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# HALOGENATED HETEROCYCLES IN REACTIVE DYES

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## *SUMMARY*

*The first reactive dyes for cellulose introduced 25 years ago were based on a dichloro-s-triazinylamino substituent. Since that time there has been a wide ranging investigation into the use of other heterocyclic ring systems and other labile atoms or groups. These are discussed in terms of their reactivity and the stability of the dye/cellulose reaction products.*

## 1. INTRODUCTION

It is of paramount importance that a dyed textile should have the property of being washable without dye being desorbed from the fibre in the washing process. To achieve such fastness to washing, it is necessary that there is some interaction between the dye and the fibre which will retain the dye on the fibre during laundering. Two such interactions are formation of a solid solution of a water insoluble in the fibre and formation of an ionic bond between an acidic group in the dye and a basic centre in the fibre or vice versa. The first of these interactions solves the problems of dyeing the many synthetic fibres which are plastic in nature, e.g. nylon, polyester and cellulose acetate. The latter solves the problems of dyeing fibres containing basic or acidic groups, e.g. wool, nylon and polyacrylonitrile.

Neither of these dye retention mechanisms can be applied to the cellulose based group of fibres which includes the largest tonnage fibre, cotton, since these fibres are not plastic in nature and do not contain any basic or acidic groups. Cellulose is amorphous, very hydrophilic and contains as functional groups only alcoholic hydroxy groups. Prior to 1956, dyeing of cotton depended upon one or other of two further dye retention mechanisms. In one of these, an insoluble dye was formed from water soluble precursors on the fibre and then caused to aggregate, physically trapping the dye within the fibre pores. Azoic and vat dyes functioned in this way.

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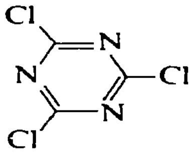
The other mechanism relied upon the formation of a multiplicity of hydrogen bonds between a long planar dye molecule and the fibre to hold a water soluble dye on the substrate. This was the retention mechanism in the case of direct dyes. The first mechanism gave good to excellent fastness at the cost of complex application procedures. The second gave easy application but poor fastness.

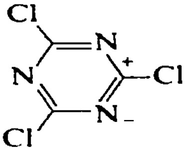
Thus there was a requirement for a type of dye which could be applied by a simple method and which would give excellent wash fastness. It had long been perceived that if a covalent link could be formed between the dye and the cellulose fibre the wash fastness requirement would be met. The difficulty lay in devising a simple method of doing this and it was this problem which was surmounted by the introduction of reactive dyes in 1956.

## 2. CHLOROTRIAZINE DYES

The first reactive dyes for cellulose were the initial members of what is now the Procion MX range.[1] They depend for their reactivity on a dichloro-*s*-triazinylamino group, the key intermediate in the introduction of which is cyanuric chloride (**I**). In this compound, the contribution of canonical forms such as (**II**) to the structure causes a deficiency of electrons on the ring carbon atoms. The greater electronegativity of chlorine compared with carbon polarizes the carbon–chlorine bonds (**III**) and enhances the positive charge on the ring carbon atoms.



(I)



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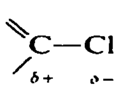
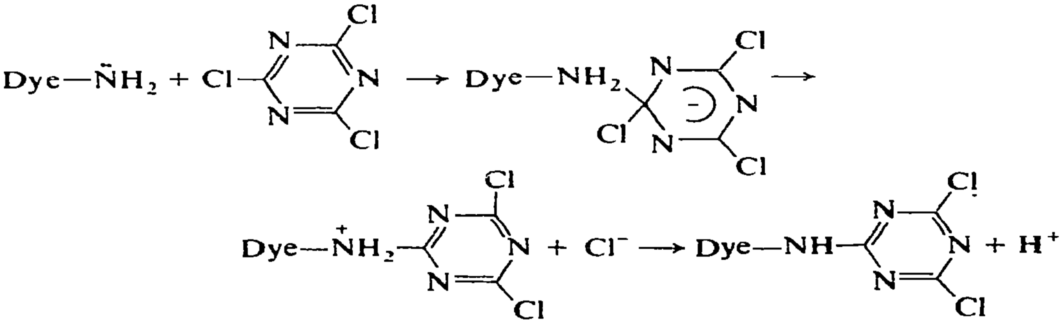


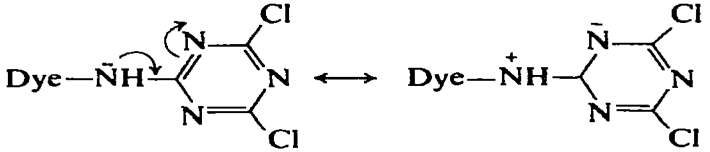
(III)

This makes the molecule susceptible to nucleophilic attack. If the attacking nucleophile is a dyestuff containing an amino group, reaction occurs thus:



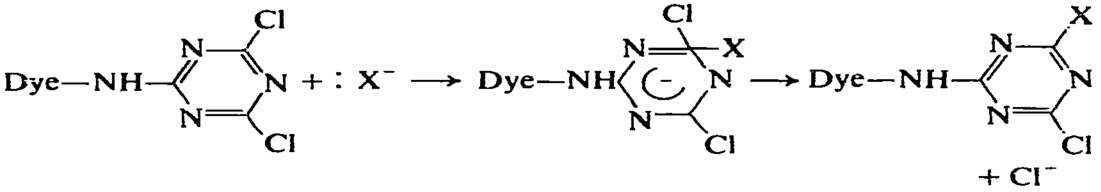
The resulting dye structure can be seen to consist of two distinct parts, the chromogen and the reactive system. The chromogen contributes the colour and so long as it contains a group, invariably amino, to which the reactive system can be attached, little else is required of it. This freedom of choice removes the need to use large dye molecules which had previously been a characteristic of water soluble cotton dyes. Very simple dye structure can be chosen, the emphasis being purely on the basis of shade and properties such as fastness to light. In practice the azo, anthraquinone and phthalocyanine chromogens predominate in the ranges of reactive dyes. All contain a number of sulphonic acid groups to confer the water solubility which is required to allow application from aqueous medium.

In the dichloro-*s*-triazinyl reactive group the influences which cause the high reactivity of cyanuric chloride persist although they are diminished by feedback of electrons from the bridging nitrogen atom into the triazine ring.

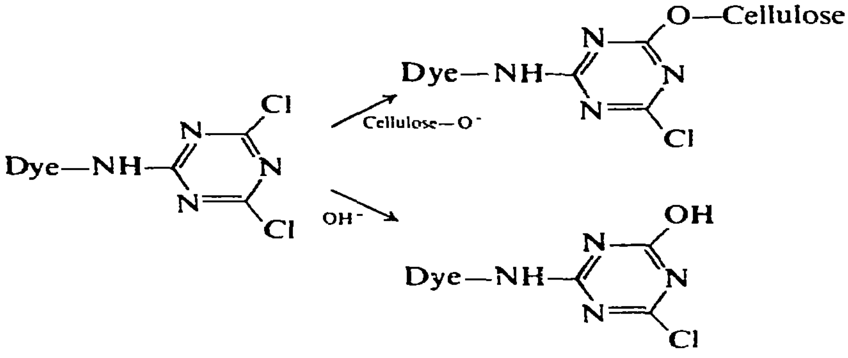


This diminishes the tendency to build up positive charge on the ring carbon atoms and lowers the level of reactivity compared with cyanuric chloride. Protonation can occur under acid conditions negating this effect and causing the lability of the chlorine atoms to increase markedly. The result is auto-catalytic hydrolysis which destroys the reactive system and it is to prevent this effort that buffer is incorporated into the dye powder.[2]

Although diminished in reactivity, the dichloro-*s*-triazinyl group is still readily susceptible to nucleophilic attack at temperatures of about 30–40 °C and it is upon this facility that the methods devised for dyeing cellulose fibres depends. In the exhaust dyeing method of application the dye is dissolved in water and, since nucleophiles are not present to any sensible extent at neutral pH values, the solution is quite stable. The cloth is immersed in the solution and salt (about 6 % on volume of solution) is then added causing the sulphonated dye to be driven out of the solution and adsorbed by the fibre. After these purely physical processes have taken place (about 30 min is necessary), alkali, usually sodium carbonate, is added to raise the pH to about 10·5. Now the nucleophiles necessary for reaction are present and attack on the dye takes place thus:



In this reaction scheme, the attacking species, $X^-$, can be either cellulose—$O^-$ leading to fixation of the dye on the fibre or $OH^-$ resulting in hydrolysis to give unfixed dye which is washed out of the cloth at the end of the dyeing process. These two reactions will be governed by the rate equations shown.

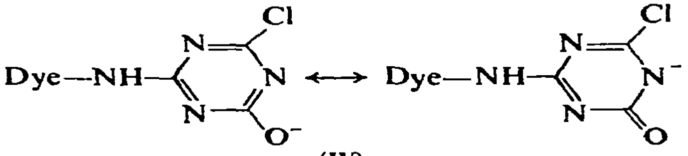


$$\text{Rate of fixation} = k_1\,[\text{Dye}]\,[\text{Cellulose—O}^-]$$

$$\text{Rate of hydrolysis} = k_2\,[\text{Dye}]\,[\text{OH}^-]$$

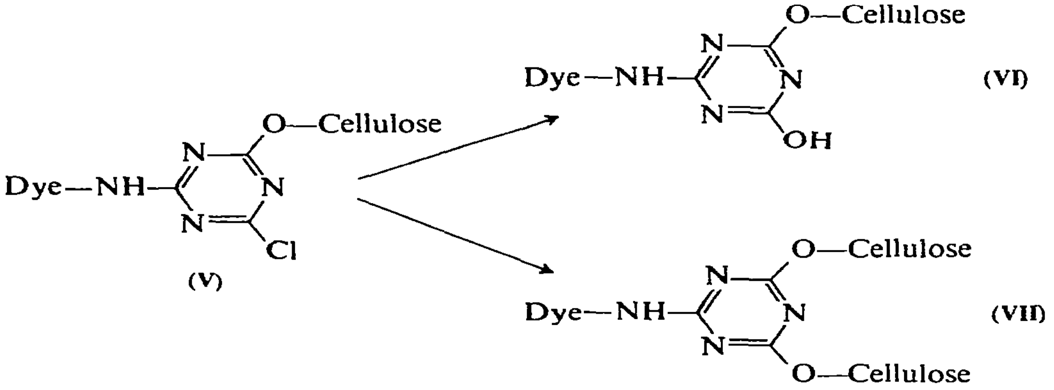
The rate constants for these two reactions are similar and thus give no inherent preference for fixation. All other things being equal, the large excess of water present (5–20 ml for each gram of cloth) should lead to hydrolysis being the overwhelming reaction. Two effects swing the reaction in favour of fixation in this heterogeneous process. First, the adsorption of the dye on to the fibre causes the concentration of dye in the fibre phase to be up to 500 times greater than the concentration of dye in solution and, second, the ready ionization of the $C_6$ primary hydroxyl group in cellulose leads to about a 25-fold excess of cellulose —$O^-$ ions over $OH^-$ ions inside the fibre. These two effects completely outweigh the vast excess of water and ensure that fixation predominates.

The dichloro-*s*-triazinyl dye has two equally reactive chlorine atoms but if hydrolysis occurs, the resulting chlorohydroxy-*s*-triazine is ionized (**IV**) in the alkaline medium employed, imparting a full negative charge to the system.

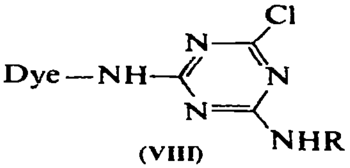


(IV)

Feedback of this into the triazine ring eliminates the positive charge on the ring carbon atoms and stops nucleophilic attack, thus denying this species a further chance to achieve fixation. In the fixed dye molecule (V) the remaining chlorine is still labile although the level of reactivity is decreased by the presence of the —O— cellulose grouping. Under severe or prolonged dyeing conditions this chlorine can be hydrolysed giving (VI) or replaced by a further cellulose—$O^-$ leading to crosslinking of the fibre (VII).[3]



Replacement of one chlorine atom of a dichloro-*s*-triazinyl dye by a non-labile, electron repelling substituent such as an amino or alkoxy group leads to the monochloro-*s*-triazinyl species (VIII) and (IX). These dyes form the backbone of the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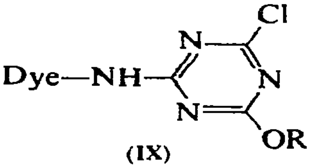
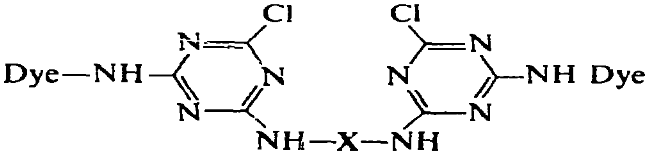
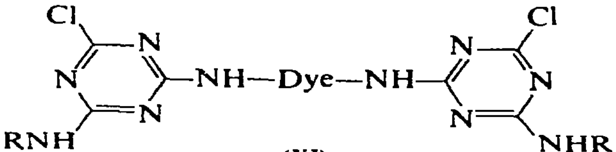

(IX)

Procion H, Procion P and Cibacron ranges of reactive dyes. The reaction readily occurs at temperatures of 20–50 °C and at such a pH that an appreciable amount of the free base is present. Thus, with arylamines a pH of 5–6 is appropriate whilst with ammonia or a strongly basic alkylamine a pH of about 9 is required. The introduction of this second amino group on to the ring causes the level of reactivity to be markedly depressed. In practical terms the temperature necessary to cause fixation on to cellulose rises from about the 30–40 °C range to about 80 °C and generally, slightly more alkaline conditions (about pH 11) are required. Dyes of the Procion H and Cibacron ranges can, therefore, be applied by an exhaust dyeing technique similar to that described above with the exception that the operating temperature is raised to 80 °C. In the case of small, simple reactive dye molecules no advantage accrues to the dyer to affect the heating costs and consequently the dichloro-*s*-triazinyl dyes are generally preferred to the simple monochloro-*s*-triazinyl. The increased dye mobility which comes with the higher dyeing temperature does, however, allow larger dye molecules to penetrate more satisfactorily and be better adsorbed by the fibre during the exhaustion stage. This fact is exploited by the dyes of the Procion HE range which comprises selected dyes conforming to the patterns (X) or (XI), each of which contains two distinct reactive systems. These dyes thus have two chances of achieving fixation and, consequently, a higher proportion of the dye is fixed and less wasted. In the Procion HE range judicious choice of structure has also been made to ensure that the members of the range are very similar to each other in dyeing behaviour, enabling a wide range of mixture shades to be obtained from a limited number of dyes.

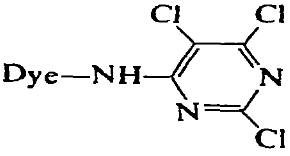

(X)


(XI)

Application techniques so far mentioned have been dyeing methods in which the whole of the cloth is uniformly coloured. The lower reactivity of the monochloro-*s*-triazines does, however, make them ideally suited to printing processes in which a pattern is produced. The dye and alkali are dissolved in water and a thickening agent added. The resulting paste is printed on to the cloth by means of an embossed roller and the cloth is then heated to 100–150 °C, at which temperature rapid dye–fibre reaction occurs, 5–15 s being sufficient time for the fixation to be completed. Finally, loose dye and auxiliaries are washed out of the fibre. Procion P and Cibacron dyes are applied in this way as are the Procion SP and Cibacron Pront dyes which are specifically tailored for excellence in this outlet.

## 3. OTHER HALOGENOHETEROCYCLIC DYES

The immediate success of the triazine based reactive dyes led to an intensive search for alternative reactive systems by the various dyestuff firms. Many are now available based on other chloroheterocyclic systems. Typical were the Reactone dyes (XII) introduced by Geigy[4] and the Drimarene Z dyes, brought out by Sandoz, these dyes being similarly prepared from tetrachloropyrimidine. Variants wherein



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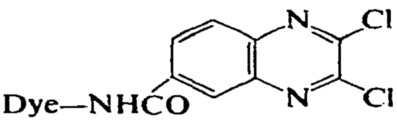

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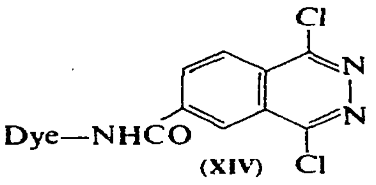

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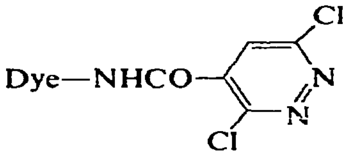


(XV)

the reactive system is attached to the chromogen via a carbonylamino grouping are the Levafix E[5] (Bayer, **XIII**), Elisiane[6] (CFMC, **XIV**) and Solidazol[7] (Cassella, **XV**) dyes formed using the appropriate chloroheterocyclic acid chloride. These heterocyclic systems contain only two nitrogen atoms in contrast to the triazine ring which contains three nitrogen atoms ideally located. Charge density calculations (Fig. 1) clearly show that this does not lead to such a pronounced positive charge on the ring carbons and consequently, the level of reactivity is lower. Dyes of these types display a level of reactivity comparable with monochloro-*s*-triazine dyes. In the pyrimidine series reactivity can be boosted to the cyanuric chloride level by means of an electron attracting group located in the 5-position. This occurs with dyes prepared from 5-cyano-2,4,6-trichloropyrimidine[9] (**XVI**) and, to a lesser extent, with the Reactofil[10] dyes (**XVII**) which were marketed by Geigy.

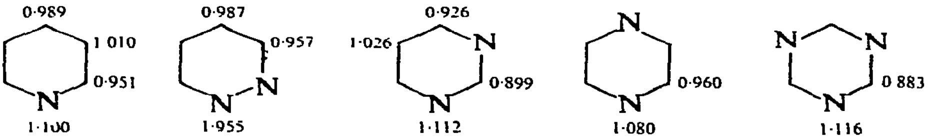
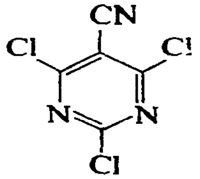


Fig. 1. Charge density calculations for heterocycles.[8]



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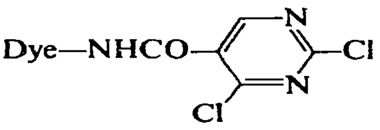
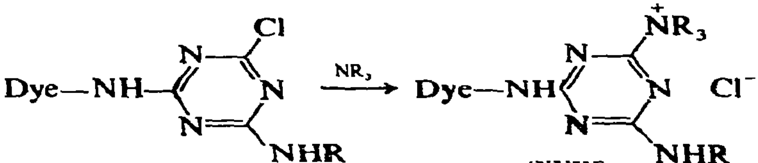


(XVII)

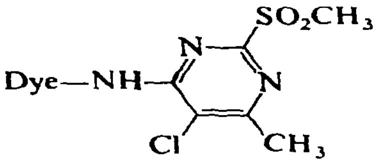
An alternative method of enhancing reactivity lies in variation of the leaving group. This can be readily achieved by formation of a quaternary ammonium salt



(XVIII)

(XVIII) from, for example, a monochloro-*s*-triazine and a suitable tertiary amine.[11] The requirement placed on the tertiary amine is that it should have a very sterically accessible nitrogen atom. Pyridine and the odourless nicotinic acid are noteworthy in the heteroaromatic series. The strongly basic trimethylamine and 1,4-diazabicyclo[2,2,2]octane form quaternary salts so rapidly that they can be used as dyebath additives to promote cold dyeing behaviour in monochloro-*s*-triazinyl dyes.

Dyes having methylsulphonyl[12] (XIX) or fluorine[13] (XX) as leaving entity have been marketed. Introduction of the former substituent into the pyrimidine ring



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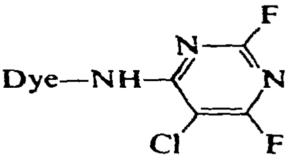
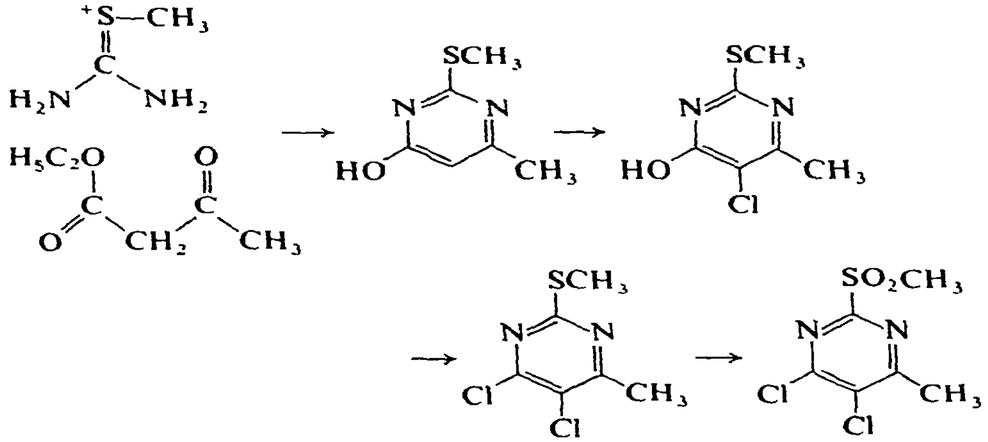
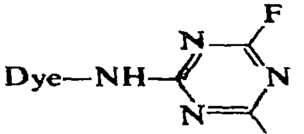


(XX)

involves a ring synthesis to produce 4,5-dichloro-6-methyl-2-methylsulphonylpyrimidine (XXI) which is then condensed with a suitable amino containing dye. 5-Chloro-2,4,6-trifluoropyrimidine, required as intermediate for the Levafix EA dyes (XX), is prepared by halogen interchange. This use of fluorine as leaving group

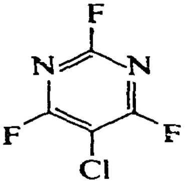


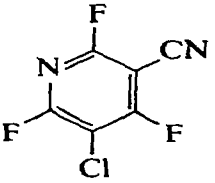
(XXI)



(XXII)

is also a characteristic of the monofluoro-*s*-triazines of the Cibacron F range (Ciba–Geigy; **XXII**) which are obtained from cyanuric fluoride after two condensations.[14] Both the Levafix EA and Cibacron F ranges are applied to cellulose at about 50 °C, which is a fairly convenient temperature, and so are considerably more reactive than their chloro analogues.





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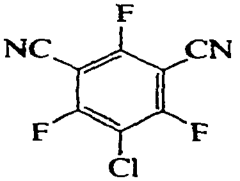
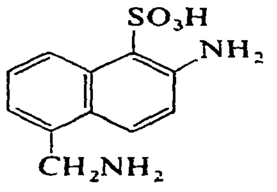


(XXIV)

Using fluorine as leaving group and progressively replacing the hetero nitrogen atoms by cyano groups one can construct a series of intermediates (**XXIII**)[15] and (**XXIV**)[16] which will yield reactive dyes dyeing at about 50 °C when condensed with suitable amino containing chromogen. A complication arises in that these fluoroheterocycles do not readily condense with as wide a range of amino compounds as do the corresponding chloroheterocycles. This arises from the preference of the soft amino containing nucleophile to displace the softer chlorine rather than the hard fluorine atom. This preference is reversed in the fixation stage when the hard alkoxide ion prefers to displace the hard fluorine atom thus leading to the lower fixation temperature. A consequence of the difficulties experienced in the initial condensation of amine with fluoroheterocycle has been the emergence of a number of new dyestuff intermediates carrying $-CH_2NH_2$ groups, which are more readily reacted than simple aromatic amino groups. Typical are (**XXV**), whose preparation is disclosed in a Bayer patent,[17] and (**XXVI**).[18]



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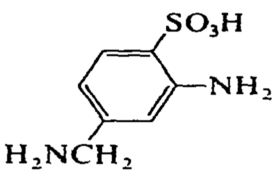
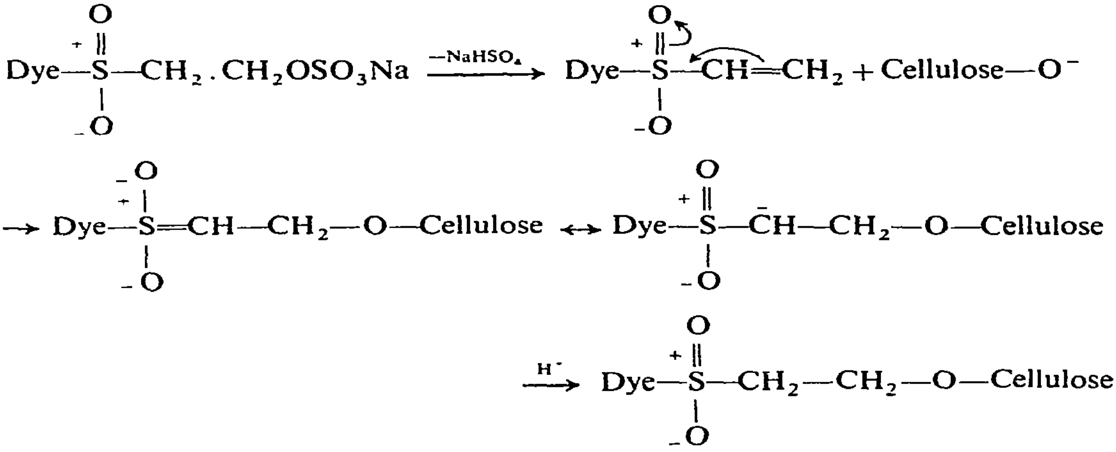


(XXVI)

## 4. β-SULPHATOETHYLSULPHONE DYES

In addition to the halogenoheterocyclic reactive dyes discussed above which fix by a substitution mechanism a second general class, fixing by an addition mechanism, has been exploited. This class is typified by the Remazol (Hoechst) dyes in which the reactive system is a β-sulphatoethyl sulphone group. In the presence of alkali, this group splits out sodium hydrogen sulphate giving rise to a vinyl sulphone. In this, the electron attracting sulphone grouping induces a positive charge on the terminal carbon atom and causes attack by ionized cellulose, or hydroxyl ions, to occur at this site. In these dyes the small alkyl reactive system is not conducive to good physical absorption by the fibre and, consequently, the majority of Remazol dyes find extensive use in printing applications where their weak physical attraction for the fibre makes washing off of unfixed dye easy.



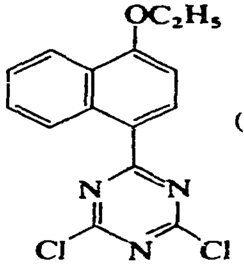
$$\text{Dye}-\underset{\displaystyle {}_{-}\text{O}}{\overset{\displaystyle \text{O}}{\overset{+\,\|}{\underset{|}{\text{S}}}}}-\text{CH}_2.\text{CH}_2\text{OSO}_3\text{Na} \xrightarrow{-\text{NaHSO}_4} \text{Dye}-\underset{\displaystyle -\text{O}}{\overset{\displaystyle \text{O}}{\overset{+\,\|}{\underset{|}{\text{S}}}}}-\text{CH}{=}\text{CH}_2 + \text{Cellulose}-\text{O}^-$$

$$\longrightarrow \text{Dye}-\underset{\displaystyle -\text{O}}{\overset{\displaystyle {}_{-}\text{O}}{\overset{+\,|}{\underset{|}{\text{S}}}}}{=}\text{CH}-\text{CH}_2-\text{O}-\text{Cellulose} \longleftrightarrow \text{Dye}-\underset{\displaystyle -\text{O}}{\overset{\displaystyle \text{O}}{\overset{+\,\|}{\underset{|}{\text{S}}}}}-\overset{-}{\text{C}}\text{H}-\text{CH}_2-\text{O}-\text{Cellulose}$$

$$\xrightarrow{\text{H}^+} \text{Dye}-\underset{\displaystyle {}_{-}\text{O}}{\overset{\displaystyle \text{O}}{\overset{+\,\|}{\underset{|}{\text{S}}}}}-\text{CH}_2-\text{CH}_2-\text{O}-\text{Cellulose}$$

## 5. NON-DYESTUFF APPLICATIONS

Returning to the halogenoheterocyclic class, in addition to their use as dyestuffs, these compounds have been seized on by academic workers who have skilfully exploited their properties in a number of chiefly biochemical applications. Thus Procion Yellow MX-4R has been widely used as a fluorescent stain for nerve cells, proving invaluable in the tracing of nerve patterns.[19] The compound **(XXIII)**, initially designed as a reactive fluorescent brightening agent is now marketed as a fluorescent label for use in sterol analysis.[20] Probably the most outstanding use at the moment is separation of enzymes by affinity chromatography on a carbohydrate substrate, usually agarose, to which has been attached a reactive dyestuff. This has



(XXVII)

been developed as a major method for the preparation of purified enzymes and has been the subject of a number of review articles.[21]

These side uses are, however, trivial compared with the use in textile colouration where reactive dyes have now captured about 20 % of the cotton dyeing market and are firmly established as a major force in dyestuffs chemistry.

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