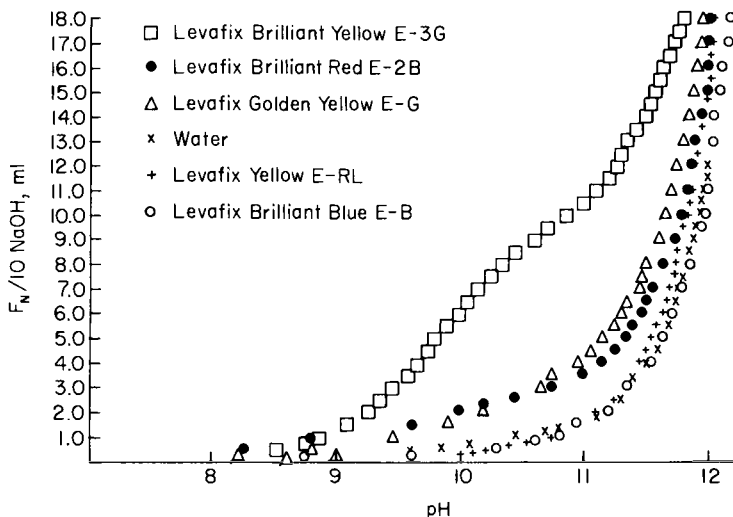


FIG. 45. Alkali consumption by dissociation of Levafix E dyestuffs when dissolved in alkaline dye and pad liquors. Titration curves with 0.1 *N* NaOH at 0°.

As a result of the different initial pH values of various dyestuff formulations, different dyestuffs in a formulation—even if they belong to the same range—are often subject to different conditions of hydrolysis and fixation. In order to get approximately the same conditions in a guiding recipe for all dyestuffs used, the quantities of alkali employed are added in sufficient excess, while alkali donors are usually employed as buffers. The most widely used chemicals are sodium bicarbonate, soda ash and its mixtures, potassium hydroxide, disodium phosphate, trisodium phosphate, metasilicate, and caustic soda and its mixtures.^{395–397} Dye liquors usually contain 50–80 g/liter of salt. The pH of

³⁹⁵ E. Ungermann, *Melliand Textilber.* **42**, 89 (1961).

³⁹⁶ H. Renziehausen, *Bayer Farben Rev.* No. 9, p. 24 (1964).

³⁹⁷ K. Greiner, *Z. Ges. Textil-Ind.* **66**, 949 (1964).

such solutions is considerably lower than that of alkali solutions of equal concentration which do not contain salt. Hence a high salt concentration will be indirectly responsible for a buffering of the dyestuff formulation.

Characteristic dye liquor pH values of reactive dyestuff solutions are shown in Table XII. However, while the dyestuff and the cellulose are

TABLE XI
PARTIAL HYDROLYSIS OF LEVAFIX BRILLIANT RED E-2B IN PAD
LIQUORS OF DIFFERENT DYESTUFF CONCENTRATION AT 25°^a

<i>Time (hr)</i>	<i>50 g/liter dyestuff 20 g/liter soda ash 100 g/liter urea</i>		<i>25 g/liter dyestuff 20 g/liter soda ash 100 g/liter urea</i>	
	<i>pH</i>	<i>Dichloro reactive dyestuff in percent of initial content</i>	<i>pH</i>	<i>Dichloro reactive dyestuff in percent of initial content</i>
0	10.70	100	10.77	100
1	10.66	98	10.74	95
2	10.64	97	10.72	92
4	10.62	95	10.70	89
6	10.60	91.8	10.65	84
22	10.55	90.3	10.61	79
24	10.37	74.2	10.40	59

^a Hildebrand.³⁹⁰

TABLE XII
pH VALUES OF DYE LIQUORS^a

<i>Additions^b</i>	<i>Soda ash (g/liter)</i>			
	1	5	10	20
Without additions	10.90	11.02	11.02	11.00
A	10.45	10.73	10.78	10.80
B	10.63	10.90	10.94	10.96
B, C	10.60	10.74	10.94	10.90
A, C	10.44	10.64	10.75	10.78

^a Hildebrand.³⁹⁰

^b A, common salt, 50 g/liter; B, Glauber's salt, 50 g/liter;
C, Levafix Brilliant Red E-2B, 1 g/liter.

TABLE XIII

pH VALUES OF COLD PAD-BATCH LIQUORS OF LEVAFIX BRILLIANT RED E-2B
AND SODA ASH SOLUTIONS OF DIFFERENT COMPOSITION^{a, b}

<i>Dyestuff</i>	<i>Dyestuff</i> <i>concentration</i> (g/liter)	<i>Soda ash</i> (g/liter)				
		2	5	10	20	50
Levafix	—	10.93	11.02	11.06	11.05	10.96
Brilliant Red	10	10.76	10.93	10.98	11.00	10.96
E-2B	25	10.50	10.74	10.87	10.92	10.92
	50	10.24	10.59	10.75	10.84	10.88

^a Hildebrand.³⁹⁰

^b Each solution also contained 100 g/liter of urea.

brought together before the soda ash is added, if dyeing is carried out in a long liquor, there can be long periods of intervening time between the alkalization of the dye solution and the dye-cellulose reaction in padding and printing processes. The time during which such a ready dyestuff formulation can be stored without a noticeable drop in reactivity has been called liquor stability (Figs. 46 and 47) or print paste stability (see Fig. 48). During this time the pH value of the dyestuff formulation drops, so that the reaction conditions change all the time, although this change is only slight. The reason for this drop in pH is probably the absorption of CO₂ from the air and the alkali consumption by hydrolysis

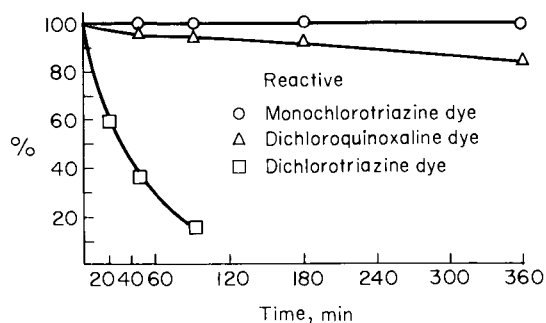


FIG. 46. Hydrolysis of reactive dyes of different reactivity in soda ash pad liquors; 10² mol/liter, 20 g/liter soda ash, 100 g/liter urea, 25°.

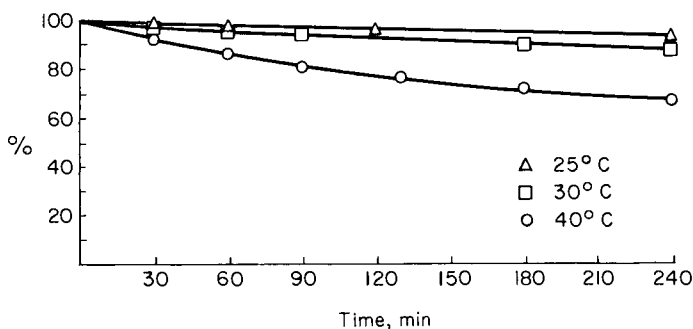


FIG. 47. Partial hydrolysis of Levafix Brilliant Red E-2B in pad liquors at different temperatures for 50 g/liter dyestuff, 20 g/liter soda ash, 100 g/liter urea.

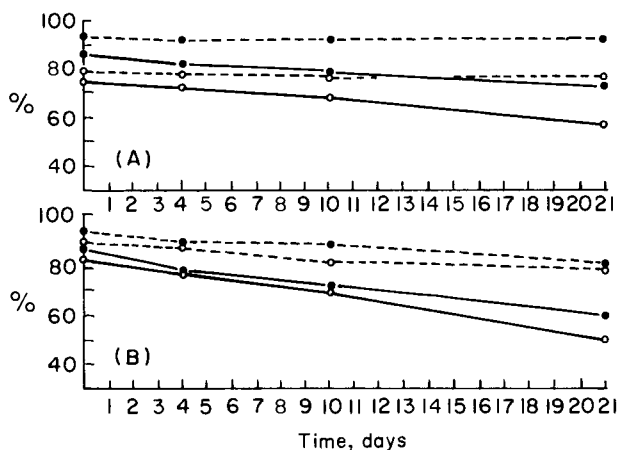
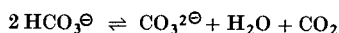


FIG. 48. Yield of fixation in percent of dyestuff used, of soda ash and bicarbonate print pastes for Levafix Golden Yellow E-G as a function of the age of the print paste in days for 1 and 8 minutes. Steaming: A, On viscose staple; B, on cotton for 40 g/kg dyestuff and 10 g/kg soda ash (—), or sodium bicarbonate (---).

of the reactive system. The alkali consumption corresponds to the neutralization of two acid equivalents for every hydrolyzed dye molecule, so that the pH drop through hydrolysis is relatively stronger than the pH drop during the fixation reaction. This will cause the reaction to slow down by itself. As a matter of fact, it will gradually come to a standstill at the low pH value which is eventually attained. This applies in particular to soda ash solutions which have only a low buffer capacity at pH 11. In contrast to pad liquors and print pastes which contain soda ash as alkali donor, the pH of sodium bicarbonate pad liquors and print

pastes will not decrease on standing, but will rather increase.^{398, 399} The pH of print pastes prepared with a soda ash-sodium bicarbonate mixture in a ratio of 1:1 (this also applies to pad liquors), on the other hand, remains largely constant, since this mixture corresponds to the equilibrium:



If a dyestuff formulation which contains sodium bicarbonate, and which is alkaline, is allowed to stand, bicarbonate is transformed into carbonate according to the state of equilibrium of $\text{HCO}_3^\ominus \rightleftharpoons \text{CO}_3^{2\ominus} + \text{H}^\oplus$, so that such formulations will show an increased rate of hydrolysis if they are allowed to stand for some time. On the other hand, when dyeing or printing with reactive formulations the pH of which has been reduced by a preceding partial hydrolysis, there is not only a drop in yield due to loss of dye, but also an increase in the optimum fixation time due to decrease in the rate of reaction. But the rate of reaction can again be stepped up by adding more alkali.

For dichloroquinoxaline and dichlorotriazine dyes, a higher yield can be obtained than would correspond to the residual content of dichloro reactive dye, if the reaction conditions of the second chlorine atom are attained. The reaction curves shown in Figs. 46 and 48 for the hydrolysis of the reactive chlorine of dichlorotriazine and dichloroquinoxaline dyes show the drop in yield which is due to the storage of dyestuff formulations before they are fixed. While a dichlorotriazine dye will hydrolyze at 25° in a soda-alkaline solution in 2 hours down to a residual reactivity of 10%, there is still 93% left of a dichloroquinoxaline dye with the same chromophoric system under the same conditions. A monochlorotriazine dye will show practically no loss due to hydrolysis even after this period. For this reason, metering devices have been developed for the highly reactive dyes which enable us to synchronize the preparation of the alkaline pad liquor with the consumption during the padding process, so that alkali and dye are united only when the actual fixation process sets in.⁴⁰⁰⁻⁴⁰² Metering devices are also used if dyes of medium reactivity are applied with relatively strong alkalis to accelerate the rate

³⁹⁸ K. Bühler, D. Hildebrand, and R. Schwaebel, *Bayer Farben Rev.* No. 13, p. 1 (1967).

³⁹⁹ D. Hildebrand and R. Schwaebel, *Textil-Praxis* **22**, 796 (1967).

⁴⁰⁰ H. U. von der Eltz and W. Hacker, *Chemiefasern* **11**, 404 (1961).

⁴⁰¹ H. U. von der Eltz, *Melliand Textilber.* **42**, 673 (1961).

⁴⁰² W. J. Marshall and I. Seltzer, *Z. Ges. Textil-Ind.* **64**, 397 (1962).

of reaction, these alkalis being stronger than the stability would warrant under optimum conditions.⁴⁰³

In analogy with the acceleration of reaction by temperature increase, it is always necessary to consider the reactivity when the usual hot dissolution of reactive dyestuffs is carried out (which is necessary to ensure quick working). To prevent slow cooling down, urea (which is usually employed as a solvent and fixation auxiliary) is added to the dyestuff powder on which hot water has been poured. The negative dissolution heat of urea is responsible for rapid cooling down of the solution. Alkali is added after the solution has cooled down to dyeing temperature. If hot dissolving is carried out in water with an alkaline reaction, hydrolysis can occur in highly reactive dyes. The same can also happen if reactive dyes are used together with alkaline disperse dyes in the continuous dyeing of polyester/cotton fabrics. Since only small quantities of urea are added to such pad liquors, the dissolving temperature can also be important in this case if we use highly reactive dyes. Since a high rate of diffusion is necessary to carry out the dyeing process, only such dyes are usually selected which are easily soluble even at ambient temperature.⁴⁰⁴ If we compare the rate of hydrolysis of a reactive dye in a pad liquor with its rate of hydrolysis in a print paste of the same initial pH, we see that the hydrolysis in the print paste takes place at a much slower rate than in a nonviscous, less concentrated pad liquor. Hence the hydrolysis of a reactive dye depends on the viscosity of the solution. This can be due to a change of the free path of the reacting particles. The fact that hydrolysis depends on the concentration is also expressed by an increase in the pad liquor stability in highly concentrated pad liquors, especially in strongly associating dyes.⁴⁰⁵⁻⁴⁰⁷

2. Exhaustion Methods

a. Long Liquor. Dyeing in a long liquor is usually done in two stages, namely, the physical adsorption process from the salt-containing liquor due to substantivity, and the reaction with the fiber promoted by alkali addition after the state of adsorption equilibrium has been reached. The first stage will usually take 30 minutes, while 90 minutes are allowed for the second stage. The position of the adsorption level which has been reached in the first stage depends on the substantivity of the dye. The

⁴⁰³ H. U. von der Eltz, *Z. Ges. Textil-Ind.* **66**, 749 (1964).

⁴⁰⁴ R. Schwaebel, *Intern. Dyer, Textile Printer, Bleacher Finisher* **138**, 337 (1967).

⁴⁰⁵ P. Rys and H. Zollinger, *Helv. Chim. Acta* **49**, 749 (1966).

⁴⁰⁶ A. Datyner, P. Rys, and H. Zollinger, *Helv. Chim. Acta* **49**, 756 (1966).

⁴⁰⁷ P. Rys, *Textilberedlung* **2**, 95 (1967).

performance of the different dyestuff ranges is different, but characteristic differences can also be observed within one and the same range.⁴⁰⁸⁻⁴¹¹ Figure 24 gives an example of a highly substantive dye by showing the adsorption and fixation process of Cibacron Navy Blue RE according to the two-stage method. Apart from this method, which is known as the *normal dyeing method*, another method has been developed which uses only one stage (*all-in method*), for which an example has been shown in Fig. 25 using Cibacron Navy Blue. Salt, alkali, and dyestuff are set at the same time. Dyeing is started at a low temperature, and level adsorption is achieved by gradual heating to fixation temperature. Technically it is quite easy to conduct a dyeing in this manner, but there are less chances of monitoring the process in such a way that the most favorable results are obtained.

Better control possibilities are given by the exhaustion process, which is known as the *migration dyeing method*. In this method, the dyestuff is used in the same way as in the normal dyeing method, but the salt additions are made in installments before the alkali is added. This enables a very good control of the adsorption process even in the case of substantive dyes, closely woven goods, and short liquors. Soda ash is mainly used as alkali, independent of the reactivity. Only in exceptional cases, e.g., at elevated temperatures, is sodium bicarbonate used to get a better penetration. In types with lower reactivity, however, it is also possible to use stronger alkalis such as caustic soda, trisodium phosphate, or a mixture of caustic soda and soda ash if we have short liquors. Hence the adjustment of the rate of reaction to the required reaction time of 2 hours is done with the help of the dyeing temperature for the highly reactive dichlorotriazine dyestuffs (Procion M) at 20–30°, for the dichloroquinoxaline-6-carbamide dyestuffs (Levafix E) at 40°, for the vinyl sulfone dyestuffs (Remazol) at 60°, for the monochlorotriazine dyestuffs (Procion H, Cibacron) at 60–70°, and for the trichloropyrimidine dyestuffs (Drimaren, Reacton) at 80°. Dyes with a satisfactory dyeing rate at 20–40° are known as cold-dyers, while dyes which are dyed at 60–80° are called warm-dyers. The substantivity drops as the temperature increases, and this is compensated for by increasing the salt addition (Fig. 49). The salt content of the liquor is approx. 50 g/liter of NaCl or NaSO₄ for cold-dyers, 50–100 g/liter for warm-dyers, in each

⁴⁰⁸ H. U. von der Eltz and F. Osterloh, *Melliand Textilber.* **40**, 1443 (1959).

⁴⁰⁹ E. L. Caswell, *Am. Dyestuff Repr.* **48**, 10 and 39 (1960).

⁴¹⁰ J. Renggli, *Ciba Rundschau* **13**, 43 (1960).

⁴¹¹ T. Flanagan, *Am. Dyestuff Repr.* **49**, 716 (1960); *Man-Made Textiles* **37**, 57 and 67 (1960).

case for short liquors up to 200 g/liter. The liquor ratio depends on the goods to be dyed and on the dyeing apparatus used. This ratio is between 5:1 and 50:1. Since the liquor ratio is important in determining the position of the adsorption equilibrium, the fixation yield will decrease, the larger the liquor ratio becomes. It goes without saying that the influence of the liquor ratio on the fixation yield will be more pronounced, the lower the substantivity of the dye. Hence this influence is relatively low in most cold-dyeing brands. The cold-dyes reach their maximum yield values (between 70 % and 90%) in the exhaustion process.

In closely woven goods, especially viscose staple, a higher dyeing temperature is preferred in order to sidestep the maximum swelling of the fiber. The higher reactivity of the cold-dyers is compensated in this

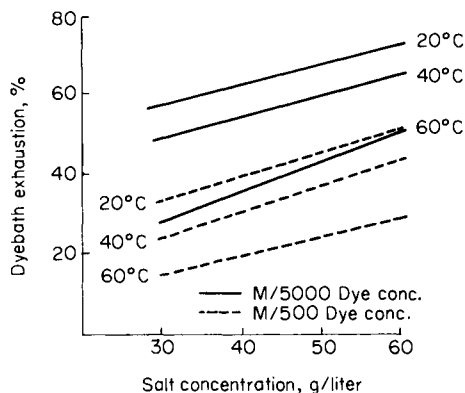


FIG. 49. Salt sensitivity of a typical cold-dyeing Procion dye at different temperatures—Procion Brilliant Red M-5BS (CI Reactive Red 2).⁴¹⁹

case by the use of sodium bicarbonate as alkali.⁴¹² Although reactive dyes do not present any serious problems in respect to levelness, it can be difficult in the case of certain qualities to get well-penetrated level dyeings without running creases. Such faults are more likely to occur in three-color mixtures, especially in blue and gray shades. Typical cases which require special attention are jig dyeings of mercerized cotton in highly twisted fabrics and dyeings on the winch beck of cotton interlock goods, as well as dyeings of wound packages of highly twisted cotton yarns or closely packed bobbins.^{414, 415} Extensive investigations have been carried out and published by dyestuff manufacturers on the dyeing

⁴¹² P. J. Dolby, *Am. Dyestuff Repr.* **55**, 422 (1966).

⁴¹³ L. G. Smirnova and T. S. Odincova, *Tekstil'n. Prom.* **23**, No. 10, p. 28 (1963).

⁴¹⁴ J. Annicq, *Melliand Textilber.* **39**, 414 (1958).

⁴¹⁵ I. J. Kalontarov and M. V. Kozlova, *Tekstil'n. Prom.* **24**, 62 (1964).

of cellulose, made up in very different ways and of a wide variety of fiber qualities, with reactive dyes, with full exploitation of the various technical possibilities. In this connection, we may draw attention to the investigations carried out by Ungermann,⁴¹⁶ Sumner and Vickerstaff,⁴¹⁷ Fowler,⁴¹⁸ Rattee,⁴¹⁹ Baur,⁴²⁰ Greiner,⁴²¹ Marshall,⁴²² Beckmann,⁴²³ Haelters,^{424, 425} Bell,⁴²⁶ and Schulze-Braucks.⁴²⁷ Table XIV compares the conditions prevailing with different methods used for the dyeing of highly reactive and less reactive dyes, using dichlorotriazine and monochlorotriazine dyes in jig dyeing. Further investigations on processes for the dyeing of Procion, Cibacron, Remazol, Levafix, Reacton, and Drimaren dyestuffs have been published by Fröhlich⁴²⁸ and by Reuben and Hall.⁴²⁹

TABLE XIV

COMPARISON OF THE DYEING CONDITIONS IN JIG DYEING WITH PROCION M AND PROCION H DYE STUFFS

	<i>Procion M</i> dyestuffs	<i>Procion H</i> dyestuffs
Temperature	30–60°	60–90°
Alkali	Soda ash or soda ash/bicarbonate	Caustic soda
Electrolyte concentration	30–60 g/liter	40–100 g/liter
Dyeing time without soaping	approx. 1 hour	approx. 1 hour

Different methods have been described to improve the levelness of exhaustion dyeings or to ensure even dyeings under special working conditions. For example, for dyes which have a tendency to produce

⁴¹⁶ E. Ungermann, *Melliand Textilber.* **42**, 89 (1961).

⁴¹⁷ H. H. Sumner and T. Vickerstaff, *Melliand Textilber.* **42**, 1161 (1961).

⁴¹⁸ J. A. Fowler, *Melliand Textilber.* **43**, 597 (1962).

⁴¹⁹ I. D. Rattee, *Am. Dyestuff Repr.* **52**, 320 (1963); *Melliand Textilber.* **45**, 782 (1964).

⁴²⁰ P. Baur, *Bayer Farben Rev.* No. 6, p. 27 (1963).

⁴²¹ K. Greiner and P. Baur, "Deutscher Färberkalender," p. 136. Franz Eder Verlag, Munich, 1964.

⁴²² J. A. Fowler, and W. J. Marshall, *SVF Fachorgan Textilveredlung* **20**, 243 (1965).

⁴²³ W. Beckmann, "Deutscher Färberkalender," p. 131. Franz Eder Verlag, Munich, 1965.

⁴²⁴ M. Haelters, *Melliand Textilber.* **48**, 191 and 314 (1967).

⁴²⁵ M. Haelters, *Ciba Rundschau* No. 1, 56 (1966).

⁴²⁶ P. F. Bell, *Textile Inst. Ind.* **5**, 13 (1967).

⁴²⁷ M. Schulze-Braucks, *Z. Ges. Textil-Ind.* **69**, 889 (1967).

⁴²⁸ H. G. Fröhlich, *Z. Ges. Textil-Ind.* **63**, 47 (1961).

⁴²⁹ B. J. Reuben and D. M. Hall, *Am. Dyestuff Repr.* **51**, 811 (1962).

unevenness if they are dyed in a neutral medium, the liquor should be adjusted to weak acidity at the beginning of the dyeing process, if necessary by adding NaH_2PO_4 as buffer and finally an acid-binding agent.⁴³⁰ In another method, the goods are treated first of all with pure water only, and the required quantity of dyestuff and salt is added as a concentrated solution after this preliminary treatment.⁴³¹ Dyeing on perforated beams has been patented as a method which is particularly suitable for reactive dyes.⁴³² According to Elzer, Greiner, and Beckmann, loose stock can also be dyed by allowing it to rest in a liquor which does not circulate.⁴³³ We can say that this method marks the transition to the cold pad-batch method.

b. Short Liquor: Pad-Batch and Pad-Roll Methods. The good diffusion capacity of the reactive dyes, as well as the possibility of obtaining fast dyeings even at low temperatures, led to an important development for the application of the reactive dyes on cellulose fibers: dyeing by the pad-batch and pad-roll processes. In these methods, usually employed for cellulose fibers, piece goods are impregnated with the dye liquor and

TABLE XV

COLD PAD-BATCH METHODS USING ALKALI: COMPARISON BETWEEN METHODS OF SHORT AND LONG REACTION TIMES^a

<i>Short reaction time</i>	<i>Long reaction time</i>
<i>Easier</i>	<i>Better</i>
Control of temperature	Coverage in special cases, e.g., in certain viscose staple goods
Sample matching	and a few mercerized cotton poplins
Levelness	
Color formulation	
<i>Greater</i>	<i>Better</i>
Latitude in reaction time	Fixation on viscose (some dyes)
<i>Better</i>	<i>Mixer</i>
Dye fixation on cotton	Not always required
<i>Less</i>	<i>Necessary</i>
Space required	For dyeings based on turquoise blue
Reaction equipment	

^a Reference 461.

⁴³⁰ ICI, *BeP* 683,681 (5.7.1966); *FP* 1,486,865 (15.7.1966).

⁴³¹ S, *BeP* 699,618 (27.1.1961).

⁴³² S, *BeP* 613,824 (12.2.1962).

⁴³³ FBy, *BeP* 655,369 (6.11.1964).

are then allowed to react after they have been batched up. The batch rotates slowly during this reaction time until the dye has been completely fixed (Table XV). Although wool can in principle also be dyed with reactive dyes, these methods have not become important for woollen goods on account of the greater diffusion resistance of the wool and also because as a rule large yardages are not handled by wool dyers. From the viewpoint of dyeing kinetics, these padding processes are really exhaustion methods with extremely short liquor ratios. But the reduction of the liquor ratio makes fewer demands on the substantivity of the dye, so that we can also use dyes of low substantivity (see Table XVI).

The cold pad-batch methods are more important than the pad-roll methods, since they require only one padder and can be carried out at room temperature.⁴³⁴⁻⁴⁵⁷ Special heat chambers have been developed for the pad-roll methods.⁴⁵⁸ The dependence of the dye-fiber reaction on the pH enables us to cut down the reaction time of dyes of low reactivity by using strong alkalis in the pad liquor. Suitable alkalis are soda ash, trisodium phosphate, metasilicate, caustic soda, and mixtures thereof. The reaction time can be adjusted to any required value in the case of highly reactive dyes by a suitable choice of the alkali. This reaction time amounts to just a few hours for dichlorotriazine and trichloroquinoxaline

⁴³⁴ H. U. von der Eltz, *Z. Ges. Textil-Ind.* **62**, 325 (1960).

⁴³⁵ M. Peter and P. Ulrich, *Ciba Rundschau* No. 152, p. 39 (1960).

⁴³⁶ H. U. von der Eltz and K. Wagner, *SVF Fachorgan Textilveredlung* **16**, 320 (1961).

⁴³⁷ K. A. Lunn, *Dyer* **125**, 341 (1961).

⁴³⁸ M. Capponi, *SVF Fachorgan Textilveredlung* **16**, 229 (1961).

⁴³⁹ H. U. von der Eltz and W. Hacker, *Chemiefasern* **11**, 404 (1961).

⁴⁴⁰ P. Ulrich, *SVF Fachorgan Textilveredlung* **16**, 211 (1961).

⁴⁴¹ R. Bugmann, *Prakt. Chem.* **12**, 288 (1961).

⁴⁴² J. F. Mawson and I. D. Rattee, *Dyer* **127**, 103 (1962).

⁴⁴³ J. F. Mawson and I. D. Rattee, *J. Soc. Dyers Colourists* **78**, 161 (1962).

⁴⁴⁴ H. A. Piggot and T. Vickerstaff, *Dyer* **128**, 362 (1962).

⁴⁴⁵ J. A. Fowler, W. J. Marshall, and I. Seltzer, *Am. Dyestuff Repr.* **51**, 917 (1962).

⁴⁴⁶ W. J. Marshall, *Dyer* **127**, 910 (1962).

⁴⁴⁷ W. J. Marshall and I. Seltzer, *Z. Ges. Textil-Ind.* **64**, 397 (1962).

⁴⁴⁸ K. Wagner, *Textil-Praxis* **17**, 273 and 354 (1962).

⁴⁴⁹ E. Ungermann, *Z. Ges. Textil-Ind.* **64**, 403 (1962).

⁴⁵⁰ M. F. Mosnier, *Teintex* **27**, 607 (1962).

⁴⁵¹ J. A. Fowler, *Tex.* **22**, 944 (1963).

⁴⁵² K. Greiner, *Z. Ges. Textil-Ind.* **66**, 949 (1964).

⁴⁵³ K. Greiner, *Bayer Farben Rev.* No. 8, p. 1 (1964).

⁴⁵⁴ H. Renziehausen, *Bayer Farben Rev.* No. 9, p. 24 (1964).

⁴⁵⁵ H. U. von der Eltz, *Z. Ges. Textil-Ind.* **66**, 749 (1964).

⁴⁵⁶ P. Perrin, *Ciba Rundschau* No. 3, p. 53 (1967).

⁴⁵⁷ W. J. Marshall, *Textilveredlung* **2**, 228 (1967).

⁴⁵⁸ J. Renggli and P. Ulrich, *Melliand Textilber.* **41**, 1537 (1960).

dyes, depending on the alkali, while chloropyrimidine dyes require 1–2 days for complete fixation. To prevent premature hydrolysis of the dye during padding, it may be necessary to use a mixing machine. The pad liquor will usually contain 50–150 g/liter of urea as an agent to promote dissolution and fixation of the dyes, as well as a rapid wetting agent besides the dye. A good preliminary treatment of the goods has a decisive influence on the dyeing. It is also important—from the viewpoint of technical application—that the unfixed portion of the dye can be washed off easily. The cold pad-batch method will generally give the highest yields since it takes place at temperatures and concentrations

TABLE XVI
COMPARISON OF DYES OF DIFFERENT SUBSTANTIVITY IN DIFFERENT
DYEING METHODS: 1% DYEING ON UNMERCERIZED COTTON^a

<i>Method</i>	<i>Amount of dye fixed (%)</i>	
	<i>Procion Brilliant Yellow H-3GS (medium to high affinity)</i>	<i>Procion Brilliant Yellow H-4GS (low affinity)</i>
Noncontinuous		
(Liquor ratio 30:1)	42	8
(Liquor ratio 5:1)	70	23
Cold pad(alkali)-batch	75	58
Pad(alkali)-dry-cure	77	75
Pad(alkali)dry-steam	78	67

^a Reference 461.

which are most favorable for the reaction. Apart from the single-phase methods in which the dye and the alkali are used simultaneously, the two-phase methods are also important, since they permit the use of stronger alkalies to get shorter fixation times in the pad liquor without hydrolysis. Fixation is then achieved by batching the goods at room temperature or by submitting them to a thermoshock treatment. Table XVII reviews the development liquors which have been formulated for Remazol dyestuffs.

An essential prerequisite for the suitability of a reactive dye for the dyeing of cellulose fibers by the cold pad-batch process is that the substantivity of the dye must enable exhaustion from the pad liquor. A special problem is the production of dyeings without tailing or ending

TABLE XVII
COMPOSITION OF THE TWO-PHASE LIQUORS^a

		<i>cm</i> ³ <i>NaOH</i> 38° Bé	<i>g</i> <i>NaCl</i>	<i>g</i> <i>Na</i> ₂ <i>SO</i> ₄ , <i>anhydrous</i>	<i>g</i> <i>Na</i> ₂ <i>CO</i> ₃ , <i>anhydrous</i>	<i>g</i> <i>K</i> ₂ <i>CO</i> ₃	<i>g</i> <i>KCl</i>	<i>cm</i> ³ <i>waterglass</i> 47° Bé
Two-phase steaming	1	30	100	—	150	50	—	—
	2	30	180	—	150	50	—	—
	3a	30	150	—	180	—	40	—
	4	30	180	—	100	100	—	—
	5	—	—	—	—	—	—	pure
Flash ageing	6	100	100	—	150	50	—	—
	7	100	180	—	150	50	—	—
Infrared fixation	8	100	100	—	150	50	—	—
Cold batch (reaction)	9	100	—	180	150	50	—	—
	10	100	180	—	150	50	—	—
	11	100	—	180	150	—	40	—
	12	—	—	—	—	—	—	pure
Wet fixation	13	70	100	—	150	50	—	—
	14	70	66	—	180	—	40	—
	15	70	200	—	—	50	—	20

^a Reference 462.

and without any change of shade from side to side and side to center.^{459,460} Initial difficulties have, however, been overcome by the construction of modern padding mangles, so that we can say that the cold pad-batch method is the safest dyeing method for reactive dyes.^{461,462}

3. Continuous Dyeing and Printing Methods

If we disregard the fact that prints can also be fixed by batch (reaction) methods, we can say that the continuous dyeing and printing processes differ from the exhaustion methods kinetically first of all by the much higher rate of fixation. The dye is transported from the liquor to the reactive sites of the fiber not by an exhaustion process which is adjusted with the help of equilibria, but by vaporization of the liquid phase. Undesirable substantivity will disturb the padding process and can lead

⁴⁵⁹ M. Capponi, *SVF Fachorgan Textilveredlung* **16**, 341 (1961).

⁴⁶⁰ M. Capponi, *Am. Dyestuff Repr.* **50**, 619 (1961).

⁴⁶¹ M. R. Fox, *Z. Ges. Textil-Ind.* **70**, 817 (1968).

⁴⁶² H. U. von der Eltz, *Z. Ges. Textil-Ind.* **70**, 824 (1968).

to tailing.⁴⁶¹⁻⁴⁶⁷ On the other hand, if the substantivity of the dye is insufficient, the dye will migrate when the padded goods are dried under inhomogeneous drying conditions. This migration will produce two-sidedness. Hence the operation of continuous dyeing processes makes it necessary to pay close attention to the immersion time, the liquor pick-up, the wetability of the goods, and the viscosity of the pad liquor. Dyes of low substantivity and high diffusion capacity are therefore most suitable for continuous dyeing and printing.^{468, 469} Fixation is done either by an alkali shock method (wet development by alkali shock, i.e., a shock fixation method in a concentrated alkaline electrolyte bath on an open-width machine) or by a thermoshock treatment, or by a combination of treatment with alkali and heat.^{470, 471} Dyes which can be fixed in an acid medium are treated with a combination of acid catalyst and heat. Depending on the simultaneous or separate use of alkali and dye, these methods are subdivided into one- and two-bath or one- and two-step processes.⁴⁷²⁻⁴⁷⁴ Special mention must be made of the one-bath pad-steam process, the two-bath pad-steam method, the one-bath pad-cure, and the two-bath pad-alkali shock methods. One-bath and two-bath methods have been developed for the printing and dyeing of reactive dyes on polyester/cellulose fabrics.⁴⁷⁵⁻⁴⁷⁸

In the one-bath method, the dyestuff is applied to the fabric together with the alkali and then fixed by steaming or curing at 100–102°. In the two-bath methods, the dyestuff is only padded with urea, given an intermediate drying treatment, and fixed after the goods have passed through an alkali bath, the fixation being done by steaming or curing. To prevent bleeding in the chemical bath, a large quantity of salt is added to the bath. Fixation can also be done by alkali shock without steaming

⁴⁶³ M. Capponi and A. Barthold, *Textil-Praxis* **17**, 155 and 255 (1962).

⁴⁶⁴ M. Capponi, *Melliand Textilber.* **44**, 720 (1963).

⁴⁶⁵ H. H. Sumner and C. D. Weston, *Am. Dyestuff Repr.* **52**, 442 (1963).

⁴⁶⁶ M. Capponi and R. Senn, *Chimia (Aarau)* **19**, 271 (1965).

⁴⁶⁷ S, *SZAS* 2,335/65 (19.2.1965).

⁴⁶⁸ K. Neufang, *Textil-Praxis* **21**, 675 (1966).

⁴⁶⁹ M. Capponi and R. C. Senn, *J. Soc. Dyers Colourists* **82**, 8 (1966).

⁴⁷⁰ P. Eltzer, *Bayer Farben Rev.* No. 14, p. 59 (1968).

⁴⁷¹ M.-O. Hueckel, *Am. Dyestuff Repr.* **57**, 479 (1968).

⁴⁷² C. D. Weston, *Hexagon Digest* **25**, 3 (1957).

⁴⁷³ R. A. Brindley and I. D. Rattee, *Melliand Textilber.* **39**, 1017 (1958).

⁴⁷⁴ G. Dierkes, *Z. Ges. Textil-Ind.* **64**, 496 (1962).

⁴⁷⁵ P. Ulrich and H. Stern, *Am. Dyestuff Repr.* **53**, 697 (1964).

⁴⁷⁶ *Ciba Rundschau* No. 2, p. 43 (1965).

⁴⁷⁷ H. U. von der Eltz, *Textil-Praxis* **21**, 523 (1966).

⁴⁷⁸ H. U. von der Eltz, *Melliand Textilber.* **48**, 1433 (1967).

or curing if the temperature of the chemical bath is increased.⁴⁷⁹ For example, neutral prints of Procion Brilliant Red M-2BS or Procion Rubine M-BS are fixed after intermediate drying, in a bath consisting of 20 parts soda ash, 0.6 parts caustic soda, 10 parts sodium sulfate, and 100 parts water, fixation time 15 seconds at 30°. ⁴⁸⁰ For dyes of low reactivity, the fixation temperature is preferably increased up to 95°, depending on the reactivity. After impregnation of the dried print or dyeing with an alkaline developing liquor, fixation can also be done by means of an air passage.⁴⁸¹ According to Kögel and others, the acid-binding agent can also be sprayed.⁴⁸² To improve the stability of the pad liquor or print paste, alkali donors have been developed which reveal their acid-binding function only when they are heated to temperatures above 80°. At this temperature they produce alkali or alkaline earth carbonates (while separating volatile by-products or other by-products which can be easily washed off).⁴⁸³ The alkali required for fixation can also be brought on the fiber by preliminary impregnation.⁴⁸⁴

In the thermoshock method, the rate of fixation depends not only on the reactivity of the dye and on the alkali used, but also on the fixation temperature and on the time required to heat the fabric (Fig. 50) (see also Fig. 31).⁴⁸⁵ Figure 51 gives a schematic comparison of the relative fixation requirements of different fixation equipment for the same pad dyeing with soda ash as alkali.⁴⁸⁶ Thermoshock can be administered by steaming with saturated steam,⁴⁸⁷ superheated steam under normal pressure,⁴⁸⁸⁻⁴⁹¹ and also with pressurized steam.⁴⁹² Other possible methods of thermoshock treatment are with hot air,⁴⁹³ contact

⁴⁷⁹ W. Gahlert, *Textil-Praxis* **23**, 754 (1968).

⁴⁸⁰ S, *SZAS* 14,667/62 (13.12.1962).

⁴⁸¹ FH, *BeP* 679,670 (18.4.1966).

⁴⁸² CIBA, *SZAS* 365/62 (12.1.1962); *BeP* 627,033 (12.1.1962).

⁴⁸³ FH, *FP* 1,295,912 (16.7.1960/17.5.1962).

⁴⁸⁴ ICI, *DAS* 1,252,622 (18.4.1957); *BP* 819,585 (18.4.1956); compare *BeP* 556,709; (18.4.1956); *BP* 819,585 (18.4.1956).

⁴⁸⁵ P. Ulrich and H. Niederer, *SVF Fachorgan Textilveredlung* **20**, 712 (1965).

⁴⁸⁶ D. Hildebrand, *Melliand Textilber.* **49**, 67 (1968).

⁴⁸⁷ I. D. Rattee and I. Seltzer, in "Procion Dyestuffs in Textile Dyeing," pp. 194-195. I.C.I., Manchester, 1962.

⁴⁸⁸ ICI, *BP* 32,707/65 (30.7.1965); *FP* 1,488,066 (29.7.1966); *DP* 6,601,761—C17/66.

⁴⁸⁹ A. P. Lockett, *J. Soc. Dyers Colourists* **83**, 213 (1967).

⁴⁹⁰ D. Hildebrand and R. Kuth, *Textil Praxis* **22**, 346 (1967).

⁴⁹¹ D. Hildebrand and R. Kuth, *Textilveredlung* **2**, 890 (1967).

⁴⁹² D. Hildebrand and R. Kuth, *Textilveredlung* **3**, 392 (1968).

⁴⁹³ I. D. Rattee and I. Seltzer, in "Procion Dyestuffs in Textile Dyeing," p. 184. I.C.I., Manchester, 1962.

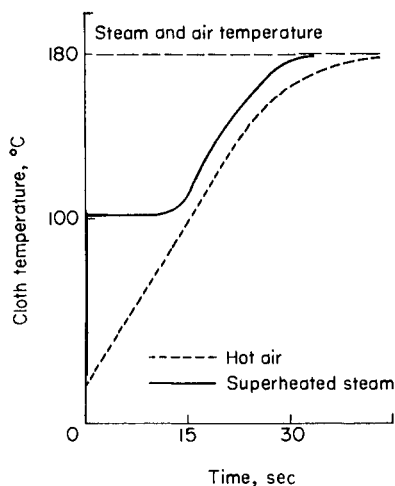


FIG. 50. Rate of heating of textile substrate in hot air (---) and in superheated steam (—).⁴⁸⁹

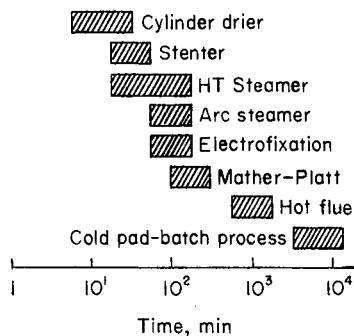


FIG. 51. Time required for the fixation of Levafix P dyes on different fixation equipment, compared with the cold pad-batch process.⁴⁸⁶ Example: 40 g/liter Levafix Brilliant Red P-3B, mercerized cotton cloth.

heat^{494, 495} by means of hot cylinders, a fluid bed,⁴⁹⁶ infrared radiator,^{497, 498} high-frequency alternating fields,⁴⁹⁹ or heated inert solvents, e.g., hydrocarbons.⁵⁰⁰ A combination of infrared radiation and steam

⁴⁹⁴ I. D. Rattee and I. Seltzer, in "Procion Dyestuffs in Textile Dyeing," p. 190. I.C.I., Manchester, 1962.

⁴⁹⁵ DuP, USP 272,221 (11.4.1963); FP 1,388,486 (28.12.1964).

⁴⁹⁶ F. G. Andas, *Dyer* **125**, 937 (1961).

⁴⁹⁷ P. Ulrich and H. Schaub, *SVF Fachorgan Textilveredlung* **16**, 162, 314 and 586 (1961).

⁴⁹⁸ Traitements Chimiques des Textiles, FP 1,343,752 (12.10.1962).

⁴⁹⁹ S, SZAS 4,671/61 (20.1.1961).

⁵⁰⁰ ICI, FP 1,495,705 (30.9.1966); BP 41,614/65 (30.9.1965); BeP 687,651 (30.9.1967).

is known as electrofixation.⁵⁰¹ For highly reactive dyes, the fixation time in modern continuous equipment is less than 1 minute, and comes down to 15 seconds in the two-bath pad-steam process with caustic soda as alkali. The times are even shorter if the alkali shock method is used. More time is required in dry heat fixation (curing). In one-bath fixation of highly reactive dyes, 25 seconds are required.

TABLE XVIII

COMPARISON OF THE APPLICATION CONDITIONS OF PROCION M AND PROCION H DYESTUFFS IN CONTINUOUS DYEING

<i>Method</i>	<i>Procion M dyestuffs</i>	<i>Procion H dyestuffs</i>
Pad(alkali)-dry	Fixed in 1-2 min by drying. Urea is added in deep shades.	Not suitable if the goods are not cured for 3-5 min at 110-125°. Urea addition in all depths of shade.
Pad(alkali)-dry-steam	Fixation by drying and subsequent steaming for 15 sec (not required in the case of pale shades).	Fixation by drying and subsequent steaming for 3-10 min.
Pad-dry-pad (caustic soda)- steam	Fixation by steaming for 15-60 sec.	Fixation by steaming for 60-75 sec.

In the one-phase fixation of pad dyeings and prints for which soda ash and sodium bicarbonate are often used to ensure stability of the pad liquors and print pastes, a fixation time of 8-12 minutes is required for dyes of low reactivity and if conventional agers are used. Highly reactive dyes can be fixed in 1-3 minutes under these conditions (Table XVIII). In superheated steam, fixation times are less than 1 minute (see Fig. 52). The speed of the goods of a continuous process always depends on the slowest step, which may be drying, fixation, or rinsing (see Fig. 53).

The manufacturers of dyestuffs have published extensive papers on the most favorable continuous dyeing and printing methods for the different ranges of reactive dyes, e.g., Procion,^{489, 502-506} Remazol,⁵⁰⁷⁻⁵¹⁹

⁵⁰¹ H. J. Korndörfer, *Melliand Textilber.* **44**, 1006 (1963).

⁵⁰² S. W. Milne in "Procion Dyestuffs in Textile Printing," p. 53. I.C.I., Manchester, 1962.

⁵⁰³ ICI, *SVF Fachorgan Textilveredlung* **12**, 518 (1957).

⁵⁰⁴ F. R. Alsberg, *Deut. Textiltech.* **12**, 369 (1962).

⁵⁰⁵ ICI/Artos, *Z. Ges. Textil-Ind.* **68**, 366 (1966).

Cibacron,⁵²⁰⁻⁵³⁰ Levafix,⁵³¹⁻⁵³⁶ Reacton,⁵³⁷⁻⁵⁴⁰ Drimaren,^{463,541-543} and Primazin,⁵⁴⁴⁻⁵⁴⁸ as well as Bafixan dyestuffs.⁵⁴⁹

Usually, the dyestuffs which are suitable for continuous dyeing and printing are water-soluble. Application by padding or printing will, however, enable the general use of water-insoluble disperse reactive

- ⁵⁰⁶ ICI, *Intern. Dyer, Textile Printer, Bleacher Finisher* **138**, 122 (1967).
- ⁵⁰⁷ H. Zimmermann, *Melliand Textilber.* **40**, 539 (1959).
- ⁵⁰⁸ H. Zimmermann, *Melliand Textilber.* **41**, 1557 (1960).
- ⁵⁰⁹ G. D. Zimmermann, *SVF Fachorgan Textilveredlung* **16**, 757 (1961).
- ⁵¹⁰ E. Ungermann, *Melliand Textilber.* **42**, 89 (1961).
- ⁵¹¹ K. Wagner, *Z. Ges. Textil-Ind.* **63**, 278 (1961).
- ⁵¹² H. U. von der Eltz, *Melliand Textilber.* **42**, 672 (1961).
- ⁵¹³ H. Zimmermann, *Dyer* **127**, 578 (1962).
- ⁵¹⁴ G. Dillman, *Melliand Textilber.* **43**, 265 (1962).
- ⁵¹⁵ W. Kretzschmar, *Melliand Textilber.* **45**, 1022 (1964).
- ⁵¹⁶ W. Gahlert, *Textil-Praxis* **20**, 594 (1965).
- ⁵¹⁷ E. Fees, *Melliand Textilber.* **47**, 1162 and 1307 (1966).
- ⁵¹⁸ H. Zimmermann, *Melliand Textilber.* **48**, 552 (1967).
- ⁵¹⁹ E. Fees, *Textil-Praxis* **23**, 335, 387, and 469 (1968).
- ⁵²⁰ H. Werdenberg, *Z. Ges. Textil-Ind.* **60**, 335 (1958).
- ⁵²¹ H. Werdenberg, *Melliand Textilber.* **40**, 1451 (1959).
- ⁵²² *Ciba Rundschau* **13**, 39 (1960).
- ⁵²³ G. Kögel, *Ciba Rundschau* **13**, 45 (1960).
- ⁵²⁴ G. Kögel, *Ciba Rundschau* No. 4, p. 40 (1961).
- ⁵²⁵ A. Schaub, *SVF Fachorgan Textilveredlung* **16**, 56 (1961).
- ⁵²⁶ W. Badertscher, *Melliand Textilber.* **44**, 829 (1963).
- ⁵²⁷ W. Badertscher, *Ciba Rundschau* No. 1, p. 44 (1963).
- ⁵²⁸ P. Ulrich and H. Stern, *Ciba Rundschau* No. 2, p. 39 (1964).
- ⁵²⁹ W. Badertscher, *Ciba Rundschau* No. 5, p. 52 (1965).
- ⁵³⁰ W. Badertscher, *Ciba Rundschau* No. 4, p. 50 (1966).
- ⁵³¹ W. Kühnel, *SVF Fachorgan Textilveredlung* **16**, 764 (1961).
- ⁵³² W. Kühnel, *Bayer Farben Rev.* No. 1, p. 8 (1962).
- ⁵³³ R. Schwaebel, *Intern. Dyer, Textile Printer, Bleacher Finisher* **138**, 337 (1967).
- ⁵³⁴ K. Bühler, D. Hildebrand, and R. Schwaebel, *Bayer Farben Rev.* No. 13, p. 1 (1967).
- ⁵³⁵ W. Kühnel, *Bayer Farben Rev.* No. 13, p. 16 (1967).
- ⁵³⁶ D. Hildebrand and R. Schwaebel, *Textil-Praxis* **22**, 796 (1967).
- ⁵³⁷ H. Rafael, *SVF Fachorgan Textilveredlung* **16**, 754 (1961).
- ⁵³⁸ *Rev. Textiles, Tiba* **59**, 89 (1960).
- ⁵³⁹ H. Schumacher, *Melliand Textilber.* **41**, 1548 (1961).
- ⁵⁴⁰ H. Schumacher, *SVF Fachorgan Textilveredlung* **16**, 747 (1961).
- ⁵⁴¹ M. Capponi, *SVF Fachorgan Textilveredlung* **16**, 341 (1961).
- ⁵⁴² F. F. Metzger, *Z. Ges. Textil-Ind.* **63**, 202 (1961).
- ⁵⁴³ J. H. Roberts, *Textile Mfr.* **90**, 118 (1964).
- ⁵⁴⁴ H. Schwab and G. Barts, *Z. Ges. Textil-Ind.* **64**, 392 (1962).
- ⁵⁴⁵ G. Meyer and H. Wirth, *Melliand Textilber.* **43**, 850 (1962).
- ⁵⁴⁶ G. Meyer and H. Wirth, *Melliand Textilber.* **46**, 190 (1965).
- ⁵⁴⁷ G. Meyer and H. Wirth, *Melliand Textilber.* **47**, 1296 (1966).
- ⁵⁴⁸ G. Meyer and H. Wirth, *Melliand Textilber.* **48**, 1446 (1967).
- ⁵⁴⁹ J. von Delden, *Melliand Textilber.* **46**, 397 (1965).

dyes. The pH dependence of the fixation has been utilized in textile printing to produce resist effects under Aniline Black^{550, 551} or with acid-fixable pigment binders.^{536, 552} Other resisting agents are organic amino compounds,⁵⁵³ cationic water-soluble and alkali-insoluble polymers,⁵⁵⁴ and resisting emulsions based on methyl polysiloxane.⁵⁵⁵ Provokov and

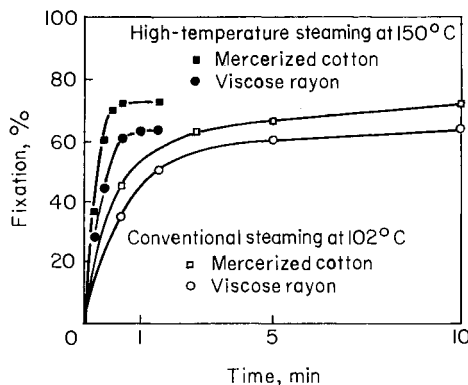


FIG. 52. Comparison of the yield of fixation of Procion Golden Yellow H-RS by conventional steaming and by high-temperature steaming.⁴⁸⁹

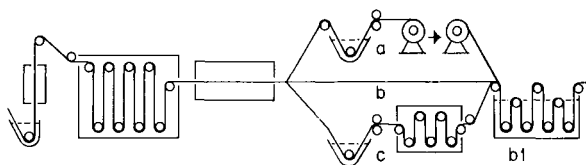


FIG. 53. Subdivision of the continuous method into individual stages.⁴⁸⁶ a, Pad-batch process; b, thermofixation process; c, pad-thermofix-pad-steam process.

others⁵⁵⁶ have described a resist based on pentamethylol melamine + ammonium salt catalyst. Resist prints under reactive dyeings can also be obtained by the printing of pastes which contain sodium hydroxymethane sulfonate.⁵⁵⁷ Discharge printing can only be carried out with reactive dyes which can be easily split by a reductive or alkaline treatment (or where the linkage systems behave in a similar manner).⁵⁵⁸ Vinyl

⁵⁵⁰ ICI, *BeP* 587,423 (9.2.1960); *BP* 875,862 (10.2.1959).

⁵⁵¹ N. A. Sokolova, A. Z. Cernomordik, and M. P. Zukeva, *Tekstil'n. Prom.* **24**, 67 (1964).

⁵⁵² N. G. Senger, *Z. Ges. Textil-Ind.* **63**, 345 (1961).

⁵⁵³ ICI, *BP* 829,443 (10.4.1957).

⁵⁵⁴ Nippon Senka Ind., *JP Appl.* No. 23,619/67 (19.11.1965).

⁵⁵⁵ Gy, *SZAS* 9,726/63 (7.8.1963); *USP* 2,016,968 (15.8.1962).

⁵⁵⁶ N. I. Provokov, A. A. Kudrjasova, and E. N. Ryvkina, *Tekstil'n. Prom.* **25**, 63 (1965).

⁵⁵⁷ Meisei Chem., *JP Appl.* No. 253/68 (29.1.1966).

⁵⁵⁸ BASF, *BeP* 680,232 (28.4.1966).

sulfone dyes are particularly suitable. The fixation yield in textile printing depends also on the choice of suitable thickening agents, apart from an optimum use of alkali. Alginate and emulsion thickenings have proved particularly suitable.⁵⁵⁹⁻⁵⁶³ Reactive dyes are now also being printed on wool and silk, in addition to the already well-known fields of application on cellulose fibers and cellulose/polyester fabrics.⁵⁶⁴⁻⁵⁶⁸ However, the use of reactives in the dyeing of wool by continuous processes remains an exception, although useful dyeings can be obtained by the one-bath pad-steam method, e.g., on tops, with the required fastness to processing.

4. Combination with Resin Finishes

Since a number of reactive dyes will also react with basic groups under acid fixation conditions (as they exist in anticrease finishing of cellulose textiles with nitrogen-containing precondensates), it is possible to dye and to give an anticrease finish in a one-bath one-step process under the conditions which apply to acid-catalyzed resin finishing of cellulose textiles.⁵⁶⁹⁻⁵⁷⁴ The reaction takes place in 1-15 minutes at 130-170°. Catalysts which have been specially developed for this method are available under the trade name Procion Resin Catalyst A. The process is known as Procion Resin Process.⁵⁷⁵⁻⁵⁸¹

⁵⁵⁹ W. A. Schotten, *BP* 856,284 (12.8.1958).

⁵⁶⁰ *Z. Ges. Textil-Ind.* **62**, 1102 (1960).

⁵⁶¹ *Textile Ind.* **124**, 74 and 132 (1960); *Am. Dyestuff Repr.* **49**, 717 (1960).

⁵⁶² ICI, *BP* 956,161 (23.10.1961).

⁵⁶³ H. Werdenberg, *DAS* 1,262,960 (26.11.1958); *BeP* 585,059 (26.11.1959); *FP* 1,241,551 (26.11.1959); *BP* 942,191 (26.11.1959); *USP* 3,068,058 (27.11.1959).

⁵⁶⁴ H. Werdenberg, *Ciba Rundschau* **13**, 34 (1959).

⁵⁶⁵ W. Badertscher, *SVF Fachorgan Textilveredlung* **16**, 194 (1961).

⁵⁶⁶ F. Talamona, *Ciba Rundschau* No. 2, p. 45 (1963).

⁵⁶⁷ F. Talamona, *SVF Fachorgan Textilveredlung* **18**, 358 (1963).

⁵⁶⁸ W. Janssen, *Melliand Textilber.* **49**, 1067 (1967).

⁵⁶⁹ ICI, J. A. Moyse and C. D. Weston, *FP* 846,505 (22.11.1957).

⁵⁷⁰ ICI, *USP* 3,054,699 (6.6.1958).

⁵⁷¹ ICI, *BP* 884,043 (5.11.1959).

⁵⁷² ICI, *BeP* 595,382 (23.9.1960); 604,457 (31.5.1961).

⁵⁷³ ICI, Tech. Inform. Dyehouse No. 546 (1960).

⁵⁷⁴ ICI, *BP* 985,189 (26.2.1962).

⁵⁷⁵ *Dyer* **123**, 495 (1960).

⁵⁷⁶ *Am. Dyestuff Repr.* **49**, 244 (1960).

⁵⁷⁷ ICI, *BP* 912,348 (12.5.1960).

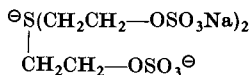
⁵⁷⁸ I. Rattee and R. Bugmann, *SVF Fachorgan Textilveredlung* **16**, 162 (1961).

⁵⁷⁹ J. A. Fowler, *Melliand Textilber.* **43**, 597 (1962).

⁵⁸⁰ I. Rattee, *J. Soc. Dyers Colourists* **78**, 69 (1962).

⁵⁸¹ *Textile Mfr.* **88**, 1046 (1962).

According to another working method, the fabric which has been padded with dyestuff and antirease agent is stored in the presence of mineral acid as catalyst for 1–3 hours at temperatures which are not higher than 60°. According to Moyse and Weston⁵⁸² the textile goods can also be finished and dyed in a one-bath two-stage process by padding with precondensate, acid catalyst (e.g., zinc chloride), and reactive dye as well as an alkaline cross-linking agent of the following structure:



The goods are dried and cured and are then passed through an alkali bath. The alkaline cross-linking agent is made to react, e.g., by steaming, and the acid content of the fabric is neutralized. Another possibility is to dye according to the cold pad-batch process and then to impregnate the goods, without intermediate scouring, with aqueous solutions of urea-formaldehyde condensates, followed by curing in the presence of suitable acid catalysts.⁵⁸³ For the widely used Procion Resin Process, compounds such as the following are suitable as aminoplasts: dimethylol ethylene urea, trimethylolmelamine, dimethylol glyoxal urea, methylol-stearamide. Migration of the dye into the resins and hence the production of uneven dyeings is prevented by adding triisobutylnaphthalenesulfonic acid or butylnaphthalenesulfonic acid. The migration inhibitor Perminal PP is a commercially available product of this kind. A plasticizer (Velan NW) is also added. According to various patents^{584–589} it is also possible to use instead of the reactive dyes other dyes which contain groups capable of condensation with the antirease agent. According to Einsele,⁵⁹⁰ it is also possible to use polyvinyl alcohol finishes with reactive dyes (Procion and Reakton dyes have been investigated) by a one-bath and two-bath process.

A similar procedure has been described in a Geigy patent.⁵⁹¹ Simultaneous dyeing and antirease finishing of textile goods consisting wholly

⁵⁸² ICI, J. A. Moyse and C. D. Weston, *BP* 982,255 (24.10.1962).

⁵⁸³ ICI, *BeP* 617,446 (9.5.1962).

⁵⁸⁴ BASF, *FP* 1,228,823 (29.10.1958).

⁵⁸⁵ CIBA, *AustP* 219,552 (24.6.1960); 212,267 (27.2.1959); *BeP* 592,257; 619,191 (20.6.1962).

⁵⁸⁶ BASF, *GE* 1,140,897 (9.6.1960).

⁵⁸⁷ BASF, *GE* 1,131,180; 1,140,171 (26.7.1961).

⁵⁸⁸ BASF, *BeP* 618,888 (13.6.1962).

⁵⁸⁹ Asahi Dyestuffs, *SZAS* 593/61 (18.11.1961).

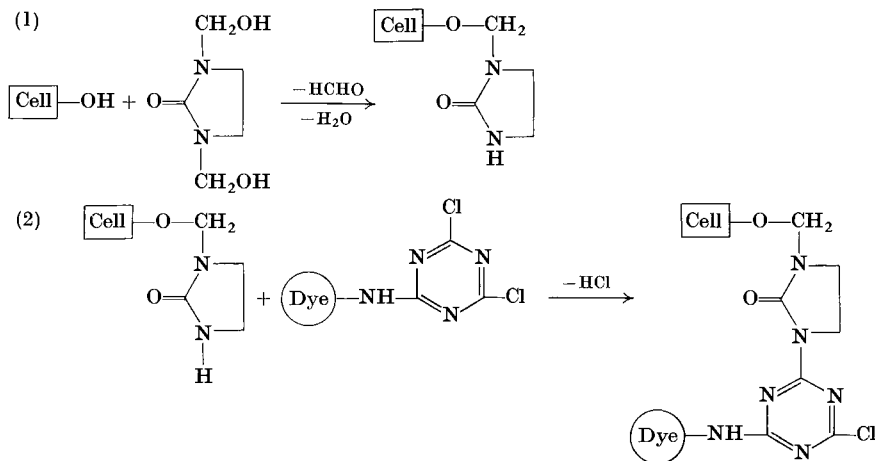
⁵⁹⁰ U. Einsele, *Melliand Textilber.* **43**, 497 (1962).

⁵⁹¹ Gy, *FP* 1,320,443 (19.4.1962).

or mostly of native or regenerated cellulose can also be done with vinyl sulfone or sulfonamide dyes which react in alkaline medium with the hydroxyl groups of the cellulose (with intermediate formation of free vinyl groups), whose reactivity is, however, preserved under acid curing conditions.⁵⁹²

On the other hand, it is also possible to finish the textile goods first with a resin-forming agent such as melamine formaldehyde or ethylene urea, and then to dye with a reactive dye which will go on such compounds in an acid medium. Fixation is then effected in the presence of acetic acid⁵⁹³ at 50–90° in a manner similar to the reaction with fibers which contain nitrogen. A method for simultaneous dyeing and finishing, using

CHART 1

MECHANISM OF DYESTUFF FIXATION VIA ACID-FIXABLE RESINS⁵⁹⁵

dyes which contain an isothiuronium salt group, has been described by Mawson and Rattee.⁵⁹⁴ A technical testing method for the finished fabrics has been reported by Loy and Gysin⁵⁹⁵ (Chart 1); see also Stamm.⁵⁹⁶ A two-stage finishing and dyeing method with triethanolamine and ammonium nitrate as catalyst has been described by Chekalin.⁵⁹⁷ Resin finishes will often change the fastness to light of

⁵⁹² FH, *BeP* 616,368 (12.4.1962).

⁵⁹³ MCI, *JP Appl.* No. 21,711/65 (22.7.1958).

⁵⁹⁴ ICI, J. F. Mawson, and I. D. Rattee, *BP* 912,348 (12.5.1960).

⁵⁹⁵ W. Loy and H. P. Gysin, *Textil-Praxis* **22**, 45 and 115 (1967).

⁵⁹⁶ O. A. Stamm, *J. Soc. Dyers Colourists* **80**, 416 (1964).

⁵⁹⁷ M. A. Chekalin, *RP* 190,863 (20.5.1965).

reactive dyeings. Relevant data have been given by the dyestuff manufacturers in their pattern cards. See also references 598 and 599.

II. Degradation of the Dye-Fiber Linkage

If a reactive dyeing has been rinsed well until the water used for rinsing has become clear, and if this dyeing is then exposed to acid and alkaline treatments, it will bleed to an extent which depends on the pH and on the temperature. Hence some of the dye which has been chemically linked to the cellulose can be split off by hydrolysis, the extent of which depends on the stability of the linkage system. This dye will stain the treatment bath or—in the usual wet-fastness tests—the accompanying fabric. Even if the amount of removable dye is low, this hydrolysis can cause the wet-fastness to drop considerably, especially when the goods are stored in a weakly acid condition for a prolonged period. The dependence of the hydrolysis on the pH gives us a suggestion of the mechanism of the dissociation reaction, while the dependence on the temperature allows us to draw conclusions on its activation energy.⁶⁰⁰ If we can determine the stability to hydrolysis of a dyeing of unknown origin, we can draw conclusions on the type of reactive system used to produce this dyeing.⁶⁰¹⁻⁶⁰⁴ This test is best carried out by treating a dyeing which has been rinsed to produce a clear rinsing water in a buffer solution in the thermostat, or by boiling the goods and by determining the amount of hydrolyzed dye quantitatively in percent of the total amount of dye present, as a function of time.⁶⁰⁵⁻⁶⁰⁷ The hydrolysis values obtained in this manner will enable us to calculate the hydrolysis constants for a given temperature,^{600, 604, 608, 609} which correspond for a number of dyes to a reaction of pseudo-unimolecular order if we consider

⁵⁹⁸ *Ciba Rundschau* **13**, No. 147, p. 41 (1959).

⁵⁹⁹ H. U. von der Eltz, *Melliand Textilber.* **42**, 929 (1961).

⁶⁰⁰ E. Elöd and Y. Nakahara, *Melliand Textilber.* **41**, 567 (1960).

⁶⁰¹ A. Bode, *Melliand Textilber.* **41**, 34 (1960) (English Ed.).

⁶⁰² E. Clayton, "Identification of Dyes on Textile Fibres," 2nd ed. Soc. Dyers Colourists, Bradford, 1963.

⁶⁰³ F. Jordinson and R. Lockwood, *J. Soc. Dyers Colourists* **78**, 122 (1962); **80**, 202 (1964).

⁶⁰⁴ G. E. Kritschewskij, F. I. Sadov, and N. N. Boiko, *Technol. Textile Ind. (English Transl.)* **25**, 100 (1961).

⁶⁰⁵ J. Benz, *J. Soc. Dyers Colourists* **77**, 734 (1961).

⁶⁰⁶ R. C. Senn, O. A. Stamm, and H. Zollinger, *Melliand Textilber.* **44**, 261 (1963).

⁶⁰⁷ R. C. Senn and H. Zollinger, *Helv. Chim. Acta* **46**, 781 (1963).

⁶⁰⁸ D. Hildebrand, *Bayer Farben Rev.* No. 13, p. 1 (1967).

⁶⁰⁹ D. Hildebrand, unpublished results.

only the beginning of the hydrolysis reaction (Figs. 54 and 55). If we plot the hydrolysis constants obtained in this manner against the pH at which hydrolysis was carried out, we get characteristic hydrolysis curves.^{600, 601}

Hydrolysis experiments by Zollinger^{606, 607} have shown that the kinetics of hydrolysis need not always follow a simple law, and that it can change during the process of hydrolysis depending on the type of linkage (Fig. 56). In the hydrolysis reactions carried out at the boiling tempera-

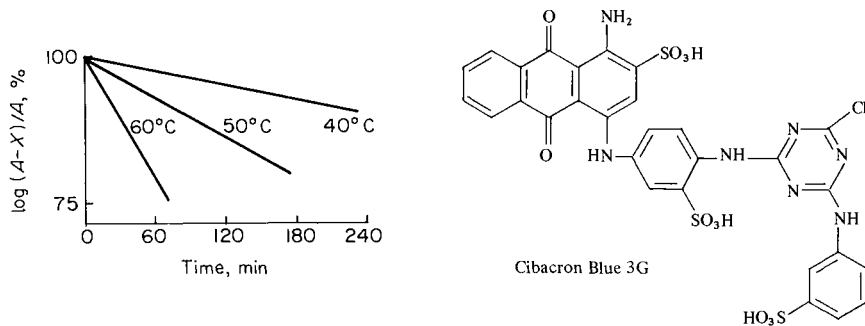


FIG. 54. Desorption of Cibacron Blue 3G from Cuprama in an aqueous 1% NaOH/CH₃OH solution.⁶⁰⁰

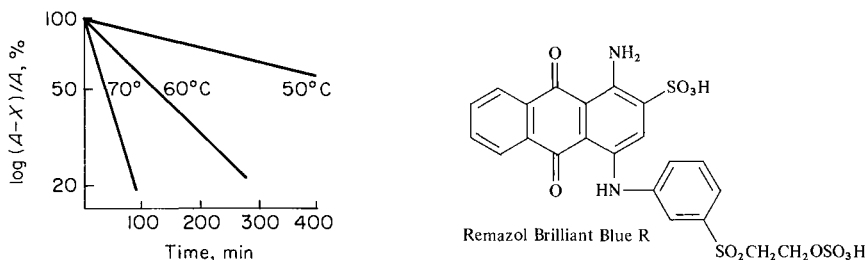


FIG. 55. Desorption of Remazol Brilliant Blue R from viscose in an aqueous 0.75% NaOH/CH₃OH solution.⁶⁰⁰

ture by Senn, Stamm, and Zollinger,^{606, 607} the hydrolysis constants were therefore not determined. A study of the hydrolysis curves published by different authors shows that, generally speaking, reactive dyeings on cellulose have their maximum stability in a pH range between 6 and 7, and that an increasing amount of dye is hydrolyzed when the pH goes up or down.⁶¹⁰ In the strongly acid range, a hydrolysis of the glucoside linkage of the cellulose is superimposed on the degradation of the actual dye-fiber linkage, while in the alkaline range the rate of hydrolysis can drop in a characteristic manner due to dissociation processes which

⁶¹⁰ E. Siegel, 3rd Intern. Farbensymp., Interlaken, 1967, p. 100. *Chimia* 1968.

depend on the pH and which take place in the chromophoric system of the dye. Similar phenomena have been observed in connection with the dependence of the hydrolysis of reactive dyes on the pH (see Section I,B,1).⁶¹¹ If these variations are considered, we can still define a pH range, both for acid and for alkaline hydrolysis, in which the dependence on the pH corresponds largely to the H^+ or OH^- concentration. This means that in many dyeings a drop in pH by 1 unit in the practically

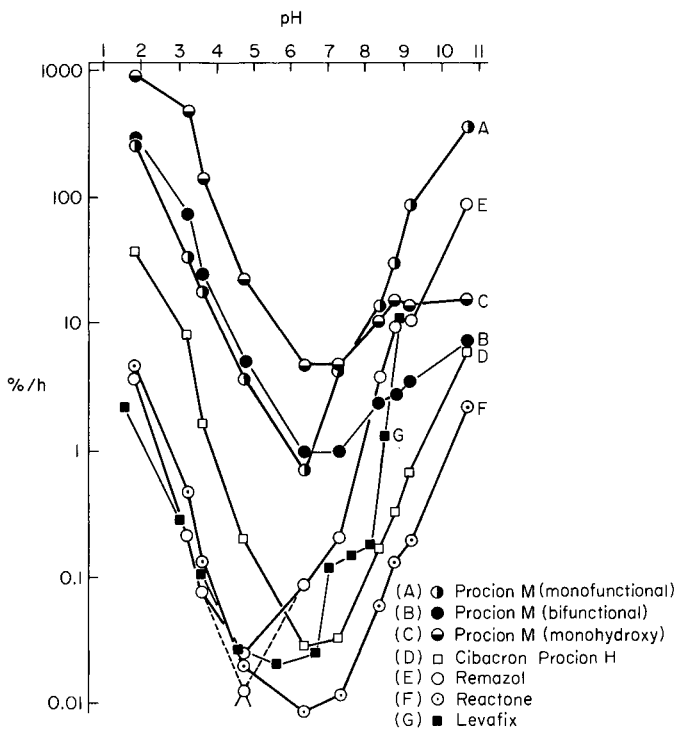


FIG. 56. Rate of hydrolysis of reactive dyeings.^{606,607}

important weakly acid pH range (pH 5–3) or a pH increase in the alkaline range (pH 11–12), hydrolysis will be accelerated by a factor of 10. The dependence of hydrolysis on the temperature at constant pH, which was determined for the first time by Elöd and Nakahara,⁶⁰⁰ showed that the activation energy for Cibacron Blue 3G on Cuprama was 22 kcal and that it was 28 kcal/mole for Remazol Brilliant Blue R on viscose rayon (Figs. 54 and 55).

⁶¹¹ D. Hildebrand and W. Beckmann, *Melliand Textilber.* **45**, 1138 (1964).

An explanation of the hydrolysis of the dye-fiber linkage is possible by considering the chemical structure of the reactive group.^{607, 612-615} The chemical structure of the reaction center is the same before and after the reaction with the cellulose. The only difference is that the leaving group (e.g., chlorine) has been replaced by a high-molecular alkoxy group. It is therefore understandable that at least in the stronger alkaline medium with hydroxyl ions, nucleophilic substitution can again take place at the C atom which has been positively polarized by neighboring N atoms (see formulas on page 437).⁶⁰⁷

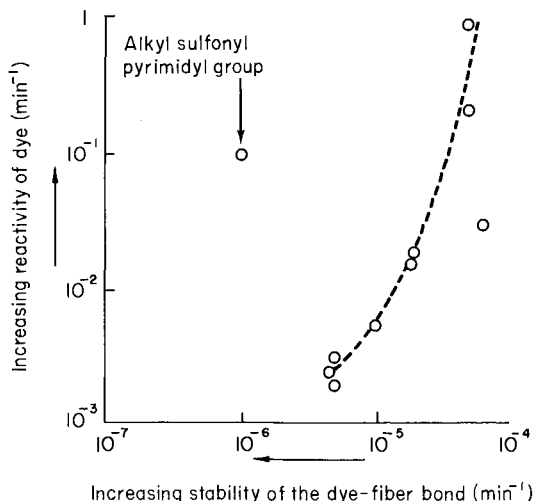


FIG. 57. Relation between reactivity of a reactive dye and alkaline stability of the dye-fiber bond.

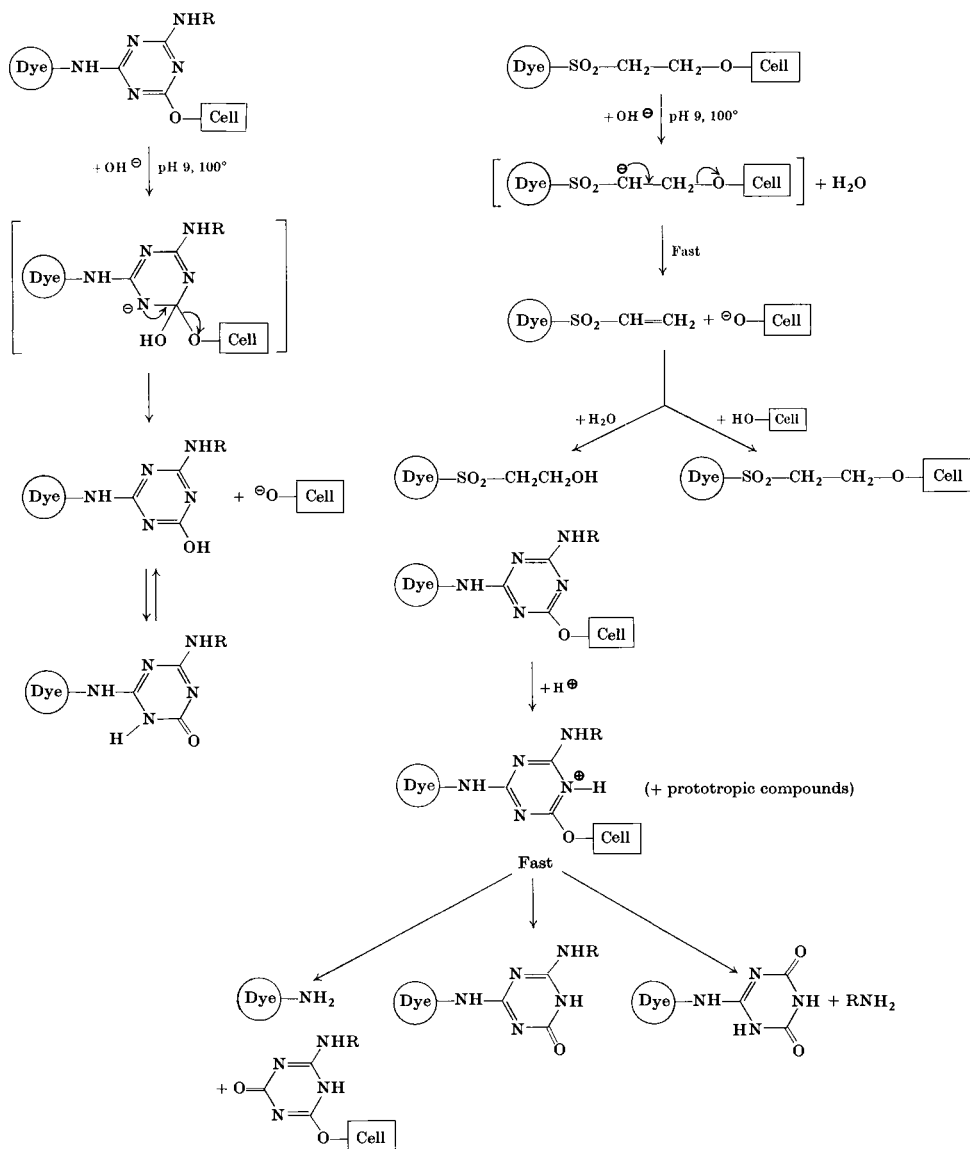
Figure 57 shows the rate of fixation plotted against the rate of hydrolysis of the dye-fiber bonds under alkaline conditions in terms of the pseudo-first-order reaction constants. The values obtained are in a line, with the exception of the alkylsulfonylpyrimidine dye. With this exception, the stability of the dye-fiber bond therefore increases with increasing reactivity of the dye. The bond stability of the alkylsulfonylpyrimidine reactive dyes (Levafix P) is thus considerably higher than would be expected from their reactivity. The combination of high

⁶¹² I. D. Rattee, *Endeavour* **20**, 154 (1961).

⁶¹³ C. Preston and A. S. Fern, *Chimia (Aarau)* **15**, 177 (1961).

⁶¹⁴ T. L. Dawson, A. S. Fern, and C. Preston, *J. Soc. Dyers Colourists* **75**, 210 (1959).

⁶¹⁵ O. Thumm and J. Benz, *Angew. Chem.* **74**, 712 (1962).



reactivity and bond stability can be attributed to the mechanism demonstrated in Fig. 58. The activation of a Levafix P dyestuff is mainly due to the polarity of the exchangeable group (X) and therefore will be eliminated by the substitution reaction [(B) in Fig. 58]. When the activation of the reactive system is mainly due to the heterocyclic system used (R), the sensitivity of the reactive system to a hydrolytic

effect is proportional to the liability to degradation of the dye-fiber bond (A).

Reactive systems in which an OH group has been produced by hydrolysis of a second exchangeable radical will assume a negative charge in an alkaline medium, which will considerably reduce alkaline hydrolysis of the dye-fiber bond (XIII). The stability to hydrolysis of

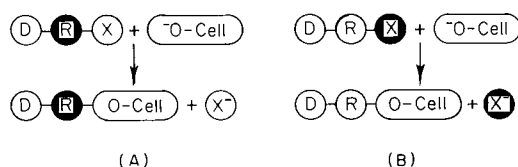
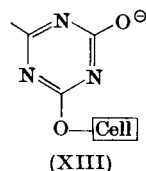
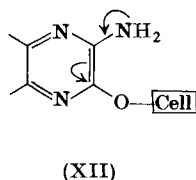


FIG. 58. Schematic comparison of internal and external activated reactive groups: A, Internal activation: involved in the dye-fiber bond; B, External activation: eliminated by the fixation reaction.

the dye-fiber bond can also be increased by introducing electron-donating substituents into the heterocycle, because the electron-attracting effect of the double-bonded nitrogen atoms (XII) is thus reduced.^{619, 620}



In the acid range, there is a fundamental difference in the behavior of reactive linkages based on nitrogen-heterocycles and vinyl sulfone. In this range, a high stability to hydrolysis is displayed especially by the β -alkoxyethyl sulfone group. Romanova and Chekalin⁶²¹ have even been able to show by careful hydrolysis of cotton fabrics dyed with Remazol dyestuffs that the dye-cellulose linkage is more stable than the glycoside bond of the cellulose. Zollinger,⁶⁰⁶ contrary to Rattee,⁶²² has concluded

⁶¹⁶ I. D. Rattee, *Chimia (Aarau)* **18**, 293 (1964).

⁶¹⁷ J. Heyna, *Angew. Chem.* **74**, 966 (1962).

⁶¹⁸ K. Schündehütte and K. Trautner, *3rd Intern. Farbensymp., Interlaken, 1967*, *Chimia* 1968 Supplementum, p. 155.

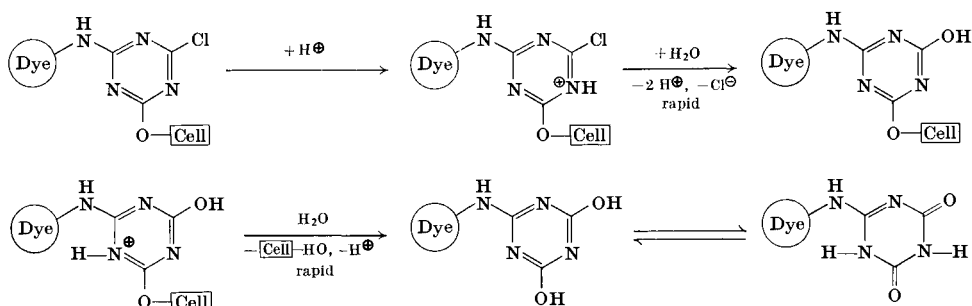
⁶¹⁹ S. Horrobin, *J. Chem. Soc. (London)* p. 4130 (1963).

⁶²⁰ I. D. Rattee, *Science* **52**, 581 (1964).

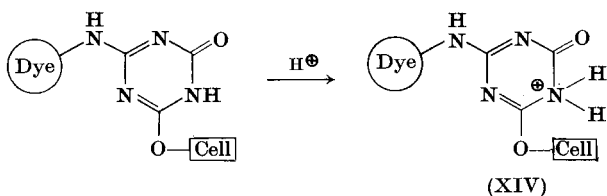
⁶²¹ M. G. Romanova and M. A. Chekalin, *Tekstil'n. Prom.* **26**, 52 (1966).

⁶²² I. D. Rattee, *J. Soc. Dyers Colourists* **77**, 739 (1961).

that there is a specific hydroxonium ion catalysis. He based his conclusions on the strong dependence of the acid hydrolysis of dye-fiber linkages based on dichlorotriazine on pH. In triazine dyeings, this kinetic finding can be explained by the formation of a triazonium ion intermediate stage. The triazonium ion has a much higher reactivity than triazine, because the positive character of the linking C atom is increased by the association of a proton, so that it becomes easier for the water molecules to attack the triazonium ion. The acceleration is proportional to the hydrogen ion concentration.^{606, 607} This mechanism has a particularly noticeable effect in heterocycles, the aromatic character of which is cancelled out by hydrolysis of a second exchangeable group.^{612-614, 616}

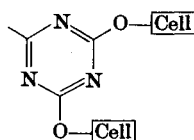
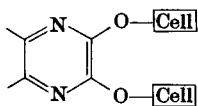


The liberated acid has an autocatalytic effect (XIV):



This mechanism is supported by the fact that no monochloro-reactive dye can be found in the products split off from dichlorotriazine and trichloroquinoxaline dyeings; only that dye is split off which is already present in the more unstable lactim-ether form.

Dyes with two exchangeable groups can also attach themselves to cellulose in a bifunctional manner. Such linkages can be responsible for variations of the kinetics of reaction of pseudo-unimolecular order.



According to investigations by Benz⁶⁰⁵ on the ability of different bridge links between the chromophoric system and the supporting group to undergo hydrolysis in pyrimidyl dyes, the dissociation between the chromophoric system and the supporting group takes place at an -O- bridge, while the -NH- and -NR- bridges are stable, so that in this case the stability of the cellulose ester bond is most important. The basicity of the bridge link is also decisive for the stability of the dye-fiber linkage,⁶⁰⁴ in analogy with the influence of basic substituents on the positive character of the bonding C atom in the heterocycle. The marked difference in the stability to hydrolysis of dyeings having the same supporting group is therefore due to the different basicity of the nitrogen which forms the bridge. The stability of the carbamide bond lies between that of the -O- bridge and the -NH- bridge. The carbamide bond is practically stable under acid hydrolysis conditions, but hydrolysis is possible under alkaline conditions. In dyeings with dichloroquinoxaline dyes, the amide bond participates proportionally in the hydrolysis under alkaline conditions, depending on the basicity of the corresponding amino group. This becomes even more noticeable in chloropyrimidine-4-carboxylic acid derivatives. In spite of the stable pyrimidine-cellulose ether linkage, the carbamide group is easily hydrolyzed in alkaline scouring, probably due to the strong electron-attracting action of the pyrimidine ring.

In dichlorotriazine dyes, one of the two free chlorine atoms will react with cellulose. The second chlorine atom has either remained unchanged, or it has been hydrolyzed by water, or it has also reacted with cellulose. To prevent the second chlorine atom being subsequently transformed by hydrolysis, e.g., during washing, into the acid-unstable keto form (XIV), the dyeing can be aftertreated with 1 g/liter solution of ethylenediamine in the scouring bath.^{623, 624} The hydrolyzed dye is retained on the fiber as a water-insoluble precipitate if the aftertreatment is carried out with dicyandiamide formaldehyde condensation products, polyquaternary compounds or guanidine derivatives: Levogen brands (Bayer), or Fixanol PN (ICI). Recent investigations by Pierce and Rattee⁶²⁵ on the

⁶²³ ICI, *SVF Fachorgan Textilveredlung* **15**, 9 (1960).

⁶²⁴ ICI, *SVF Fachorgan Textilveredlung* **16**, 708 (1961).

⁶²⁵ J. H. Pierce and I. D. Rattee, *J. Soc. Dyers Colourists* **83**, 361 (1967).

acid-catalyzed hydrolysis of dye-fiber linkages of type 3 (see also Section III,A,1) of dichlorotriazine dyes have shown that the bimolecular rate of hydrolysis constant is independent of the ion concentration of the reaction medium. Kinetically we can distinguish between two kinds of this type of linkage, one of which is present in a relatively low concentration and is hydrolyzed very quickly, while the other is more stable.

The stability of the dye-fiber linkage is not only important for the fastness properties, but also for the stripping of faulty dyeings. For example, a treatment of 2 hours with a 4% aqueous soda ash solution at the boil will restore the solubility of the fiber, which has become insoluble in cuprammonium solution, but the amount of stripped dye is low. On the other hand, according to Nevell,⁶²⁶ 20 Procion dyestuffs listed by him (10 hot-dyers and 10 cold-dyers), with the exception of Procion Brilliant Blue H-7G, can be stripped completely by treatment at the boil with a 40% hydrazine solution. No noticeable decomposition of the cellulose was observed. For wool and polyamide fibers, the possibility of hydrolysis of the dye-fiber linkage is only of secondary importance, since these fibers are not exposed to alkaline boiling and since the amide bonds are sufficiently stable under acid conditions. Unsatisfactory wet-fastness properties of reactive dyeings on wool are therefore not due to fission of the dye-fiber linkage, but to the difficulty in removing the chemically unfixed portion of the dye. Rattee has pointed out that solubilized, reactive-dyed protein components of the wool keratin can go into solution under washing conditions.⁶²⁷

III. Proofs for the Existence of a Covalent Dye-Fiber Linkage

A. CELLULOSIC FIBERS

In the preceding sections, several indirect proofs for the existence of a genuine chemical bond between a reactive dye and cellulose have been discussed. We can say that neither the kinetics of reaction of the dyeing process, nor the mechanism of dye redissociation which has been established, nor the different methods of analysis based on the solvent stability of the dye-cellulose linkage can be properly understood without assuming that there is a covalent dye-cellulose bond. On the other hand, the indirect conclusion that a covalent bond is formed between the dye and cellulose under dyeing conditions cannot be accepted without direct

⁶²⁶ T. P. Nevell, *J. Soc. Dyers Colourists* **77**, 158 (1961).

⁶²⁷ D. M. Lewis, I. D. Rattee, and C. B. Stevens, *3rd Congr. Intern. Rech. Textile Lan., Paris, 1965*, Vol. III, p. 213 (1966).

structural proof, so that several special methods have been developed which attempt to provide the required proof.

1. *Mono- and Dichlorotriazine Dyes (Procions; Cibacrons)*

According to Vickerstaff⁶²⁸ the following facts can be considered as proof for the existence of a covalent bond between a dye of the mono- or dichlorotriazine type and the cellulose fiber; (a) Direct and vat dyeings can be removed from the fiber by boiling with solvents such as pyridine, *o*-chlorophenol or chloroform. This cannot be done with reactive dyeings. (b) The solubility of polyvinyl alcohol and of cellulose in water and in cuprammonium solution, respectively, is reduced by treatment with a reactive dye in presence of alkali. (c) A reactive azo dye fixed on cellulose can be reduced, and the amine which remains on the fiber can be diazotized and coupled with a coupling component to produce a dyeing with wet-fastness properties which are as good as those of the original reactive dyeing.

Schwertassek⁶²⁹ used swelling and solubilization in sulfuric acid to follow the reaction of cellulose fiber with Procions and Cibacrons. Diminished solubility suggested cross-linking by a cold-dyeing Procion; but there was no effect on solubility when Cibacrons and hot-dyeing Procions were used. Sorption of iodine suggested blocking of the hydroxyl groups of cellulose, but not cross-linking. Kinetic studies of the desorption of reactive dyes dyed on cellulose have shown that a first-order chemical reaction between dye and fiber takes place.⁶³⁰

Wegmann⁶³¹ succeeded in synthesizing a dye on cellulose by bringing the fiber to react first with a chlorine atom of dichloroanilinetriazine, and then by replacing the second chlorine atom on the fiber by a dye with a free amino group. The dyeing produced in this manner was identical with the dyeing in which the corresponding reactive dye had been used.

Trials conducted by Dawson,⁶³² according to which reactive-dyed cotton cannot be oxidized as extensively as undyed cotton, indicate that part of the OH groups is blocked by the reactive dye. Einsele⁶³³ acetylated cellulose which had been dyed with Cibacron Brilliant Yellow 3G and found that the degree of acetylation had decreased. Furthermore, the reactive-dyed cellulose dissolved without difficulty in chloroform

⁶²⁸ T. Vickerstaff, *J. Soc. Dyers Colourists* **73**, 237 (1957).

⁶²⁹ K. Schwertassek, *Faserforsch. Textiltech.* **9**, 321 (1958); **11**, 159 (1960).

⁶³⁰ E. Elöd and Y. Nakahara, *Melliand Textilber.* **41**, 567 (1960).

⁶³¹ J. Wegmann, *Melliand Textilber.* **39**, 1006 (1958).

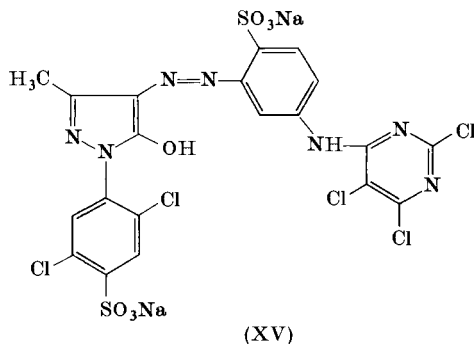
⁶³² T. L. Dawson, *J. Soc. Dyers Colourists* **74**, 584 (1958); see also E. H. Daruwalla and P. Subramaniam, *ibid.* p. 296.

⁶³³ U. Einsele, *Melliand Textilber.* **42**, 427 (1961).

or methylene chloride, although the reactive dye itself is insoluble in these solvents. The chromatographic behavior of the dyed and acetylated cellulose was similar to that of acetylated cellulose, rather than that of adsorbed and not chemically linked dye. An indication (but by no means a proof) of the formation of a covalent dye-fiber bond was derived from the interpretation of the infrared spectra of dyed cellulose.⁶³⁴ To this end it was first necessary to determine the exact position of the C—O—C band of aromatic substituted alkoxytriazines. This was found to be a double band between 8.8 and 9.1 μ . 2-Chloro-4-anilino-6-(*p*-carboxyanilino)-*s*-triazine was used as model substance, since this compound will not absorb in this range.

2. Trichloropyrimidyl Dyes (*Drimarenes*; *Reactones*)

To identify a covalent bond between the trichloropyrimidyl dye (XV) and cellulose, Möck⁶³⁵ subjected dyed cellulose to acetolysis with acetic anhydride and perchloric acid. The dye-glucose compound was taken up in boiling water, in which pentaacetylglucose remained undissolved. The existence of the dye-glucose bond was established, after electrophoretic separation, by treatment with alkaline silver nitrate when glucose was liberated and responded to the usual tests.



3. Sulfonyl Fluorides

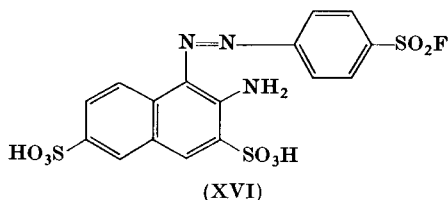
The covalent bonding of sulfonyl fluoride dyes to the primary OH of cellulose was proved by the analogy of the substitution of tosyl esters of primary OH groups by iodine, a reaction known in carbohydrate chemistry.⁶³⁶ Cotton dyed with (XVI) by the pad-steam process was

⁶³⁴ H. Rath and M. Pässler, *Melliand Textilber.* **42**, 787 (1961).

⁶³⁵ U. Möck, *Melliand Textilber.* **45**, 655 (1964).

⁶³⁶ B. Krazer and H. Zollinger, *Helv. Chim. Acta* **13**, 1513 (1960); H. Zollinger, *Chimia (Aarau)* **15**, 185 (1961); *Angew. Chem.* **73**, 125 (1961).

heated for 24 hours in absolute acetone with an excess of sodium iodide at 110–120° in a pressure tube, and the amount of iodine absorbed was determined after the excess iodide had been removed. The data show that



approximately three-quarters of the dye which had been fixed on the cotton can be exchanged for iodine. This proportion of fixed dye behaved like the tosylate of the primary alcoholic group of a sugar. Dyeings prepared with ω -chloropropionyl and mono- and dichlorotriazine dyes were not affected by the action of sodium iodide. For that portion of sulfonyl fluoride which had not been exchanged, substitution of secondary hydroxyl groups of cellulose was assumed.

4. Vinyl Sulfones (Remazols)

The high activation energy (15–30 kcal/mole) of the liberation of the dye which has been bound by the fiber has also been considered as a proof for the existence of a chemical bond.^{637, 638} Some authors have been able to prove the existence of a chemical linkage by starting with the dyed, insoluble substrate and progressing by chemical decomposition to low molecular weight, soluble compounds until they were able to prove the chemical structure with the help of synthesis. Such work was conducted by Chekalin⁶³⁹ and Bohnert⁶⁴⁰ as well as Zollinger and co-workers,^{641–643} using vinyl sulfone dyeings. Vinyl sulfone reactive dyes (Remazols), being sulfuric esters of β -hydroxyethyl sulfones, are particularly suited for supplying chemical proof for the dye–cellulose linkage, since they will color cellulose by the formation of an ether, which is relatively resistant

⁶³⁷ ICI, BP 824,960 (17.10.1956); DBP 1,052,946 (12.9.1956); CFM, BP 827,570 (6.12.1956); FP 1,193,706 (6.12.1956); CIBA, FP 1,192,485 (18.1.1957); FH, BeP 578,517 (8.5.1959).

⁶³⁸ E. Bohnert and R. Weingarten, *Melliand Textilber.* **40**, 1036 (1959).

⁶³⁹ M. A. Chekalin, *Tekstil'n. Prom.* **21**, No. 1, 40 (1961); **23**, No. 8, 67 (1963).

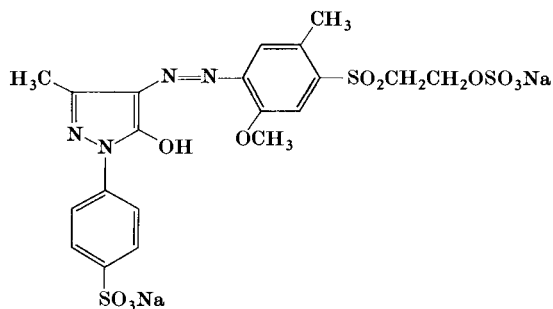
⁶⁴⁰ E. Bohnert, *Melliand Textilber.* **42**, 1156 (1961).

⁶⁴¹ O. A. Stamm, H. Zollinger, H. Zähler, and E. Gäumann, *Helv. Chim. Acta* **44**, 1123 (1961); H. Zollinger, *Palette* **28**, 32 (1968).

⁶⁴² R. C. Senn, O. A. Stamm, and H. Zollinger, *Melliand Textilber.* **44**, 261 (1963).

⁶⁴³ O. A. Stamm, *Textil-Rundschau* **19**, 245 (1964).

to decomposition of cellulose by acid hydrolysis. Bohnert⁶⁴⁰ dyed Remazol Golden Yellow G (CI Reactive Yellow 17) on viscose to saturation by dyeing 15 times. A fraction isolated from the products of acid degradation was found to be identical in chromatographic behavior and IR spectrum with a reaction product of glucose and dye, which was obtained as a crystalline gold-yellow substance.



Remazol Golden Yellow G

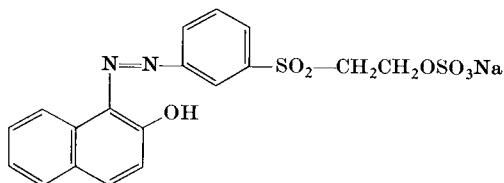
Stamm, *et al.*,⁶⁴¹ were able to supply chemical proof for the existence of the dye-cellulose linkage with the help of partially hydrolyzed cellulose powder which had been dyed with Remazol Brilliant Blue R and which had been subjected to microbiological decomposition by *Cellulomonas uda*. A dyed soluble degradation product was isolated by chromatography as a homogeneous substance; after complete hydrolysis by sulfuric acid, it yielded glucose. Homogeneous dye-sugar derivatives consisting of 1 mole each of dye and glucose were subsequently isolated from the sulfuric acid hydrolysate of dyed cellulose. The compounds were permethylated with methyl iodide and silver oxide in dimethylformamide, and the dye radical was then hydrolyzed with alkali, while the glucosidic methyl group was hydrolyzed with acid. By comparison with synthetic methylglucoses it was concluded that glucose had been substituted in the 2- and 4-positions. A quantitative total balance revealed a 60% substitution at the C-2 hydroxyl group and about 20% substitution at each of the two ends of the chain.⁶⁴⁴

Chekalin⁶³⁹ dyed viscose with Remazol Brilliant Blue R and degraded the cellulose by treatment with 58% sulfuric acid at room temperature for 6 days. Dyed glucose was separated by chromatography, and by using chemical reactions (periodate oxidation, osazone formation, and

⁶⁴⁴ O. A. Stamm, *Helv. Chim. Acta* **46**, 3008 and 3019 (1963); P. Hagen, E. T. Reese, and O. A. Stamm, *ibid.* **49**, 2278 (1966).

interaction with trityl chloride) it was shown that about 70% of the dye was attached to the 6-hydroxyl and about 30% to the 2-hydroxyl of the glucose unit in the cellulose chain.

Bhagwanth, Rama Rao, and Venkataraman have provided direct physical evidence for the formation of covalent bonds between cellulose and reactive dyes.⁶⁴⁵ NMR spectral data showed that monochloro- and dichlorotriazine dyes form ester-type linkages with primary and secondary alcohols and with cellulose; and that dyes of the vinyl sulfone type form true ethers. The NMR spectra of the products obtained by reacting α -methylglucoside with a simple dye (XVII) of the Remazol type as model compound were determined as the acetates. The products



(XVII)

obtained by hydrolysis of dyed viscose were similarly examined, and it was demonstrated that both C-6 and C-2 hydroxyls of the cellulose molecule were attacked. The relative amounts of the C-6 and C-2 dyed glucose were 60–70% and 30–40%, but it was realized that these proportions depend on steric and other factors in the structures of the dyes as well as the conditions of dyeing. In a recent communication, Bhagwanth *et al.*⁶⁴⁶ have suggested that Bohnert's statement⁶³⁸ referring to the vinylsulfonyl group as the true reactive group of the Remazol class of dyes needs to be reconsidered, and that an S_N2 reaction between the arylsulfonyl ethyl sulfate and the cellulose anion cannot be excluded.

Apart from the chemically exact proof of the existence of a dye-fiber linkage, methods which make it possible to prove that a dyeing has been produced with reactive dyes and to differentiate between a reactive dyeing and a dyeing produced by other means are of interest for dyers and printers. The confirmatory test for reactive dyeings is generally based on the covalent linkage of the dye with the cellulose fiber, which distinguished reactive dyeings from dyeings produced on cellulose with all other types of dyes. An essential feature of reactive dyeings should

⁶⁴⁵ M. R. R. Bhagwanth, A. V. Rama Rao, and K. Venkataraman, *Indian J. Chem.* **7**, 1065 (1969).

⁶⁴⁶ M. R. R. Bhagwanth, E. H. Daruwalla, V. N. Sharma, and K. Venkataraman, *Textile Res. J.* **40**, 392 (1970).

therefore be that such dyeings cannot be stripped from the fiber by means of powerful dye solvents. An essential prerequisite is that the unfixed portion of the dye is completely washed off and there is no effect of the solvent on the dyeing in the sense of a hydrolytic reaction. Suitable solvent systems are pyridine, 1:1 pyridine–water, dimethylformamide, 1:1 dimethylformamide–water, and saturated urea solution. Dyeings with reactive dyes show the expected high resistance to these solvent systems.^{647–653} The fact that the great majority of such dyeings will not bleed or will bleed only in traces, if at all, distinguishes them very clearly from dyeings produced with all other types of dyes. But there are a few exceptions. Among these are a few reactive turquoise blue brands,^{649, 653} as well as reactive systems which produce insoluble pigments as by-products during the fixation process.⁶⁵⁴ We cannot reasonably expect the relatively alkali-sensitive Remazol dyeings⁶⁴² to be stable to boiling aqueous pyridine. A reactive dyeing or a reactive print can be recognized with the help of extraction tests even if combinations of several dyes have been used. However, it is usually difficult to completely identify the individual dyes which have been used in a combination to produce reactive dyeings and prints. Since the properties of a dyeing are determined both by the reactive group and by the chromophoric system, both have to be investigated independent of each other. Hints on the reactive system can be found from the stability to hydrolysis of the dye–fiber linkage (see Section II). The conventional methods of dyestuff analysis are used to identify the chromophoric system.⁶⁵⁵

B. WOOL AND POLYAMIDE FIBERS

From the time the reactive dyes were first developed, much has been published to prove the existence of homopolar linkages between dye and

⁶⁴⁷ AATCC, New York Section, *Am. Dyestuff Repr.* **47**, 9 (1958).

⁶⁴⁸ A. Bode, *Melliand Textilber.* **40**, 1304 (1959).

⁶⁴⁹ F. Jordinson and R. Lockwood, *J. Soc. Dyers Colourists* **78**, 122 (1962).

⁶⁵⁰ C. H. Giles, M. B. Ahmad, S. D. Dandekar, and R. B. Mokay, *J. Soc. Dyers Colourists* **78**, 125 (1962).

⁶⁵¹ E. Clayton, "Identification of Dyes on Textile Fibres," 2nd ed., Soc. Dyers Colourists, Bradford, 1963.

⁶⁵² F. Jordinson and R. Lockwood, *J. Soc. Dyers Colourists* **80**, 202 (1964).

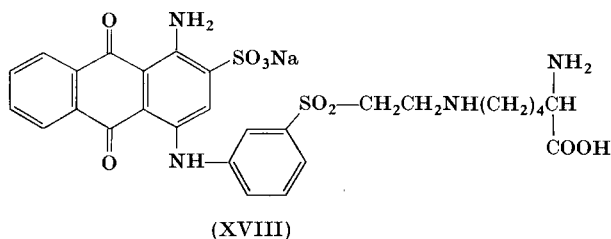
⁶⁵³ O. Thumm and J. Benz, *Chimia (Aarau)* **19**, 286 (1965); *Am. Dyestuff Repr.* **55**, 15 (1966).

⁶⁵⁴ W. Kühnel, *SVF Fachorgan Textilveredlung* **16**, 764 (1961).

⁶⁵⁵ *CSD II*, p. 1304.

protein. Although we have already reviewed a number of indirect conclusions that such linkages actually exist (see the preceding sections dealing with the chemical fundamentals of reactive dyeing of protein material), the fact that this is so has only been recently established by chemical methods. The confirmatory test would be the isolation of amino acid derivatives of a suitable reactive dye, which are chemically pure (*pro analysi*), such isolation being effected from the protein hydrolysate of the dyed fiber, plus the proof of the chemical structure by synthesis. The indirect proofs are based on the characteristic changes of the fiber protein caused by the reactive dyeing process, e.g., by means of solubility tests or by determining the change in the number of functional groups in terms, for instance, of a reaction between the fiber and dinitrofluorobenzene. The decrease of the functional groups which can be dinitrophenylated—such decrease being established as a difference value—has been considered as definite proof of the existence of a chemical linkage. The first proof of a covalent bond between a fiber protein and a commercially available reactive dye was given by Zahn and Reinert,⁶⁵⁶ who used a collagen sheeting dyed with Remazol Brilliant Blue. Dye derivatives of lysine and hydroxylysine were identified in the total hydrolysate (6 *N* HCl, 110°, 20 hours). Both the dyed amino acids were isolated in analytically pure form and identified by means of preparative layer chromatography on silica gel.

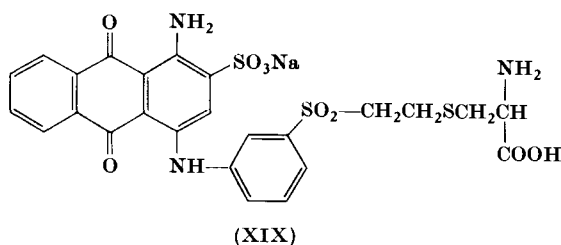
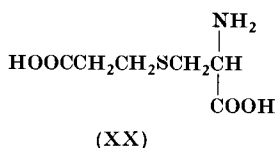
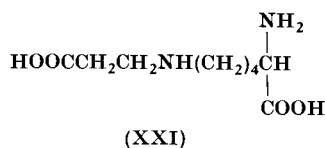
Zahn and Rouette⁶⁵⁷ isolated the product (XVIII) from wool which had been dyed with Remazol Brilliant Blue. They were also successful in isolating *S*-Remazol Brilliant Blue-cysteine (XIX) from reduced wool, and in isolating *S*-carboxyethylcysteine (XX) and *N*-carboxyethyllysine (XXI) from wool which had been dyed with an acrylamide dye.



ϵ ,*N*-Remazol Brilliant Blue—lysine

⁶⁵⁶ G. Reinert, "VTCC-Vortrag," Baden Baden, 1968; H. Zahn and G. Reinert, *Kolloid-Z. und Zeitschrift für Polymere* **226**, 1 (1968).

⁶⁵⁷ H. Zahn and P. F. Rouette, *Textilveredlung* **3**, 241 (1968).

*S*-Remazol Brilliant Blue—cysteine*S*-Carboxyethyl cysteine ϵ -*N*-Carboxyethyl lysine

This supplies definite chemical proof for the existence of a covalent linkage between reactive dye and fiber protein. The isolation and identification of dichlorotriazine dye derivatives of amino acids from reactive-dyed collagen has not been successful to date, since the covalent dye-protein linkage is not more stable to hydrolysis than the peptide bond or the acid amide bond and is therefore also susceptible to degradation under the conditions of total hydrolysis.

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