CHAPTER 1

REACTIVE DYES - A BRIEF REVIEW

1. REACTIVE DYES - A BRIEF REVIEW

1:1. INTRODUCTION

The achievement of dye fastness on cellulose by chemical combination of the dye with the fibre represents the most recent truly new concept added to the dyer's palette. It took exactly 100 years following W.H. Perkin's preparation of the first synthetic dye-Mauvine - before the first reactive dyes for cellulose were used commercially. The introduction of "Procions", by ICI in 1956 heralded an era of an entirely new type of synthetic dyes for textile fibres. Prior to this date, the methods available for the colouration of cotton and viscose relied heavily on aggregation of the dye molecules within the fibre pores in order to physically trap the dye within the fibre. This was true for both water-soluble (e.g. direct) and water-insoluble (e.g. azoic, vat) colours. Because of the weak, reversible nature of the forces involved, in the dyeing processes, the washing fastness was limited. In the case of the water-soluble direct dyes, which have the advantage of direct applicability, washing fastness was totally inadequate for many reasons. Thus to over come this deficiency for achieving satisfactory wet fastness had long been realised to lie in forsaking the weak reversible aggregation forces and attaching the dye molecule to the fibre by a covalent bond.

1:2. THE DISCOVERY OF REACTIVE DYES.

Very little work seemed to have been done to achieve fastness by chemical combination with fibres since Cross and Bevan's work in 1895 (1). The goal of bright, truly wet-fast dyeings on cellulose via the reactive route seems to have been considered a chemist's pipe dream; references do occur with this goal in mind, but they used rather impractical approaches (2-21).

During the late 1940s CIBA, Hoechst and ICI worked in the area of reactive dyes for wool. In 1952 Hoechst marketed a range of fibre reactive, Remalan reactive dyes for wool (22). Later, after the appearance of Procion dyes, the Remazol reactive dyes for cellulose appeared based on the same chemistry as the Remalan dyes. The discovery of the first commercially workable dyes for cellulose grew from research conducted on reactive dyes for wool. In 1952 the work (23) on the reaction of cyanuric chloride with soda cellulose inspired Rattee and Stephens at the ICI laboratories (Manchester, England) to turn their attention from wool to cellulose. As a result of their work, ICI marketed the first commercial range of reactive dyes for cellulose the Procion-M possessing dichloro-s-triazinyl group as a reactive unit. The commercial success of Procion-M range gave the impetus to the development of several other ranges of reactive dyes possessing different reactive systems and these are listed in chart-1 and chart-2.

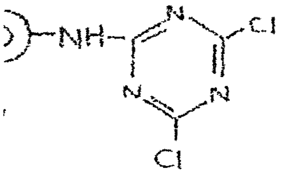
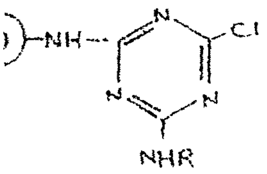
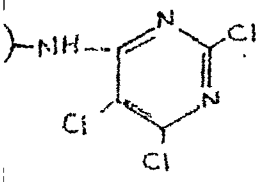
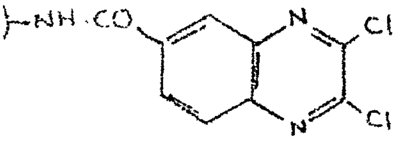
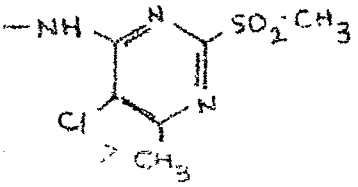
1:3. CONSTITUTION OF REACTIVE DYES.

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 ($\text{Dye} - X + \text{Cell-O}^- \longrightarrow \text{Dye} - O - \text{Cell} + X^-$), or an activated C = C bond which is able to add to a hydroxyl group of cellulose ($-CH{=}CH_2 + \text{Cell} - OH \longrightarrow -CH_2-CH_2 - O - \text{Cell}$).

Thus the majority of reactive dyes can be distinguished into two categories by their reaction modes as:

CHART - 1

Major Commercial Types Of Reactive Dyes in Cellulose

STRUCTURE	COMMERCIAL NAME	FIRM	YEAR OF INTRODUCTION
	Procion	ICI	1956
	Procion-H	ICI	1957
	Cibacron	CIBA	1957
)$-SO_2CH_2CH_2O\cdot SO_3Na$	Remazol	Hoechst	1958
	Reaclon	Geigy	1959
	Drimaren	Sandoz	1959
	Levafix E	Bayer	1961
	Levafix P	Bayer	[illegible]

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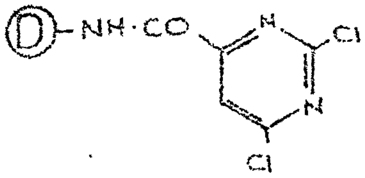
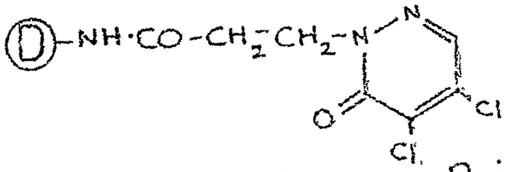
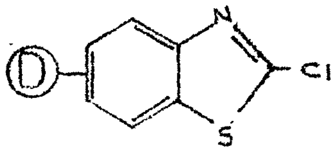
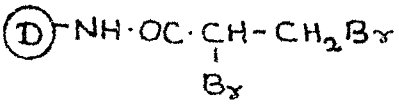
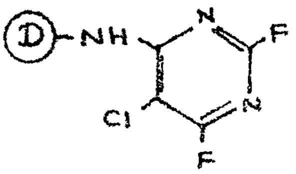
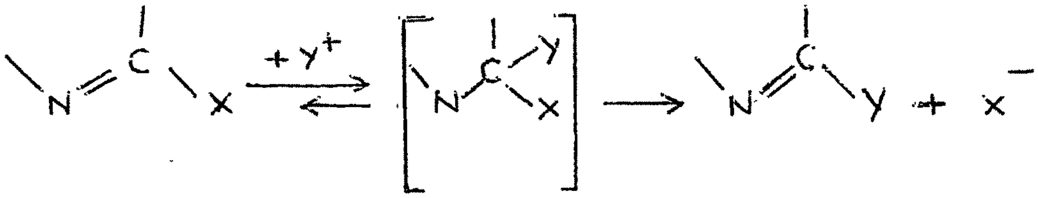
STRUCTURE	COMMERCIAL NAME	FIRM	YEAR INTRODUCED
	Reactofil.	Geigy	196[illegible]
	Primazin P	BASF	1964
	Elisiane	Francolor	1963
Ⓓ$-SO_2-NH\cdot CH_2CH_2\cdot O\cdot SO_3Na$	Levafix	Bayer	1958
Ⓓ$-NH-OC-CH_2-CH_2\cdot SO_2\cdot C_6H_5$	Solidazol	Cassella	1964

CHART - 2

MAJOR COMMERCIAL TYPE OF REACTIVE DYES FOR WOOL AND POLYAMIDE

STRUCTURE	COMMERCIAL NAME	FIRM	YEAR INTROD.
—	Procinyl	ICI	195[illegible]
1:2 Metal complex dye- $-NH \cdot OC \cdot CH = CH_2$	Procilan	ICI	19[illegible]
 $\text{D}-NH \cdot OC \cdot \underset{Br}{CH} - CH_2Br$	Lanasol	CIBA	1966
	Verofix	Bayer	197[illegible]
	Drimalan F	Sandoz	1970

(i) nucleophilic addition - elimination dyes



(ii) nucleophilic addition dyes

$$-CH = CH_2 \overset{+y^-}{\rightleftarrows} -\overset{-}{C}H-CH_2-y \overset{+H^+}{\rightleftarrows} -CH_2-CH_2-y$$

The general formula of a reactive dye is given as

s - C - b - R

Where 's' is a water solubilizing group. Generally $-SO_3Na$ and $-COONa$ groups are used as a water solubilizing group. 'b' is a bridging group which links together chromophoric 'C' and reactive 'R' systems. The commonly used bridging groups are $-NH$, $-C-$, $-CH_2O-$, $-\underset{CH_3}{\underset{|}{N}}-$ etc. The bridge unit is affecting to a great extent the reactivity of the dye and the tendency of the corresponding dyeing to hydrolyze.

Chromophoric system 'C' is mainly responsible for the colour of the dye. Various types of shade can be obtained by changing the chromophoric system. From the large number of suggested chromophoric systems, azo, anthraquinone and phthalocyanine derivatives have achieved greatest economic importance up to the present date. 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 mainly from 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 shades.

'R' is a reactive group. The dye-fibre compound may have the properties of an ester or ether; the precise nature and stability of the dye-fibre bond will depend on the reactive group.

A brief literature survey of the development in this field is discussed here. However, it has not been considered necessary to include a generalised review of the reactive dyes, because this subject has been dealt with in considerable details by Venkataraman (24), Beech (25) and others (26-34).

1:4. VARIOUS REACTIVE SYSTEMS:

Reactive systems can broadly classified as aliphatic, aromatic and heterocyclic reactive systems. In the following section relevant publications are dealt with in accordance with the scheme adopted by Venkataraman (24) for the reactive groups.

1:4:1. Aliphatic Carrier Systems of Labile Groups:

1:4:1:1. Substituted Alkane Monocarboxylic Acid Amides.

The first genuinely reactive dye for wool placed on the market was Supramine Orange R(35). The unusually high wet fastness is due to reaction between the labile chlorine atom of chloroacetylamino group and the amino groups in the wool fibre. The dyeing of cellulosic fibres with dyestuffs containing chloroacetylamino groups was first described by BASF in 1957 (36) and later by other firms (37,38). The use of chloroacetylamino groups together with other aliphatic carbonamide systems, is claimed predominantly by Japanese firms in special dyes (39-42). Dyes containing β-chloropropionylamino groups are recognised as wool reactive dyes (43,44). α,β-Dihalopropionamides were developed by CIBA in cellulose-reactive dyes (45). The use of dichloro or dibromo-propionic acid is claimed in a number of new dyes (46-48). Among other substituted aliphatic carboxylic acid amides, substituted isobutyric acid amides are claimed as new reactive components (49).

In a BASF patent relating to β-sulphonylpropionamide dyestuffs, sulphonyl group is described and claimed in anthraquinone, azo and phthalocyanine dyes (50) (chart-3).

Recently Guise et al. have suggested the isothiouronium system, which has long been known as a wool-reactive group possess improved properties in the β-isothioureidopropionalide residue ($-C_6H_4-NHCOC_2H_4-SC(NH_2)_2^+$) (51).

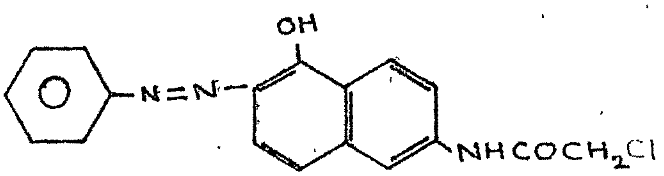
1:4:1:2. Substituted Alkane Monocarboxylates.

This new reactive dyestuff group was discovered in 1962 by General Aniline and Film Corporation. In such dyes saponification of propionic ester bond is taking

CHART-3

1:4:1:1 SUBSTITUTED ALKANE MONOCARBOXYLIC ACID AMIDES

REFERENCE



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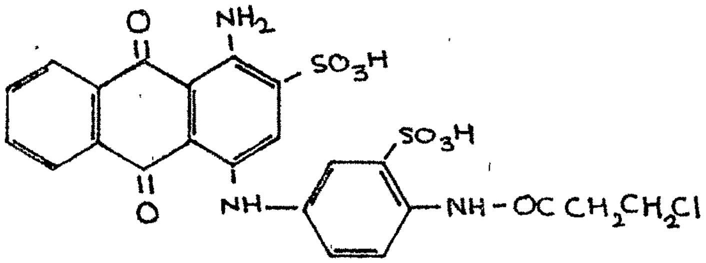

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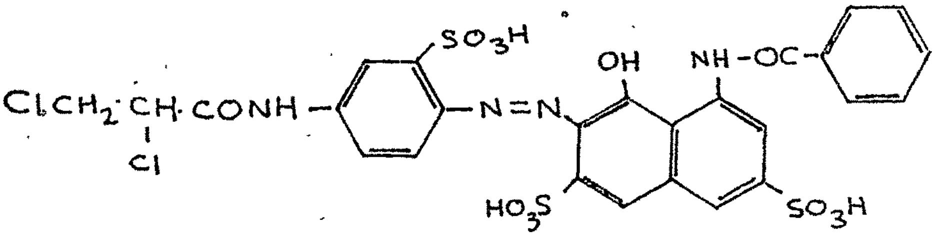

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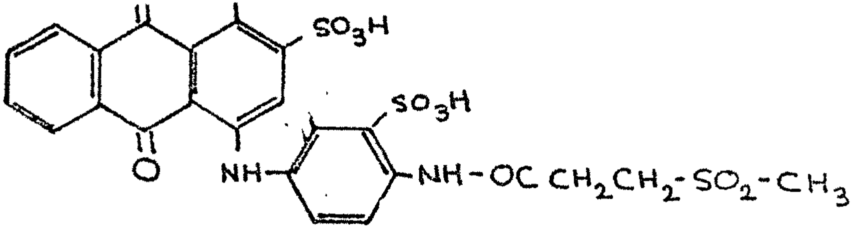

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place resulting in the fixation yield and fastness to washing (52) (chart-4).

1:4:1:3. Substituted Cycloalkane Carboxamides.

From ethylene tetrafluoride and acrylonitrile or -cyanobutadiene or their derivatives, fluorocyclobutane-carboxamides are obtained (53), which are useful reactive dyestuff group. **Farbwerke** Hoechst has claimed number of patents on this group (54) (chart-4).

1:4:1:4. Substituted Aliphatic Ketones.

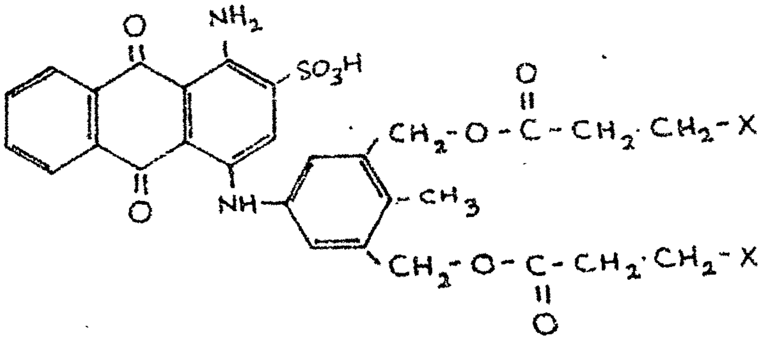
It was recognised by BASF in 1957 (55) and General Aniline in 1962 (56) that chloromethyl or β-chloroethyl aryl ketone groups posses good reactivity with cellulose (chart-4). Disperse dyes derived from ω-chloro-4-aminoacetophenone have been investigated with respect to their dyeing properties on polyester blends (57).

1:4:1:5. Amides of Substituted Aliphatic Sulphonic Acids.

The dyes containing chloromethyl sulphone group is claimed to react with cellulose with difficulty and in moderate yield (58). In 1958 BASF patented

CHART-4

1:4:1:2 SUBSTITUTED ALKANE MONOCARBOXYLATES REFERENCE



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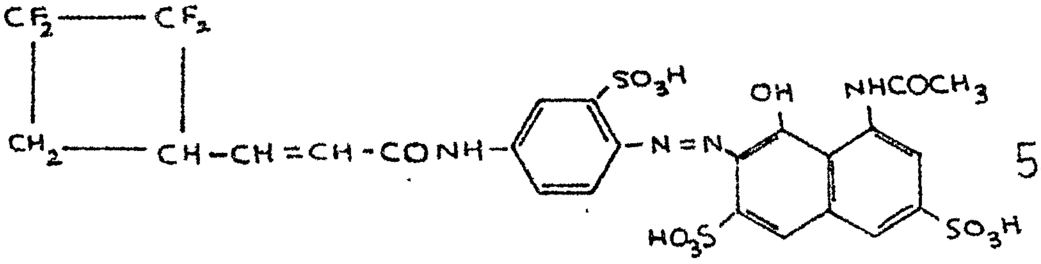
1:4:1:3 SUBSTITUTED CYCLOALKANE CARBOXAMIDES



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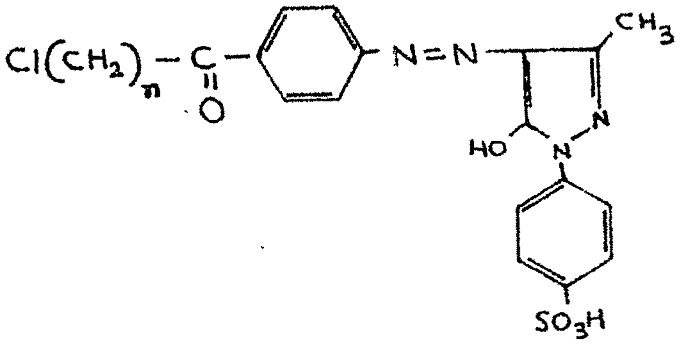
1:4:1:4 SUBSTITUTED ALIPHATIC KETONES



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vinylsulphonamide group as cellulose reactive group (59) (chart-5).

1:4:1:6. β-substituted Ethyl Sulphones-Vinyl Sulphones.

The following reactive systems are frequently referred to as 'Vinyl Sulphones' to simplify matters, though strictly speaking they are vinyl sulphone intermediates.

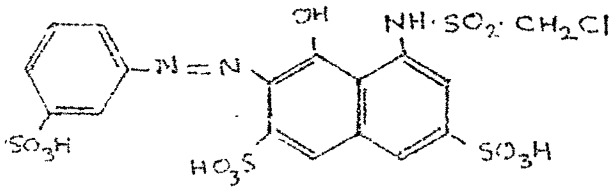
For this reason, the majority of papers and patent specifications refer to a multitude of β-substituents (X), which are quite easy to eliminate, e.g. X- = Cl-

Reactive dyes containing β-haloethyl sulphone groups are recommended by CIBA for the dyeing of cellulose (60). Generally, β-substituent X- = Cl-, $(Alkyl)_2N$-, HO_3SS-, H_2O_3PO-, but primarily HO_3SO is used. In the case of azo dyes the vinylsulphone group is usually substituted directly into the aryl nucleus of the diazo component or (sometimes) that of the coupling component. In a number of patents, however, bridges are included e.g., -NH-, $-(CH_2)_n-$, $-CONR(CH_2)_n-$, $-SO_2NRAryl-$, -CONRAryl-, -NRCOAryl-, and $-NRSO_2Aryl-$, between the aryl nucleus and the vinyl sulphone group. In this

CHART - 5

1:4:1:5 AMIDES OF SUBSTITUTED AIPHATIC SULPHONIC ACIDS

REFERENCE



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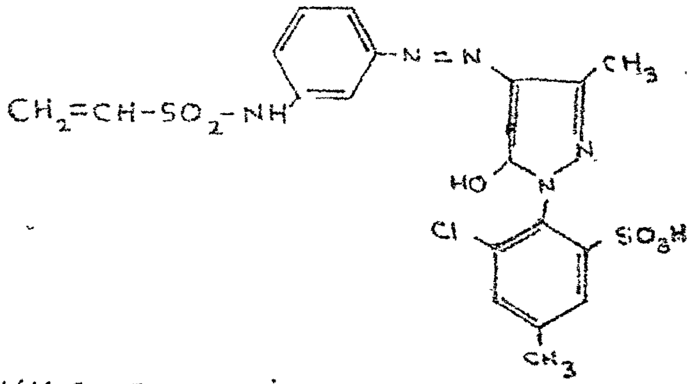

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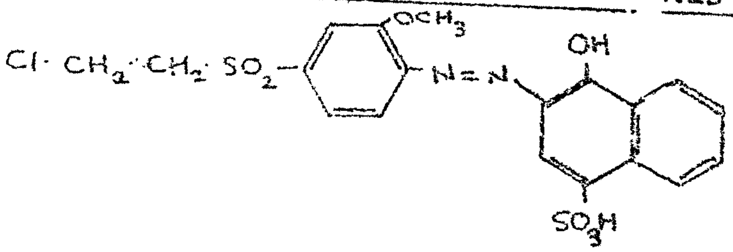
1:4:1:6 β-SUBSTITUTED ETHYL SULPHONES-VINYL SULPHONES



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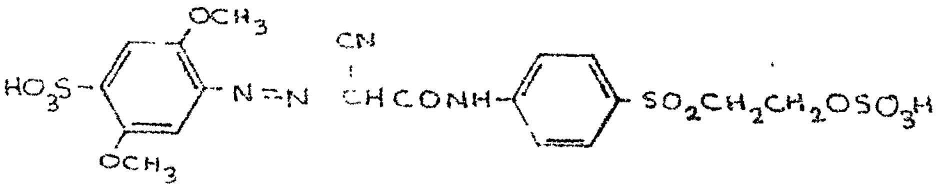

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connection references must be made to a large number of the patents-primarily from Farbwerke Hoechst, as well as Sumitomo and other Japanese firms - covering this reactive group (61-67) (chart-5). In some reviews, attension is focussed on the development of vinyl sulphone dyes and their general fields of application (68-73).

1:4:1:7. β-Substituted Ethylamine Derivatives.

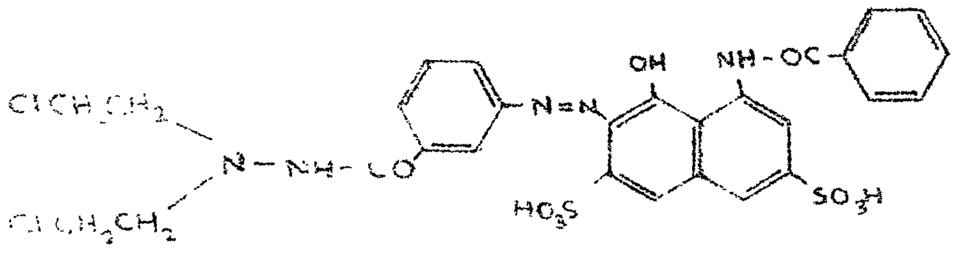
In 1956 dyestuffs containing β-haloethylamines group for dyeing cellulosic materials was described by BASF (74). The N, N-bis(β-chloroethyl)-hydrazide group claimed by Sandoz is interesting from chemistry point of view (75). Thus all ethylamine derivatives, containing a group in the β-position which is capable of splitting off together with the bonding electron pair under alkaline medium, have been mentioned as reactive groups used in reactive dyes for the dyeing of cellulose, nylon and wool (chart-6).

1:4:1:8. β-Substituted Ethylamides of Sulphonic Acids.

ICI recognised that the water-soluble dyes containing N-β-haloethylsulphonamide groups are fixed on

CHART-6

1:4:1:7 β-SUBSTITUTED ETHYLAMINE DERIVATIVES



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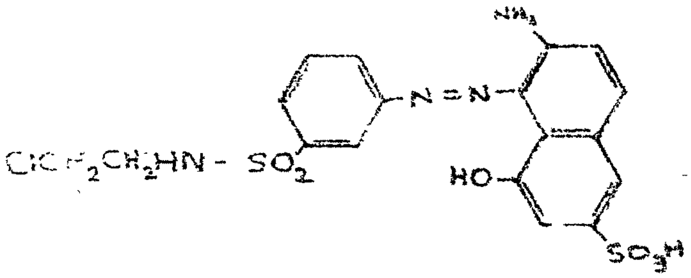
1:4:1:8 β-SUBSTITUTED ETHYLAMIDES OF SULPHONIC ACIDS



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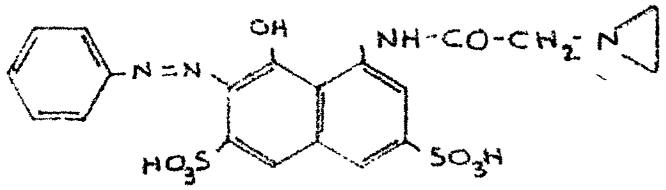
1:4:1:9 ETHYLENEIMINE DERIVATIVES



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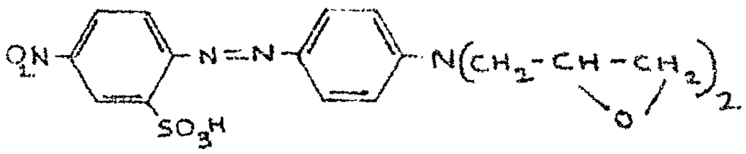
1:4:1:10 EPOXIDE DERIVATIVES



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cellulosic fibres from an aqueous alkaline medium shades which possess excellent wet-fastness properties (76) (chart-6).

1:4:1:9 Ethyleneimine Derivatives

Water-soluble reactive dyes containing an ethyleneimine residue have been described by CIBA (77), (chart-6). C-linked aziridines as reactive groups are usually obtained by condensation with primary aliphatic amines or ammonia (78). The dyes may be subjected to ring opening by means of H^+ and may polymerize, they also represent interesting reactive dyes for fibres containing -NH-groups. They are able to combine with cellulosic fibres in the presence of resin-forming agents and acid catalysts at 100-170°C.

1:4:1:10 Epoxide Derivatives

This reactive group, which is not successful in practice, was developed by CIBA, BASF and Bayer (79).

These compounds and their precursors, e.g. special variants of the epichlorohydrin group ($-CH_2CHOH-CHCl-Cl$ and $CH_2-CHOH-CH_2-CCl_3$) are claimed for incorporation in disperse dyes for synthetic-polymer and semi-synthetic fibres (80) (chart-6).

1:4:1:11 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 (81). These groups - particularly the corresponding chlorides-were developed intensively by BASF (82), (chart-7).

1:4:2 Aromatic Carrier Systems

Due to the equivalence of the groups N and O_2N-C with regard to the activation of halogen atoms in the o- or p- position in heteroaromatic or aromatic rings, the aromatic carrier systems are rarely used. The virtual absence of papers on the use of well known aromatic carrier systems shows that they are of little practical importance. Some of interesting systems are given in chart-7 (83-90).

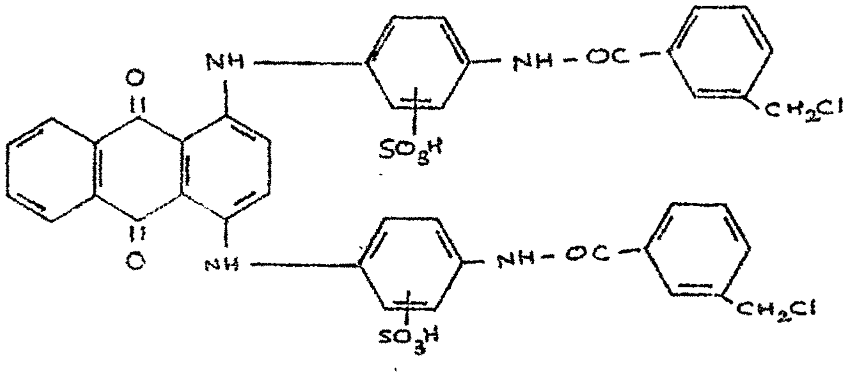
1:4:3 Heterocyclic Carrier Systems

1:4:3:1 Five - Membered Heterocycles

Numerous references are available in patents for the use of reactive halogeno heterocyclic systems of five

CHART - 7

1:4:1:11 ALLYL, PROPARGYL AND BENZYL DERIVATIVES



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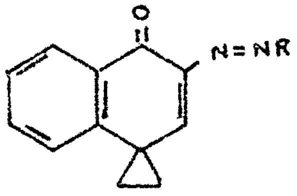
1:4:2 AROMATIC CARRIER SYSTEMS



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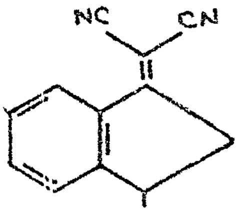

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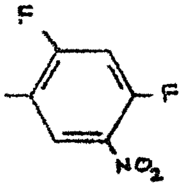

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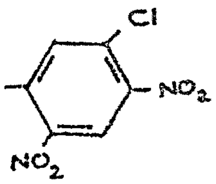

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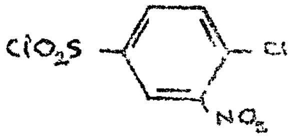

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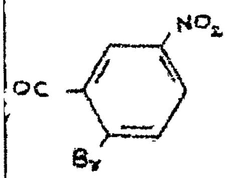

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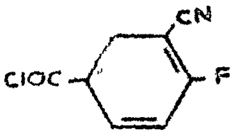

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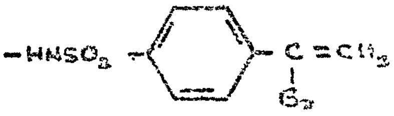

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members and their benzo derivatives, the most important of which is 2-halogeno-benzothiazole (91), (chart-8).

1:4:3:2 Pyridine Derivatives

Halogen substituents attached to pyridine or quinoline systems are not sufficiently reactive to form covalent bonds with cellulose under normal dyeing or printing conditions unless suitably situated electron-attracting groups are also present in the ring to give enhanced reactivity. By condensation of amino dyestuffs with 3,5-activated 2,6-dichloro-pyridine derivatives, easily fixed reactive dyes are obtained (92), (chart-8).

1:4:3:3 Pyridazine Derivatives

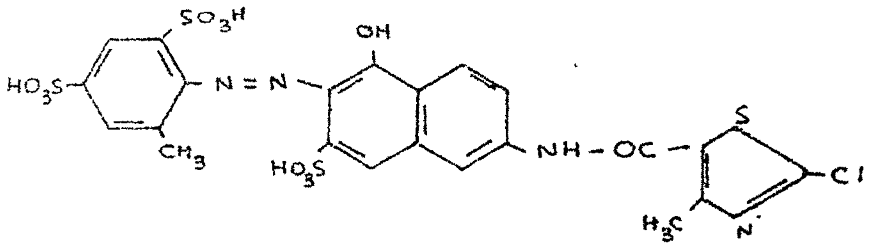
Dyestuffs containing chloropyridazine groups are suitable for the printing and continuous dyeing of cellulosic fibres with subsequent fixation in dry heat or in steam (93), (chart-8).

1:4:3:4 Pyridazone Derivatives

This reactive group has been comprehensively described by Hensel and Lutzel (94). The commercial production of the Primazin-P dyestuffs, based on this

CHART-8

1:4:3:1 FIVE MEMBERED HETEROCYCLES



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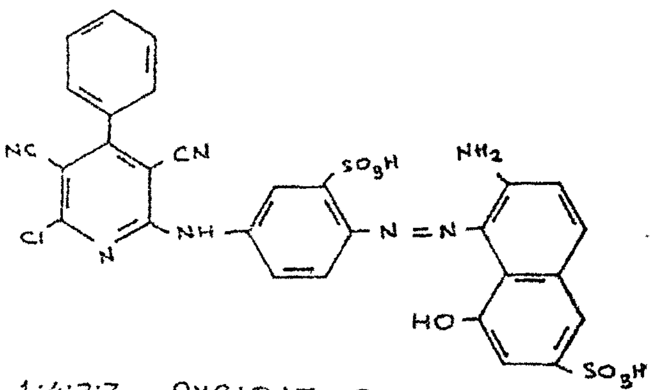
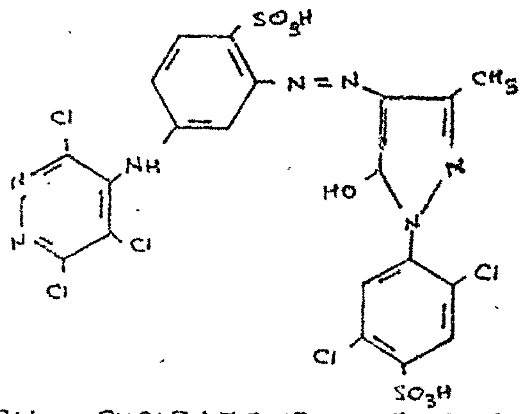
1:4:3:2 PYRIDINE DERIVATIVES



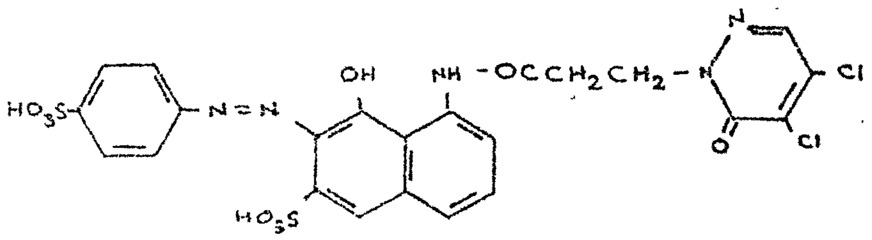
92

1:4:3:3 PYRIDAZINE DERIVATIVES



93

1:4:3:4 PYRIDAZONE DERIVATIVES



95

reactive group is claimed by BASF (95) (chart-8).

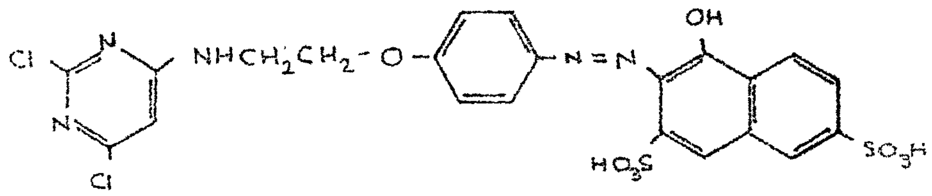
1:4:3:5 Pyrimidine Derivatives

These are used as the reactive component in many commercial ranges-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 the less reactive monoamino-monohalogen stage dyeings stability to hydrolysis doesn't attain this of pyrimidyl-cellulose bonds. Some of representative dyes are shown in chart-9.

Becuase of their economic importance, formazanes (101) and azo dyes (102) are claimed primarily in the fluoropyrimidine range. The literature revels on general aspects of their uses (103,104), particularly on cellulosic fibres (105-107), nylon and wool (108-110) have been published. Control of the reactivity of the 5-substituted difluoropyrimidylamine

CHART - 9

1. 4 3:5 PYRIMIDINE DERIVATIVES



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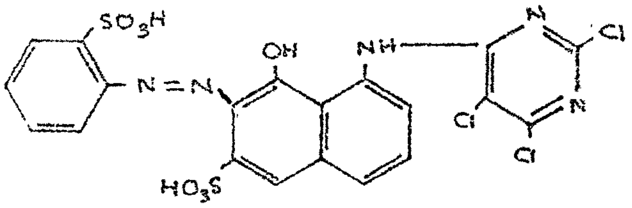

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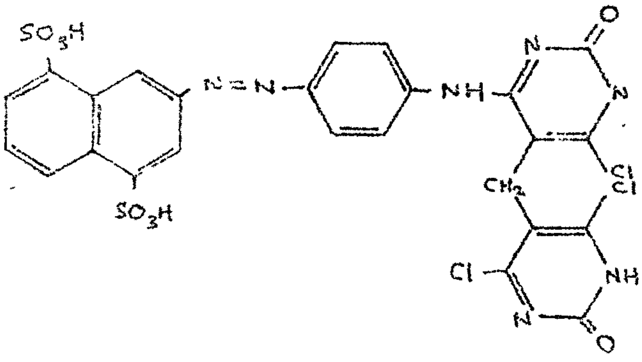

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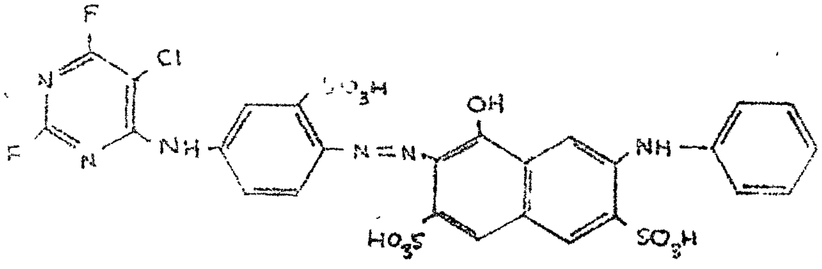


100

reactive group is achieved by replacing one fluorine atom by an O- or S- ethyl, aryl or heteryl group (111).

1:4:3:6 S-Triazine Derivatives

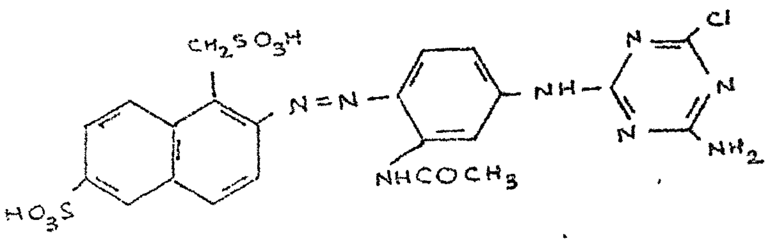
These dyes, based on s-triazine reactive systems, are, for simplicity frequently termed 'triazine dyes'. Triazine reactive systems with two leaving groups are usually very sensitive to hydrolysis. By replacing either of these groups with a suitable group, an attempt was made to influence the stability of the remaining leaving group. At the same time, the solubility and the affinity of the dyes for a particular substrate were improved. Incidentally, further reactive systems can be introduced via this remaining leaving group.

The various aspects of triazine dyes are published by several workers (112-119). Generally there are four types of s-triazine derivatives : monohalo- and dihalosubstituted s-triazines, halo-substituted s-triazines with non-imino bridge links, and s-triazines with mobile groups other than halogen. Examples of reactive dyes, based on this group, recently claimed by different firms are given in chart-10.

1:4:3:7 Benzazole Derivatives with Reactive Mobile Groups in the 2-Position.

CHART-10

1.4.3.6 S-TRIAZINE DERIVATIVES



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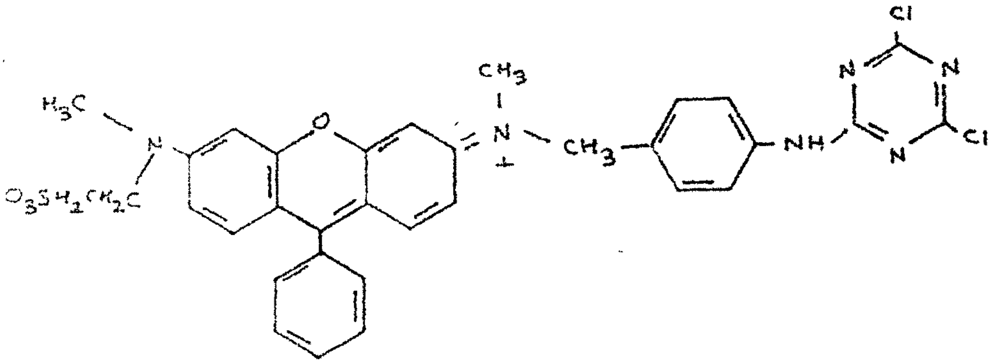

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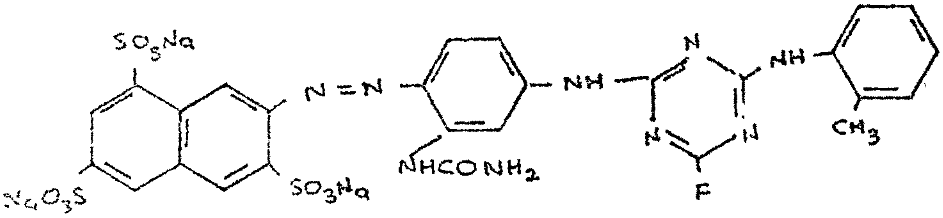

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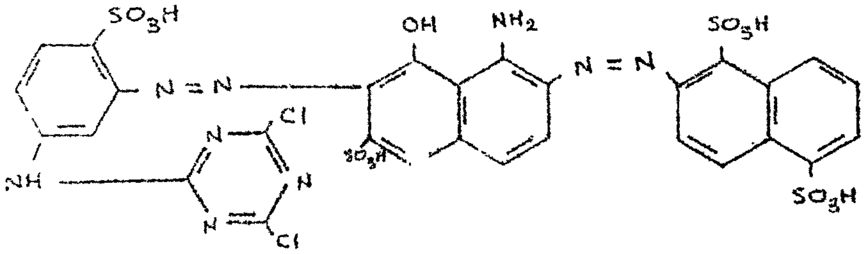


123

All benzazoles (benzoxazole, benzothiazole, benzoselenazole, benzimidazole, indolone-(3) with all important mobile groups in the 2-position are claimed as reactive components (124-126).

1:4:3:8 Quinoxaline Derivatives

Only one dichloroquinoxaline having both chlorine atoms in the hetero ring is possible viz. 2,3-dichloroquinoxaline. It has been found difficult to condense this compound satisfactorily with amino-containing dyebases. It is known that replacement of one chlorine atom by a substituted amino group powerfully deactivates the other, so that even if dyes of this type were easy to prepare, their reactivity would almost certainly be too low to be practically useful (127, 128).

It is, however, possible to introduce chlorocarbonyl or chlorosulphonyl groups into the carbocyclic ring of 2,3-dichloroquinoxaline comparatively easily, the most readily accessible compounds being 2,3-dichloroquinoxaline-6-carbonyl chloride and 2,3-dichloroquinoxaline-6-sulphonyl chloride; and as the chlorine atom borne by the carbonyl or sulphonyl group is considerably more reactive than those attached to the hetero ring, it is possible to condense these compounds with amino-containing dyebases to form reactive dyes, as indicated in chart-11.

1:4:4 Acid Derivatives as Reactive Groups

In contrast with the commercial products, acid derivatives, with heterocyclic and aliphatic carrier systems, have found no practical application up to the present date. This may be explained by an excessive 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. Some examples are shown in chart-11.

1:4:5 Formaldehyde Derivatives as Reactive Groups

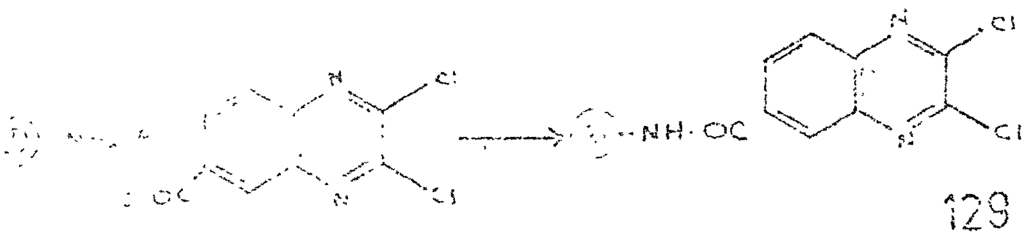
These derivatives have virtually failed to achieve any practical significance. BASF has claimed the dye for cellulose with good wet-fastness properties (132), (chart-11).

1:4:6 Other Reactive Groups

The dyeing of the more hydrophobic synthetic-polymer fibres with reactive dyes is described.

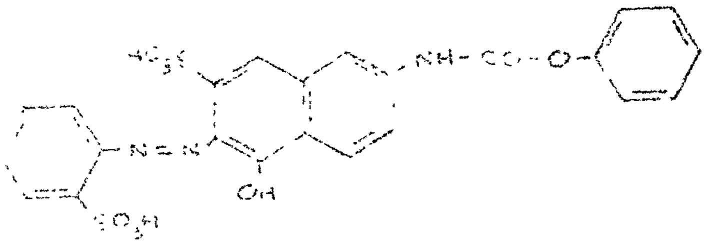
CHART - II

[illegible] QUINOXALINE DERIVATIVES



129

[illegible] ACID DERIVATIVES



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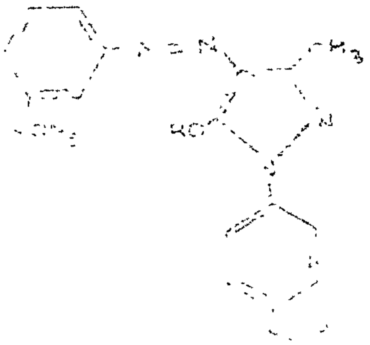
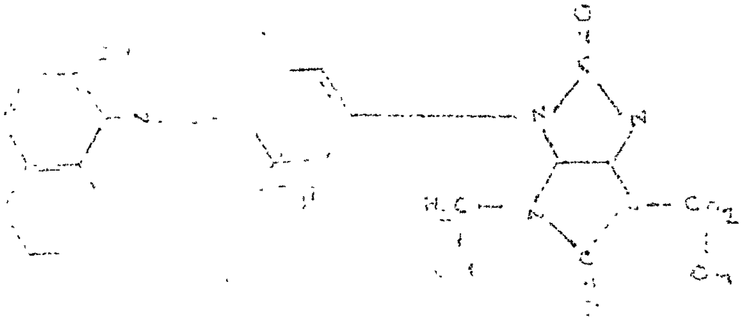


131

[illegible] FORMALDEHYDE DERIVATIVE



132

1:4:6:1 Reactive Centres Giving Rise to Nitrenes and Carbenes

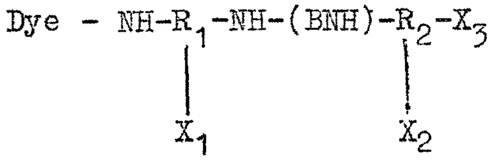
Dyes, having sulphonylazide group (133), particularly in reaction with -CH in hydrophobic fibres, as well as colouring systems with other nitrene formers viz. $-N_3$, $-OCON_3$, $-NSO_2N_3$ and $-SON_3$ or carbene formers eg.$-SO_2CHN_2$, $-COCHN_2$, $-CHR_2$, CR_3 (where R = Cl, Br or I) (134) and diazomethane triazines (135) have been patented. Tilak et al. have mentioned the importance of azides as reactive group (136). Recently they have synthesized dyes containing sulphonazide groups, which react with inert fibres such as polyster fibres which have no reactive functional group (137). This work has opened up many fascinating opportunities for synthesis of tailor-made polyester fibres. Very recently dyes containing aliphatic amino end groups for polyester fibres via transmidation is described (138).

1:4:6:2. Aliphatic Double Bond Systems as Reaction Centres.

These systems are of considerable interest. From a number of patents which have been published in the past few years, it can be seen that in the beginning of 1968 ICI were experimenting with polymerizable dyes(139).

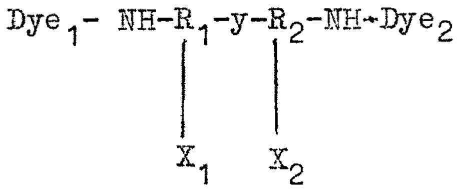
1:4:7. Dyes Containing Several Reactive Groups

Dyes with more than one reactive group have been known for a long time. They have, however, gain the importance during the past few years to achieve an increase in the fixation yield. Consequently, it is also not surprising that a number of special polyfunctional reactive groups or dyes have been patented. Dyes containing several chloro-s-triazinylamino groups are particularly important (140-141). In such dyes, dyes structure are:



$$\text{Dye} - \text{NH}-\underset{\substack{|\\X_1}}{R_1}-\text{NH}-(\text{BNH})-\underset{\substack{|\\X_2}}{R_2}-X_3$$

or



$$\text{Dye}_1 - \text{NH}-\underset{\substack{|\\X_1}}{R_1}-y-\underset{\substack{|\\X_2}}{R_2}-\text{NH}-\text{Dye}_2$$

where Dye = colouring system, R = reactive hetrocyclic group, X = leaving groups, B or y = bridges.

1:4:8. Dyes Applied in Conjunction with Separate Reactive Components.

The so-called 'two-component' systems have not yet gained a firm foothold, but examples of new polyfunctional linking agents are appeared. Of particular interest is a new method for the fixation of phosphonic acid dyes, which react in the presence of a carbodimide under acidic or weakly alkaline conditions via pyrophosphorous acid (142).

1:5. CHROMOPHORE SYSTEMS

In combining chromophores and reactive systems to produce a reactive dye, the properties of each are affected by the other. Care is needed to keep unfavourable effects to a minimum and at the same time to achieve maximum tinctorial strength, to adapt the solubility and affinity to suit the substrate, to improve resistance to finishing agents, and to impart good fastness properties. In the following section only some recent developments are discussed.

Phenazines (143) and derivatives of triphenodioxazines (144) have been quoted as new chromophores for reactive dyes. For yellow dyes of the pyrazolone type, 3-methyl (145) or 3-aryl-5-iminopyrazolones (146) are being used at present as well as 3-sulphonemethylpyrazolones

(147). Pyridones have gained importance as new components for yellow dyes. Apart from 4-alkyl-6-hydroxypyrid-2-ones (148), many 3,4-disubstituted pyridone compounds are described (149-152).

Of the acetoacetic acid arylide and analogous reactive dye types, those with acetoacetyl-p-phenylenediaminedisulphonic acid (153) and with cyano- or carbonamido acetic acid arylides as the coupling component (154) are noteworthy.

2-Aminonaphthalene-1-ω-methanesulphonic acid and its derivatives are mentioned as diazo components in various reactive dyes (155,156). In red to yellow monoazo dyes, naphthols are used as coupling components with diazotated unsubstituted β-sulphatoethylsulphonylnaphthylamines (157).

In some brown to violet vinylsulphonedisazo dyes, the monoazo dyes, which are obtained by coupling aminobenzene derivatives to 1-naphthylamine-6-(or 7) sulphonic acid, are further coupled to naphthols or acylaminonaphthols (67). Other brown reactive dyes have aromatic aminohydroxy compounds as double coupling components, e.g. 2-phenylamino-8-hydroxynaphthol-3,6-disulphonic acid (158).

To produce highly light fast reactive dyes in the shade range of yellow, rubine, violet, blue, brown, olive, and black, metal complexes obtained from o,o'-disubstitued azo compounds are mainly used. Reactive dystuffs are synthesised not only from copper complexes, which are used mainly as direct cotton dyes, but also from chrome and cobalt complexes. Asymmetrical 1:2 Cr-complexes (159) which contain H-acid as the diazo component and asymmetrical 1:2 Co-complexes (160) have been described.

1:6 PROPERTIES AND APPLICATION OF REACTIVE DYES

1:6:1 Relation Between Molecular Structure and Reactivity

Simultaneously with its reaction with the fibre, the reactive dye molecule undergoes hydrolysis by the water of the dyebath. The efficiency of the dyeing process has therefore been defined as (rate of fixation)/(rate of hydrolysis), which is proportional to Kf/Kn, where Kf and Kn are the first-order or psudo-first-order rate constants of the fixation and hydrolysis reaction (161). The reactivity of a given dye, or the above expression for the dye-fibre-water system, is governed by the nature of the reactive group. The first-order rate constants for the hydrolysis of a series of dyes having the same chromogen attached to different reactive systems illustrate the wide variation between dyes incorporating different reactive groups (162).

Assessments of the reactivities of whole ranges of reactive dyes have been published (163). The reactivities of dyes in each particular range are designed to be similar, though in fact quite wide variations within ranges do occur (164).

The Procion M (ICI) dichlorotriazinyl dyes have been shown to possess two different reactivities for water, one at low and the other at high concentrations of OH^- (165). This has been interepreted by Horrobin as being due to ionization of the bridging group (166). This has been claimed as an advantage in practice, since the substantivity of dichlorotriazinyl dyes is often low in the pH range 10.5 - 12.5 at which point the dyes have acquired an adequate degree of reactivity (167).

The reactivities of all dyes are increased with increase in pH and temperature, and in dyeing applications, many factors must be considered in choosing between dyes of high and low reactivity (163). Generally speaking, high reactivity is economically desirable, e.g., in continuous dyeing methods, where highly reactive dyes require shorter steaming times or shorter batching times.

1:6:2 Substantivity and Diffusion Properties

Since the efficiency of a reactive dyeing is determined by the ratio (rate of fixation)/(rate of hydrolysis), and since the fixation rate depends ultimately on the concentration of absorbed reactive dye, high substantivity or affinity might be considered a desirable feature in reactive dyes. However, in order to achieve suitable standards of wetfastness and levelness, most reactive dyes have only low to medium substantivity, representing a compromise between the parts played by that property in influencing the kinetics of the dye-fibre reaction, where a high value is desirable, and the requirement that hydrolyzed dye should be easily removed by washing, which demands a low value. The overall structure of the dye regulates substantivity and diffusional properties largely through the molecular weight and steric effects within the chromogen, as well as influencing other physical properties such as dye aggregation in solution.

1:6:3 Application of Reactive Dyes to Cellulose by Batch Method

Despite their early development for continuous processing, it has been estimated that 65% of chlorotriazinyl dyes sold in 1970 were used in batch processing (168), and in this area, a relatively high substantivity is desirable, low substantivity dyes giving high yields only when applied by pad methods. The desire for high substantivity for efficient fixation coupled with good washing off properties to remove unfixed dye has resulted in the development of the Procion H-E (ICI) dyes (168). This consideration of balance between high and low substantivities and different levels of reactivity is also applied in general way to Remazol ranges, which are based on the reactivity of the vinysulphone group. These dyes have lower alkali stability than the chlorine containing heterocyclics, and reaction with the fibre cannot take place until the reactive vinylsulphone is formed. The importance of the rate at which the latter is produced using different precursors has been described by van der Eltz (169).

1:6:4 Use of Reactive Dyes in Printing

The requirements of a reactive dye that make it suitable for application by printing have been given as (i) high solubility (ii) low substantivity, coupled with good diffusional properties; (iii) high degree of fixation ; (iv) reactivity high enough to achieve good fixation, but low enough to ensure print paste stability in all-in printing methods (170).

The fixation of prints of reactive dyes to cellulosic textiles is carried out in two ways, by (a) one-phase printing method and (b) two-phase printing method. The printing aspects with reactive dyes has been given by Stead (171) and Davies (172).

1:6:5 Reactive Dyes for Wool

Though reactive dyes for wool were commercially available before the introduction of the first Procion dyes for cellulose, they have become widely used only in the last ten years. The main practical difficulties facing the dyer in early trials were an unacceptable degree of unlevelness and inefficient removal of unfixed dye during subsequent washing. This was the result of incomplete reaction of dye with the fibre. The reasons for this are reviewed by Hildebrand and Meier (173). One approach to the improvement of the level-dyeing properties of reactive dyes on wool has been to modify the structure of the reactive group so that it forms only during dyeing. Particularly suited to this modification are the vinylsulphone precursors, typified by the Hostalan (FH) dyes (174). By dyeing at pH 5, the Hostalan dye is slowly converted to the reactive vinylsulphone at the boil. Recently 'masked' isocyanate group is incorporated into the dye molecule to give level dyeings of the required depth (175). Isocyanates react readily with nucleophiles, such as water, alcohols, amines, etc.

$$R-N=C=O \quad + \quad H\text{-}NuC \rightarrow RNHCO\text{-}NuC.$$

The term 'Masked' means that the isocyanate is protected by a group which can be removed by a mild chemical treatment.

A very useful review of the dyeing of wool with reactive dyes has been published (176).

1:7 MISCELLANEOUS ASPECTS

A number of developments in the field of reactive dyes originate from ecological considerations, success in experiments to increase fixation and to eliminate rinsing would lead to a reduction effluent load. In this context it must be mentioned about the biological degradation experiments with vinylsulphone dyes (177), and the application of reactive dyes from solvents (178-180).

Reactive dyes with special properties are used in a wide variety of fields, e.g. for producing an antimicrobacterial effect (181-183), for dyeing gelatin in silver-dye bleaching processes (184), for the manufacture of non-staining reagents for amylase determination (185), in indicator materials (186) and as reagents for the identification of fibrous materials (187).

The light fastness of reactive dyes is governed by the depth of colour, by the type of dye-fibre bond (188) and by the substrate (189). Light fastness on nylon has been investigated with respect to dyes of various types (190) and as a function of dye fixation (191).

1:8 ANALYTICAL TECHNIQUES FOR REACTIVE DYES

1:8:1 Purification and Purity Determination of Reactive Dyes

Commercial reactive dyes are the homogeneous chemical compounds standardized for their end use. Pure reactive dyes are easily undergoing hydrolysis during storage and the first systamatic study of loss of reactivity on storage was carried out by Stephen (192).

For most of the analytical work, it is desirable and essential to purify the reactive dyes. For purifying reactive dyes diluents, buffers and different contaminants should be removed. For removing diluents the method reported by Robinson and Mills is used (193). The more convenient and quicker method for purifying the dyes is solvent-non-solvent technique (194-196). Recently Datyner and co-workers have purified reactive dyes by recrystallizing from a mixture of water-ethanol (197).

The purity of the dye can be checked by paper chromatography and thin-layer chromatography. A good amount of work on paper chromatography and thin-layer chromatography of reactive dyes is done by Sramek and is reviewed (198,199). For purity determination use of chromatography is made by different workers (200-204).

As reactive dyes have high substantivity for cellulose, in paper chromatography, large interference and restraint on the migration of a number of reactive dye is arised. In thin-layer chromatography no much interference arises. Perkavac and Perpar have studied thin-layer chromatography on silica gel with different solvent mixtures for several reactive dyes (203). They have concluded that better separation can be done by thin-layer chromatography than paper chromatography.

1:8:2 Visible and Infrared Spectra

After purity determination, the dye is subjected for its visible and i.r. spectra. Although it is difficult to establish the structure of a unknown dye from visible spectra alone, it is frequently possible to identify its chromophoric system, by comparing its visible spectra with that previously obtained for similar dyes or chromophores. Ofcourse, identical curve shapes are not proof of identity, although they are usually indicative of similar chromogens.

Using the i.r. spectra, the functional groups can be detected, also the groups involved in chromophore can often be detected. The pattern for recognising these groups remains the same as in the other cases. Some important groups in the reactive dyes are -N = N-, $-SO_2$, $-SO_3^-$ etc. The vibrations for -N = N- group are reported in the region 1450-1400 cm^{-1} (205,206). The SO_2 group, an important group in the vinyl sulphone reactive dyes, gives strong asymmetric and symmetric stretch bands. The SO_3^- group, present in nearly all reactive dyes, shows a strong broad absorption around 1200 cm^{-1}. It is generally accompanied by one or more, weaker and sharper bands in 1080-1010 cm^{-1} region (207).

1:8:3 Examination of Reactive and Chromophore System

Different reactive systems are split off from chromophores with varying degree of ease, according to the nature of bridging group. The reagents usually employed are hydrochloric acid or aqueous sodium carbonate. After splitting off two systems, they are characterized in the usual manner, by elemental analysis, and comparision of UV, visible and i.r. spectra.

1:8:4 Identification of Reactive Dyes on Fibre

Before deciding which type of reactive dye is on the fibre, first of all one has to decide what type of dye it is. There is no direct test for determining reactive dye on the fibre. So the possibility for other class of dyes has to eliminate. When the coloured fibre is boiled with 40% pyridine in a test-tube and if the colour is remained unchanged, then it can be reactive dye, azoic dye, sulphur dye or vat dye. All other dyes are soluble in boiling pyridine.

Now azoic dyes are soluble in cold chloroform solution. Vat and sulphur dyes can easily be reduced with sodium hydrosulphite, while reactive remains intact. Bode has published another method for distinguishing reactive dyeings (208); azoic, vat, and sulphur dyes are soluble in pure dimethylformamide while reactive dyes are insoluble.

Thus reactive dyes cannot be extracted from cellulosic fibres. So for determining what type of reactive dye it is, dissolution method for cellulose is used. For this dyed fibre is dissolved in 90% sulphuric acid, cadoxen (209,210) or zincoxen (211). After dissolving the fibre, the dye is isolated and identified by TLC, etc.

PRESENT WORK

In the present work, following investigations are carried out :

(i) Synthesis of reactive coupling components having -C-C- bridge system.

(ii) Synthesis of series of reactive dyes possessing -C-C- bridge system.

(iii) Evaluation of the synthesized reactive components for azoic dyeing of cotton and wool.

(iv) Determination of the efficiency of halo aromatic amines as diazo component in reactive azoic dyeing of cotton and wool.

(v) Optimisation of the dyeing conditions for cotton and wool with the newly synthesized reactive dyes.

(vi) Examining the dyed fibres for different fastness properties viz. washing, rubbing, light etc.

(vii) Study of the absorption spectra of dyed fibres in visible region of the light.

(viii) Assessing the possibility of solvent dyeing — non-aqueous dyeing of the dyes.

(ix) Study of the rate of hydrolysis of reactive coupling components.

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