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Research-Problems in the Field of Fibre-Active Dyes*

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In general lectures on fibre-reactive dyes fall, as do lectures on any other class of dyes, into one of three categories, practical, physicochemical or organo-chemical. Each of these approaches is, of course, valuable and has its important part to play depending on the intentions of the author. This kind of separate approach is in general permissible when dealing with conventional or non-reactive dyes since although the organic chemistry of colour preparation and the physical-chemistry of colouration impinge on one another, the processes of synthesis and dyeing are totally separated. With fibre-reactive dyes on the other hand the chemical synthesis intrudes upon the dyeing process itself. The physical chemistry of the deying operation using fibre-reactive dyes is conditioned by the fact of the dye-fibre reaction and the nature of the original dye-synthesis is conditioned by the fact that the dye is more an intermediate than a final product. The presentation of the basic factors involved in fibre-reactive dye research requires, therefore, a unified treatment of their organic and physical chemistry.

In order to establish a basis for discussion it is necessary to discuss briefly the nature of bonds formed between dyes and fibres. The dyeing process depends upon the migration of a dye from a solvent (usually water) into a fibre phase resulting in a concentration change. In short the dyeing process depends upon the formation of some kind of association or bond between the dye and centres in the fibre phase. The stronger the associative forces and the higher the concentration of associating centres, the greater will be the extent of transfer form the aqueous to the fibre phase.

The associating bonds are, in general, individually weak and are of the same order of strengths as those involved in solvation or aggregation. Like such forces, the associating bonds are formed reversibly. They may be of a simple ionic character as in the case of anionic or cationic dyes with amphoteric fibres. They may derive from dispersion, van der Waals' or hydrogen bonding forces or they may arise from electronic interactions such as induced dipole effects or non-localised π-electron-hydrogen atom interactions. In no case is the stability of such forces sufficient to give significant fastness to washing or other wet treatments. The dye-fibre interactions serve only to bring about absorption of dye molecules from solution into the fibre micellar surfaces.

Fastness to washing is obtained by the colour chemist deliberately imposing limitations on the reversibility of dye-fibre bond formation. Two general methods are employed. The first involves using molecular structures which not only possess a large number of possible bonding positions in relation to the fibre, but also are capable in high concentration of bringing about inter-molecular associations between dye molecules themselves. This results in slow diffusion in the fibre under mild washing conditions so that acceptably small colour bases are experienced. This approach offers only limited possibility of success however except in such cases as exist with fibres which must always be washed under mild conditions for reasons not connected with colour fastness, for example with wool. More generally successful is the approach which imposes virtually complete non-reversibility by some technique of aftertreatment. Typical of this mode of dyeing are the vat dyes which are applied reversibly as the soluble leuco compounds and then fixed *in situ* by oxidation to the insoluble quinone. Of the many variations of this approach, the most recent, and possibly in the long term, the most important, involves the reaction of a group in the dye molecule with a group in the fibre substrate with the formation of a covalent bond, namely the fibre reactive dyes.

The most important developments in this field have been in connection with the dyeing of cellulosic fibres and it is interesting to consider the reasons why it is possible to bring about an efficient reaction between a dye and hydroxyl groups in cellulose in the presence of water. The explanation of this apparent contradiction lies in the existence of affinity effects to which reference has already been made. A good analogy to the situation lies in the field of catalysis. It is well known to employ catalysts in certain reactions which have the capacity of building up on their surface high concentrations of the reagents with a consequent acceleration of the reaction rate. In such cases the reaction products must be readily desorbed in order to maintain the activity of the catalytic surface. In the dye-cellulose reaction also high concentrations of dye are built up on the micellar surface lead-

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ing to very rapid reaction with the substrate as compared with the reaction rate in the much more dilute aqueous phase. The scale of the concentration differences which are likely to exist is indicated below.

Dye solution:

1000 ml containing 1 gm of dye.
In this dyebath is placed 100 gm of cotton and the dye exhausts to the extent of 50%.

At equilibrium:

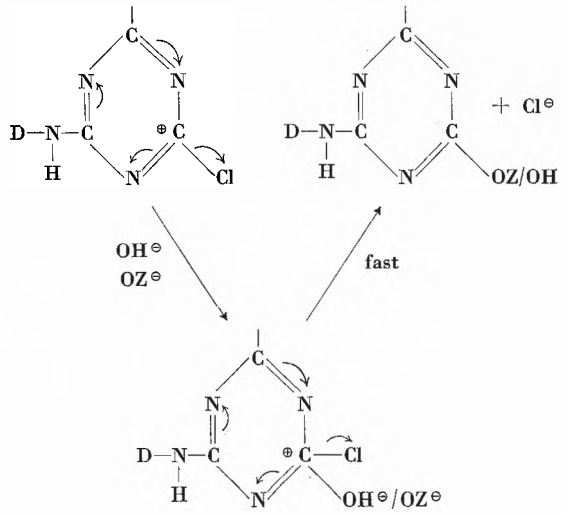
Dye concentration in solution = 0.5 g/l.
Dye concentration in the fibre = 0.5 g/100 g.

The specific volume of cellulose is ca. 0.22 l/kg.
The dye concentration in the fibre = $\frac{0.5}{.022}$ g/l = 22.7 g/l.

The dye concentration in the fibre at equilibrium is 54 times greater than the dye concentration in solution at 50% exhaustion.

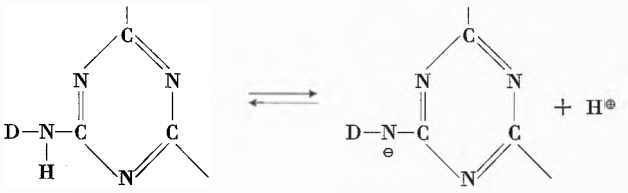
If instead of an insoluble polyhydroxylated substance, a soluble compound is used, no major affinity effects can arise and the dye-cellulose reaction is in a less favourable position relative to the hydrolysis reaction. Nevertheless the formation of a "reaction complex" is still possible and there are in any case differences between the hydroxyl groups in celluloses and in water. These differences will affect the respective reaction rates. One such effect arises from the relatively higher concentration of cellulosate ions in cellulose at a given *p*H than in water. However the major factor arises from the affinity effect irrespective of any others when considering insoluble celluloses.

The reaction mechanism involved between a typical cellulose-reactive dye and cellulose and water involves the reaction between the reactive system and the negatively charged cellulosate or hydroxyl ion via a nucleophilic substitution e.g.



The reaction kinetics are pseudo first order, that is the pseudo first order reaction constant is proportional to the concentration of hydroxyl or cellulosate ions, all other factors being equal. The reaction is exothermic and increases in rate with temperature. The majority of reactive dyes for cellulose are based on the halogeno triazinyl or halogeno pyrimidinyl group attached to the chromophore via an amino bridge. This is because this mode of attachment is by far the most stable. The imino bridging group does however give rise to an interesting effect which is important in considering the effect of *p*H on the reactivity of these dyes.

Horrabin has shown that at about *p*H 8 in the triazine series the imino bridging group ionises.



The ionisation of the imino group exercises a very strong deactivating influence on the active centres in the heterocyclic ring since the negative charge is not necessarily localised. This cannot occur with dyes containing an N-alkylated bridging group and with dyes based on H-acid, ionisation has little effect on activity presumably due to hydrogen bonding with the nearby hydroxyl group. Three effects are thus to be observed in connection with the effect of *p*H on reactivity which are best illustrated by studying the relationship between log K' (the logarithm of the pseudo first order hydrolysis constant) and the *p*H (Fig. 1).

Thus the relationship between log K' and *p*H is not simple and it is not always possible to be sure that an

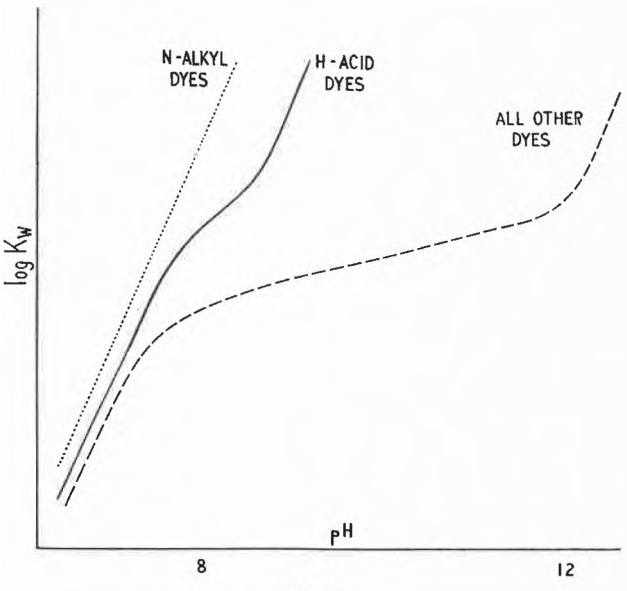


Fig. 1

increase in *p*H will have all the effects which a superficial consideration of the problem might cause to be expected especially in view of the possibility that the rate of increase of the cellulosate ion with *p*H is not necessarily the same as the rate of increase of hydroxyl ion concentration. The effect of *p*H is not, therefore, confined to its effect on reaction rate but can also affect the relationship between the reaction rates with cellulose and with water.

It is clear even at this early stage in this discussion that the physical chemistry of the dye-fibre reaction system is an essential part of the general chemical picture.

SUMNER has shown that the reaction between a reactive dye and a textile substrate may be described by a simplified version of the Danckwert's equation describing the diffusion of a reacting substance

$$Q_F = D_F \left[t + \frac{1}{2K_F} \right] \sqrt{\overline{D} \cdot K_F} ,$$

in which Q_F is the quantity of dye reacting in time t. K_F is the dye-fibre reaction velocity constant, $\overline{D}$ is the diffusion coefficient and D_F is the concentration of dye in the fibre.

Thus the rate of reaction with the fibre is given by

$$\frac{dQ_F}{dt} = D_F \sqrt{\overline{D} \cdot K_F}$$

and the rate of reaction with water is given by

$$\frac{dQ_W}{dt} = D_S \cdot K_W .$$

The efficiency of the reaction in a two phase system where the reactions compete is given by

$$\frac{dQ_F/dt}{dQ_W/dt} \sqrt{\quad} = \frac{D_F}{D_S} \frac{\overline{D}}{K_W} \cdot \frac{K_F}{K_W} = E$$

while the fractional fixation of dye on the fibre is given by

$$F = \frac{E}{1+E} .$$

Both reaction rate and efficiency are *p*H dependent. As will be shown later the substantivity ratio and the diffusion coefficient are similarly changed by *p*H.

SUMNER has shown for a given dye the ration of the bimolecular reaction constants for dye-cellulose and dye-water reaction is a constant irrespective of *p*H, and the efficiency equation may therefore be rewritten as

$$E = \overline{Z} \cdot \frac{D_F}{D_S} \sqrt{\frac{\overline{D}}{K_W}}$$

where $\overline{Z}$ is a constant for a given dye at given *p*H.

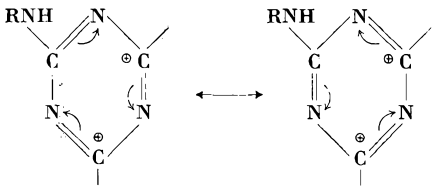
The main point to realise in considering these equations is the fact that the efficiency and rate of reaction are direct functions of dye concentration but are only root functions of the reaction velocity constant and diffusion coefficient. The role of affinity in this system is thus further emphasised.

The primary research problem in reactive dye studies is that of finding a satisfactory organic chemical solution to these equations. In searching for a suitable reactive system and appropriate chromophores to which it can be attached, the research chemist has to bear in mind many things among which not the least important is the fact that the ultimate user requires to fix the dye at a rate acceptable to production demands and with a certain economic level of efficiency. While temperature and to a lesser extent *p*H conditions can be varied to accelerate fixation hith systems of lower intrinsic reactivity it has to be recognised that both factors will also operate in the reverse direction in that they will reduce the all important substantivity ratio, unless some compensating factor is introduced. The effect of temperature on dyebath exhaustion is well enough known not to need amplification. The effect of increasing the *p*H of the system is to increase on the one hand anion competition between hydroxyl ions and dye anions for the fibre and on the other to increase the nett negative charge on the micellar surfaces. The latter effect results in increased repulsion between the micellar surfaces and the dye anions. Both effects bring about a reduction in dye absorption which under most circumstances more than offsets any increase in the reaction velocity constants and can lead to a reduction in reaction rate rather than an increase.

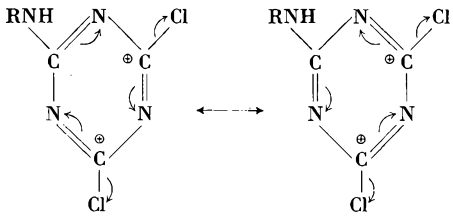
The change from one reactive system to another is not, therefore, a simple matter of organic chemistry. It presents the colour chemist with problems which demand a grasp of dyeing theory for a solution. The fact that a few examples of dyes bearing a reactive system are of little value as dyes indicates very little regarding its suitability in other contexts except, of course, in cases where the strength of the covalent bond formed is insufficient to confer fastness. This last point regarding bond stability is of course one of great importance in this field and must be considered equally with the chemistry of the dye fibre reaction. It is a factor which is a distinctive feature of the reactive system employed and attention may now be turned to a consideration of some of the particular reactive systems which are employed from this and the physico-chemical point of view.

The largest group of reactive dyes for cellulose is that based on the halogeno-s-triazines. Two ranges of dyes of this type are available—the first using the 4:6 dichloro s-triazin-2-yl amino reactive system and the other using monochloroanalogues in which the other active position is occupied by a non-labile or semi-labile group. These two ranges are rather different from the practical point of view, but from that of their chemistry they may be regarded as a single sub-class.

The triazine heterocycle attached to a chromophore via an amino bridging group has two centres subject to nucleophilic attack by negatively charged agencies as a result of the migration of electrons towards the nitrogen atoms.

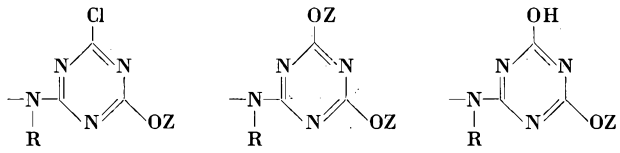


In the halogeno triazinyl system further susceptibility to attack arises from the electronegativity of the chlorine atoms.

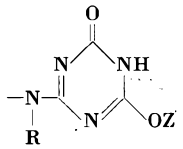


Where two chlorine atoms are present they may be regarded as mutually activating. As a result when one chlorine atom is replaced, the activity of the remaining chlorine atom depends upon the nature of the substituent. Consequently it is possible to regard the mono- and dichloro triazinyl dyes as part of a single series of monochloro triazines bearing substituents of varying electronegativity. At the extremes there will be dyes of very low reactivity and dyes which are so active that they exhibit bi-functionality.

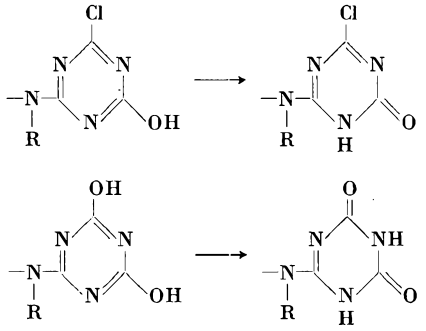
With the dichlorotriazinyl dyes the latter is in fact the case and three primary reaction products with cellulose are formed.



In fact the third form does not exist, rapid ketonisation occurring to yield



These reactions are exactly paralleled by the hydrolysis reactions which yield



The evidence for ketonisation lies in the fact that no evidence of enolisation can be obtained by U.V., I.R., or titration measurements in the case of the hydrolysis products below *p*H 12.5 when one of the groups in the bi-ketonic form is ionised. The hydrolysis products of monochloromonamino triazines show no enolisation even at *p*H 14. It is reasonable to suppose therefore that the forms I and III on the fibre are iso ammelide and iso ammeline ethers.

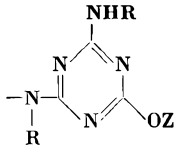
In hydrolysis, the ketonisation destroys much of the activating effect of the conjugated heterocyclic ring, and this leads to an effective deactivation of the residual chlorine atom in the primary hydrolysis product in alkali. In acid on the other hand there is every indication that protonation of the —NH— group in the heterocyclic ring occurs. This leads to intensive withdrawal of electrons from the adjacent carbon atoms and very rapid hydrolysis.

An exactly similar situation is found with the dye-cellulose reaction products. From a consideration of their molecular structures marked differences would be expected between the conjugated iso ammeline forms I and II and the iso ammelide form and this is in fact found to be the case. Treatment of the monochloro form with mild alkali brings about further reaction to give the doubly linked compound. The chlorine atom in this form is still quite active since the electronegative cellulosyl group provides some activation. With more severe alkaline treatment two effects occur. Firstly there is nucleophilic attack by hydroxyl ions at both active centres leading on the one hand to the iso ammelide or keto form and on the other to rupture of the carbon-oxygen bond involved in attaching the dye to the cellulose. At the same time any doubly linked compound which is formed will be converted to the iso ammelide form since the two cellulosyl groups in such compounds provide some mutual activation. The iso ammelide form which results from this chain of events is very stable to alkali and behaves as an ether as very little activating influence persists in this form.

Acid treatment on the other hand will bring about slow hydrolysis of the chlorine in the first of the iso ammeline forms to give the iso ammelide ether. Under these conditions there is evidence that protonation then occurs leading to very rapid rupture of the dye fibre bond. The

doubly linked iso ammeline di ether is on the other hand very stable to acid.

If the monochloro monocondensation product is reacted with an amine, a fourth form is produced.



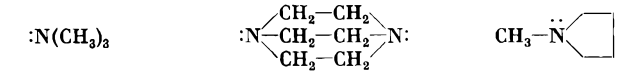
This form is very stable to acid treatments due to the electropositivity of the new substituent. On the other hand it is less stable to alkaline hydroysis than is the ketonic iso ammelide ether since the heterocyclic conjugation is preserved. This latter form may be produced, of course, either by the direct use of a monochloromonoamino triazinyl dye or by aftertreatment of a suitably produced dyeing of a dichloro triazinyl dye.

These differences are reflected in both the fastness of dyeings to storage in the atmosphere and in reproducibility factors in the bulk production of dyed materials. Where the iso ammeline ether structure is produced fixation of dye to fibre will increase with time until a point is reached where the alkali lability of the bond expresses itself and fixation falls. Thus careful control of dyeing times is required. On the other hand the problems arising from the iso ammelide ether structure arise after the dyeing operation is completed. The acidity in the atmosphere, particularly in industrial towns, causes the *p*H of regain moisture in cellulosic fibres to fall to the *p*H 3–4.5 region. Articles which are stored for long periods without washing are as a result in an acid condition. Articles which are regularly washed are, on the other hand, in a neutral or alkaline condition. Thus under certain circumstances depending on the nature of the article or the habits of the consumer, dyeings in the iso ammelide ether form are liable to suffer acid hydrolysis and show the phenomenon known generally as "bleeding". Whether this is a problem generally with dichloro triazinyl dyes depends upon the mode of application which conditions the extent to which the iso ammelide ether form is present, the use conditions of the article, whether it is resin finished and so on. It is a defect which is absent in the iso ammeline form whether produced by aftertreatment or directly. There do, however, exist certain unknown factors which require solution.

From one point of view the inknown factors are of special importance from a research point of view since most dichloro triazinyl dyes give dyeings which are adequately stable to acid storage conditions. The question arises as to why the dyes based on dichloro triazinyl H-acid are so much worse than the other dyes, and why certain H-acid derivatives are so much better than others. It is quite clear that the chromophoric system plays an important part in this differentiation and since it is invariably a substituted amine it is clearly a deactivating influence. Secondly dyeings on viscose rayon are generally superior in this regard to dyeings on cotton. There is clearly a great deal to be done to clear up these difficulties in the way of a full explanation and work proceeding in England and in Switzerland may help matters forward.

The main advantage of the triazine system in reactive dyes for cellulose, and this outweighs any of the problems so far discussed, is its versatility from the point of view of reactivity coupled with the affinity conferred on dyes containing it by virtue of the strongly resonating heterocyclic ring with its electron system in a planar structure. The affinity effect enables a wide range of conditions to be employed in dyeing which in turn enables dyes of greatly varying reactivity to be developed for specific end uses. In fact the dyeing conditions with this subclass range in *p*H from *p*H 8 upwards and in temperature from 20 to 140 °C.

The major shortcoming of the monochloro triazinylamino dyes in comparison with their dichloro analogues resides in their lower reactivity. Consequently much effort has been expended in the search for catalysts which will enable fixation rates to be enhanced. The first hint of some success in this direction arose when it was found that certain tertiary amines could be used to quaternise monochloro triazines and that the resultant dye had a high reactivity comparable with that of the dichloro triazinyl dyes. Normally tertiary amines such as triethanolamine, triethylamine, do not react with monochloro compounds except as bases leading to hydrolysis. However where the disposition of the nitrogen valencies and the nature of the substituents on the nitrogen are such that there is little or no steric impediment to approach to the lone electron pair on the nitrogen, quaternisation will take place. Suitable amines of this kind include,



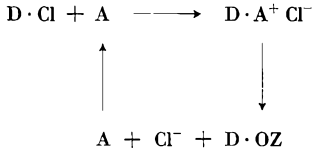
trimethylamine 1:4 diazo 2:2:2 bicyclooctane pyrrolidine

N:N dimethylhydrazine pyridine

The conditions for the quaternisation vary with the amine used and the kinetics of the reactions depend upon a number of steric and energetic factors. For example the multiple bonding of the nitrogen in pyridine brings about the absorption of the lone pair of electrons into the π-electron system of the pyridine ring. Quaternisation is therefore difficult, requiring a high temperature and fairly prolonged treatment. The quaternary compound once formed is however very reactive. Thus there is no general correlation between the reactivity of the quaternary compound and its ease of formation. The latter depends upon the nature of the amine used as already shown for

pyridine and also upon the steric or electronic distribution factors involved with the dye itself.

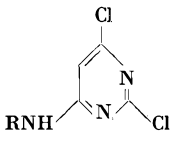
These variables do not present serious difficulties if the object is to prepare a quaternary dye. However if the amines are used as catalysts in a dyeing operation difficulties can soon be encountered. The possibility of using an amine as a catalyst in the fixation of reactive dyes arises of course from the fact that the reaction of a quaternary dye with cellulose results in the liberation of free amine.



By using amines which are able to quaternise at a satisfactory rate the fixation process can be accelerated. However the rules which govern the quaternisation reaction are different from those governing the fixation reaction. When the quaternisation rate is fast compared with the fixation rate, the amine is consumed and after a short period the reaction rate is governed by the fixation rate of the quaternised dye. Where the fixation rate is fast, the rate determining step is quaternisation. DAWSON has recently shown that the effect of this complication ist to amplify the differences existing between dyes and to give rise to compatability and other problems when a standard range of dyes is employed. It is nevertheless true that a range of dyes suitable for use with a particular catalytic system could be specially devised.

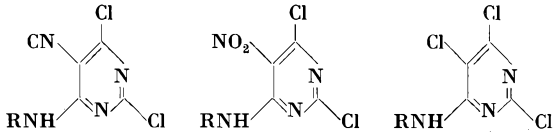
As an alternative to the triazine system, the diazine system has also been investigated. For the most part studies have been concentrated on the 1:3 diazine, pyrimidine but more recently a derivative of 1:4 diazine has been employed.

The basic reactive system in the pyrimidinyl series is the 2:4 dichloro pyrimidin-6-yl reactive system.



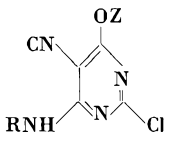
Basically this system suffers from two disadvantages as compared with the triazine system. The π-electron system of pyrimidine is less developed and the contribution of the reactive system to affinity is slight. Secondly the reactivity of the chlorine atoms is relatively low since the positivity of the 2- and 4-positions is less. The two positions are moreover not equivalent and the chance of reaction favouring collisions is reduced. On the other hand the dye-cellulose bond once formed is extremely stable to acid or alkaline media and the lower affinity makes it more easy to develop dyes which do not stain adjacent white materials in washing. The main problem facing the research chemist is that of obtaining rapid reaction under conditions which inevitably lead to poor exhaustions. To some extent it has been possible to raise the affinity level to an acceptable degree by the use of standard devices in chromophore design, but the major problem, that of low reactivity, has remained.

The clearest starting point for an attack on the reactivity question is the modification of the pyrimidine ring structure by substitution in the 5-position with a number of groups e. g.

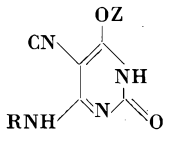


The reactivity of the carbon in the 6-position is considerably affected by the nature of its ortho substituent. Where it is strongly electronegative the chlorine atom becomes extremely labile. Thus the 2:4 dichloro 5-nitro pyrimidinyl dyes are very reactive indeed. Unfortunately the powerful inductive effect of the 5-nitro group persists after fixation rendering the dye fibre bond extremely susceptible to attack by hydroxyl ions. Thus the dye-fibre bond is ruptured at a rate only slightly less than that at which it is formed and even if, by some special means, efficient fixation is achieved the bond is readily ruptured in washing.

The use of a 5-cyano group is more satisfactory. The level of reactivity is sufficient to carry the dyes into the category of the monochloro monomethoxy triazinyl dyes which lie in between the dichloro and monochloro monoamino triazines in this regard. However even here the slight permanent activation is sufficient to cause an undesirable drop in washing fastness. At the end of the dyeing operation the dye-cellulose product takes the form



It is interesting to speculate regarding the possibility of hydrolysing the chlorine atom in the 2-position to give

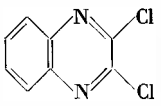


possibly by means of the use of a quaternising amine catalyst. The deactivation resulting from the destruction of the ring conjugation would if this were possible offset the activating influence of the 5-cyano group and give good washing fastness. Some loss of stability to acid

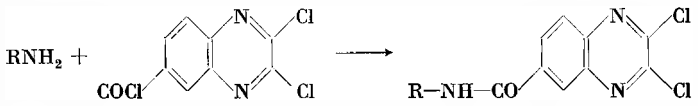
hydrolysis might occur however. As far as is known no attempts have been made to explore this kind of approach.

The use of a 5-chloro substituent has been extensively studied. This provides some activation, sufficient to extend the useful range of dyes which can be made without basically affecting application methods, but does not cause loss of fastness. The steric effect of a chlorine atom is such that free rotation of the heterocyclic ring system is prevented. The reactive system is therefore not ω-planar with the chromophoric system and cannot be regarded as entering into the general resonance system of the molecule. Consequently it would be expected on theoretical grounds that the range of reactivity over a series of dyes of this type will be small and that compatability will be high. How this factor might affect the utility of amine catalysts with that system is not known but it might be expected to be advantageous.

Studies in the 1:4 diazine system have been limited largely to the condensed 2:3 dichloro quinoxaline



While both chlorine atoms in this system might be expected to be labile, the use of one of them to bring about condensation with a chromophore would produce a dye of low reactivity and one which would be considerably sterically hindered in any reaction with cellulose. BAYER who have been most active in work on this system have therefore employed an ingenious variation, the 6-carbonylchloride derivative. This can be readily condensed with an amino dye molecule to give,



A highly active chlorine is thus left in the reactive system to give the Levafix E dyes which can be reacted with cellulose under conditions only a little more severe than required for dichloro triazinyl dyes. The main shortcoming with this system is the general weakness of the dye-fibre bond to acid conditions. In general the bonds which are formed are more readily ruptured by acid hydrolysis than are those of any other commercially available reactive dyes. The reasons for this deficiency are as yet obscure. It would be expected that the bond strength under acid conditions would be similar to that obtained with the iso ammeline form of fixed dichloro triazinyl dyes. However there are important differences, not the least of which may be the powerful permanent activation from the ortho-chlorine in the fixed dye. On the other hand hydrolysis may be occurring at the amidic bridge in the 6-position.

The 2:3 dichloroquinoxaline-6-carbonyl reactive system is particularly interesting from the fundamental point of view. It is the only reactive system which rivals the dichloro triazinyl system in reactivity and exemplifies the use of an essentially monofunctional reactive system attached to a dye by special means. The effectiveness of the reactive system, neglecting for the moment the instability of the bond formed, does not lie necessarily in the reactivity of the chlorine atom alone. With the Levafix E dyes there exists a planar angular structure in which the resonating reactive system is at right angles to the only slightly larger chromophoric system. The dye is therefore capable of attaching itself (prior to reaction) to the cellulose chain in two ways, with either the reactive system or the chromophoric system lying along the cellulose chain length.

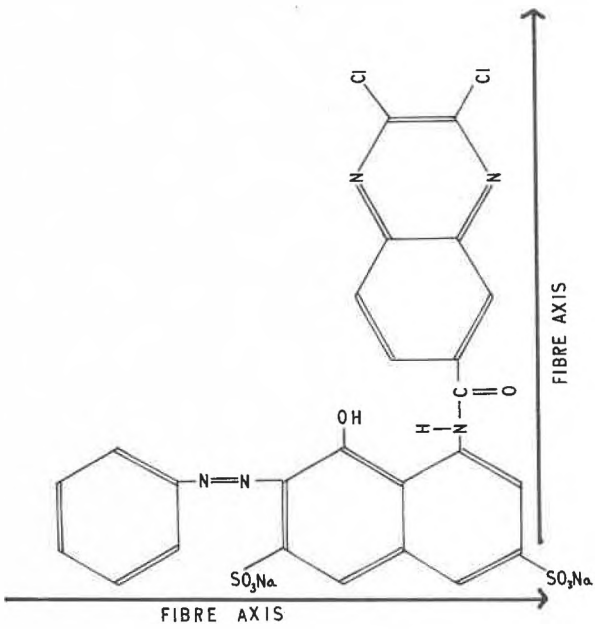


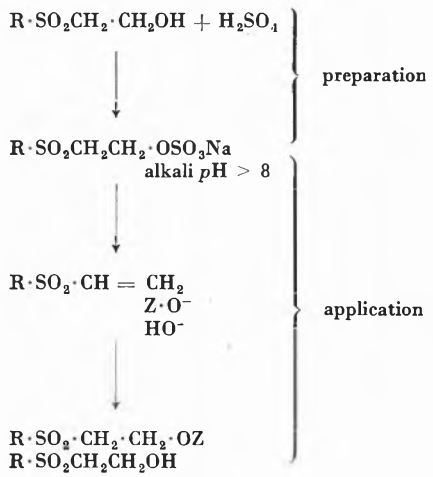
Fig. 2

Under fixation conditions (i.e. alkaline conditions) the cellulose chain largely exists as negatively charged cellulosate ions and consequently electronic repulsion forces are likely to favour the second mode of attachment. The extensive π-electron system of the reactive group, coupled with the potential H-bonding capacity of the amide bridging group, is therefore likely to favour very close approach between the reacting species. One might expect therefore a high reactivity ratio and a low activation energy of reaction. Studies of this kind of approach to the reactive dyes have only just begun and it would be premature to conclude that this theoretical treatment gives a complete picture.

So far the products of reaction between dyes and cellulose have fallen into the general class of cellulose esters, the reactive dyes being regarded as bein the acid chlorides of the esterifying acids. In some cases stability to acid or alkaline attack comparable with that normally

associated with an ether is obtained but when this is found the application conditions required make the dye unattractive from the application point of view. The formation of a stable cellulose ether, rapidly, under reasonably mild conditions remains therefore an important target in reactive dye chemistry. At one time it did seem that this objective had been achieved with the Remazol dyes of Hoechst but careful consideration suggests that this is not so.

The sequence of reactions with these dyes is as follows:



In this sequence of reactions, it appears that despite the fact that the reaction scheme implies ether formation, $-CH_2 \cdot CH_2 \cdot O \cdot CH_2-$, what has actually been formed is the cellulosate ester of the hydroxyl ethyl sulphone, which has analogous behaviour to the sulphate ester originally employed. In other words strong alkali should cause a reversal of the fixation reaction to liberate the vinyl sulphone. There is fairly strong indirect evidence that this is a correct interpretation of the Remazol linkage. Whereas a true ether linkage should be resistant to alkaline hydrolysis, the Remazol linkage is not. The dye which is removed is capable of fixation to adjacent white material to give a permanent stain under unfavourable conditions* implying that the dye which is removed is reactive.

This undesirable effect is normally avoided in the commercially available dyes by appropriate selection of dyes of low affinity. However the problems cannot be evaded by the colour chemist who is faced with the problem of achieving efficient dyes when the required level of substantivity for the achievement of this objective is barred. A choice has to be made in research between an expensive and difficult search for dyes suitable for dyeing methods where substantivity is a decisive property e.g. in batch production and the less versatile range of dyes designed for use in methods where the conditions of application render substantivity less important in a relative sense e.g. textile printing. It is interesting how an objective appraisal of a reactive system from a purely physical chemical point of view can lead directly to important commercial considerations of this kind.

There remain of course several reactive systems in commercial use which have not been mentioned and many more of practical value described in the patent literature. However to discuss all of them would not introduce any new features and would involve repetition of much of what has been said. In conclusion therefore it is worthwhile to consider how the two branches of colour chemistry, organic and physical, have come together in the subject of reactive dyes in such a way that to neglect one branch or the other is to lead to confusion rather than clarity. It is to be hoped that the lessons of this will not be missed by those who are working in other branches of colour chemistry where the value of such a fusion of disciplines may not be quite as spectacular but is nevertheless likely to be the basis of any major progress.

* Treatment: 150 min s. at 90 °C in 30 g/l sodium chloride and 10 g/l sodium carbonate; resoaped in neutral detergent at 100 °C.