The Fixation of Dyes, Containing a Dichloro-*s*-Triazinyl Group, on Cellulose

By C. Preston and A. S. Fern

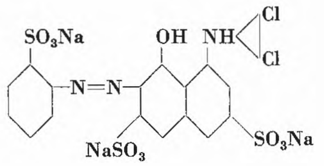
Imperial Chemical Industries Limited, Dyestuffs Division, Manchester

In 1956, precisely one hundred years after the discovery, by **Perkin**, of the first synthetic dye, the first commercial range of reactive dyes for cellulose appeared in England. This event marked not only the culmination of over sixty years of searching by chemists all over the world for a reactive dyeing system, but was also the first step into a transformation of dyeing practice, perhaps comparable in importance to the discovery of mauveine by **Perkin**. The historical stepping stones to the discovery of reactive dyes have been discussed by **Dawson, Fern** and **Preston**[1] and by **Rattee**[2] and the advantages expected and now realised from this new approach to dyeing have been summarised by **Vickerstaff**.[3]

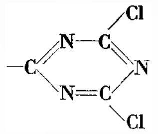
An outstanding feature of dyeing by fibre-reaction is its simplicity in operation and this is especially evident in the case of the earliest of the dyes—the dichloro-*s*-triazinyl dyes, or cold-dyeing Procion dyes, introduced in 1956. With these very reactive dyes, which form the subject of this communication, extremely attractive level dyeings can be obtained in one or two hours at room temperature, either in conventional dyeing machinery or merely by batching the cloth on a roller; at higher temperatures dyeing can be completed in a matter of seconds—again using conventional equipment. Indeed the versatility of the dichloro-*s*-triazine system is one reason why these dyes have been quickly exploited by all the markets of the world, where the dyeing of cellulosic fabrics is practised to any extent.

It is therefore of interest to examine the basic mechanisms underlying the dyeing and fixation processes, and to understand the chemical and physical factors associated with this ease and versatility of application.

The structure of a typical Procion dye is shown below:

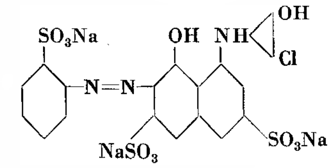


in which, for convenience, the triazine residue

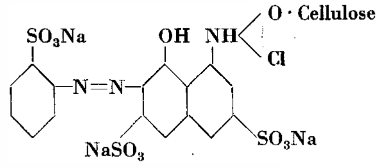


is replaced by the shorthand version .

Reaction with cellulose occurs negligibly slowly under neutral conditions, but in alkali the reaction proceeds rapidly. Simultaneously, of course, reaction with the hydroxyl groups of water also occurs to some extent. Under conditions of mild alkalinity and cold-to-moderate temperature the reaction, both with water and with cellulose, involves one chlorine per molecule only, giving the following reaction products:



and



Under more drastic conditions of alkalinity and temperature both chlorine atoms may react and a highly complex series of reactions is possible as shown in Figure 1.

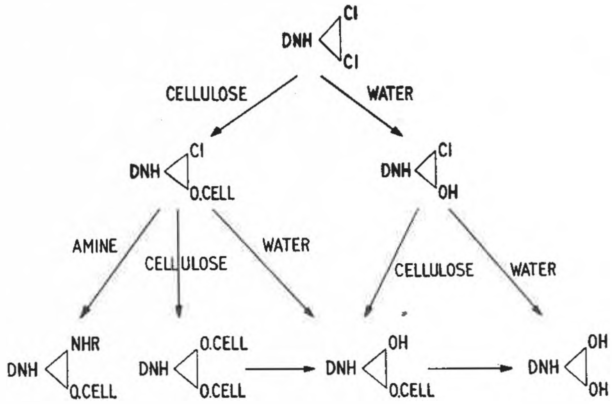


Figure 1

The reaction with cellulose will be treated later in some detail, but first it is necessary to examine the side reaction with water. This is important for two reasons. First, because the *extent* to which it occurs during dyeing governs directly the efficiency of the dyeing process, and second, because the rate at which it occurs at a given *p*H value is an indirect measure of the reactivity of the particular dye for cellulose. This second factor is not, perhaps, immediately obvious and there are a number of steps in the argument which will now be unfolded.

---

[1] Dawson, Fern and Preston, *J. Soc. Dyers Colourists 76* (1960) 210.

[2] Rattee, *Research 12* (1959) 15.

[3] Vickerstaff, *J. Soc. Dyers Colourists 73* (1957) 237.

Side Reaction with Water

The rate of hydrolysis of a dichloro-*s*-triazinyl dye in water can be found by a number of methods. If, as in this case, we are concerned only with the hydrolysis of the first chlorine atom the colour reaction between a pyridine/caustic soda reagent and the dichloro dye[1] provides a simple technique. Using this method the reaction constants for each dye have been determined over a wide range of *p*H values. Figure 2 shows the curves obtained and demonstrates the wide variation in reaction rate from one dye to another, as well as the dependence of reaction rate on *p*H.

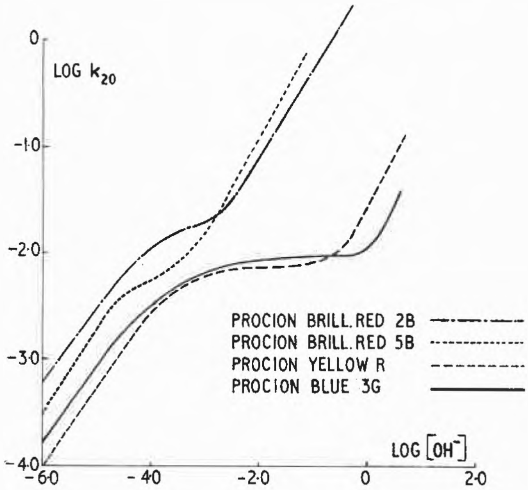


Figure 2

At *p*H 10 the reactivity with water of the most reactive dye is about 7 times greater than that of the least reactive. It would be expected that a similar spread of reaction constants would exist for the reaction of these dyes with hydroxyl-containing bodies other than water and this has been tested by carrying out reaction with the carbohydrate sorbitol:

$$\begin{array}{c} CH_2OH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

In this case (since the sorbitol/dye reaction product itself gives a colour reaction with pyridine/caustic soda reagent) the reaction was followed electrometrically. To avoid reaction at the second chlorine of the triazine residue the *p*H was maintained at 10.5 or less at room temperature and to reduce concentration effects a swamping concentration of sorbitol was employed. Under these conditions *pseudo* first-order reaction constants could be calculated. Table 1 shows the reaction constants for the water and sorbitol reactions for eight cold-dyeing Procion dyes and the expected wide spread of reaction constants both with water and with sorbitol is apparent. The ratio of the reaction constant for sorbitol to the reaction constant for water is, however, reasonably constant. A similar constancy of ratio, although at a different figure, has been found for other soluble carbohydrates—for example, 2 methyl glucoside.

Table 1: Reaction Constants at *p*H 10

Procion Dye	k_{water} sec^{-1}	$k_{sorbitol}$ sec^{-1}	$\frac{k_{sorbitol}}{k_{water}}$
Yellow R	1.0×10^{-5}	4.6×10^{-4}	46
Brilliant Yellow 6 G	5.7×10^{-5}	2.3×10^{-3}	40
Brilliant Red 2 B . .	1.8×10^{-4}	7.6×10^{-3}	42
Brilliant Red 5 B . .	7.6×10^{-5}	3.0×10^{-3}	40
Blue 3 G	6.1×10^{-5}	2.4×10^{-3}	40
Brilliant Blue 3 R . .	1.8×10^{-5}	8.5×10^{-4}	49
Scarlet G	1.1×10^{-5}	4.9×10^{-4}	46
Brilliant Orange G .	1.4×10^{-5}	6.0×10^{-4}	43

The increase in reactivity with increasing *p*H has been studied for the mannitol/water system. Reaction rates for the dye with water alone and for dye with aqueous mannitol were investigated over a wide range of alkalinity, varying from 0.1 N to 2.5 N caustic soda. For experimental convenience estimation of reaction rate was made by the pyridine/caustic soda method and to avoid the complications caused by the reaction products giving a colour reaction with the reagent a monochlorotriazinyl dye was used. This is unlikely to affect the conclusions drawn since it has been shown (Figure 3) that the reactivity of the first and of the second chlorine on the triazinyl residue is affected in a parallel way by *p*H change.

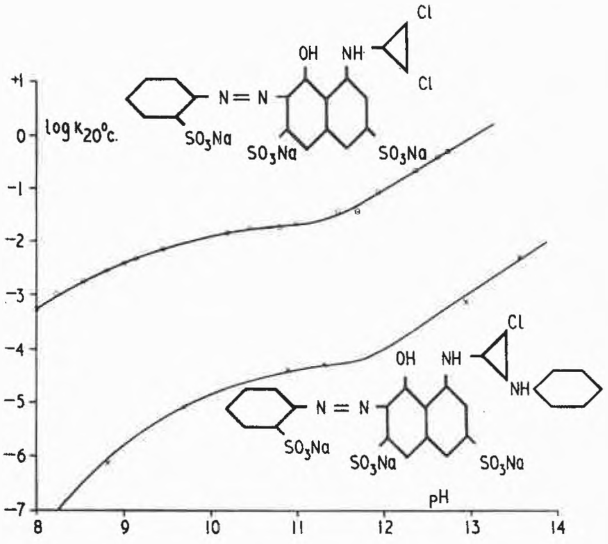
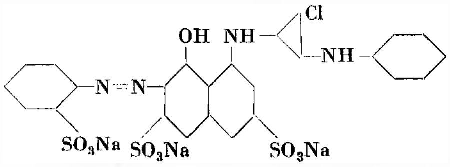


Figure 3

Table 2 shows the ratio of the measured first-order reaction constants for mannitol and for water over a range of alkalinities and it is seen that the ratio is progressively reduced as the alkalinity is increased. Again, as for sorbitol, the measured rate with mannitol is dependent on the concentration of mannitol, i. e. it is a

Table 2



(NaOH)	$\frac{k_{\text{mannitol}}}{k_{\text{water}}}$	$\frac{k_{\text{mannitol O}^-}}{k_{\text{OH}^-}}$
0.1 N	1.05	13.5
0.2	0.89	13.5
0.4	0.66	14.3
0.6	0.58	14.7
0.8	0.40	12.2
1.0	0.41	14.5
2.5	0.20	15.8
	Mean	14.1 ± 1.2

pseudo first-order rate constant. This, together with the effect of pH suggests that reaction takes place with the hydroxyl ions of water and with the *ionised* hydroxyl groups of the carbohydrate. On this assumption the falling values of the $\frac{k_{\text{mannitol}}}{k_{\text{water}}}$ ratio as pH increases reflects the increasing proportion of ionised water to ionised carbohydrate hydroxyl groups as the pH rises. The pK value for mannitol is known and the concentration of ionised hydroxyl groups at any pH can be calculated. When these values and the concentration of hydroxyl ions in the water are included in the calculation, a series of bimolecular constants is obtained for the dye/mannitol ion and dye/water ion systems. The ratio of these is constant at all pH values (Table 2).

So far a simple picture of the reaction mechanism has emerged. The reaction between Procion dye and a soluble carbohydrate is governed by the concentration of carbohydrate *ion* present and the various dyes, despite their wide range of reactivity from one member to another, all show the same ratio of reactivity $\frac{\text{carbohydrate ion}}{\text{water ion}}$ for a given carbohydrate.

The application of this reaction mechanism to the dyeing of cellulose is complicated by the heterogeneous nature of the cellulose/water/dye system. The complications are of three kinds. First, the calculation of the concentration of the reactants must now involve considerations of affinity and diffusion, and the assumptions implicit in such measurements. Second, it still remains to be shown that cellulose ions are present during dyeing. Finally, steric factors may intervene in the solid phase.

Measurement of rates of reaction in heterogeneous systems is important in fields other than dyeing and Danckwerts has evolved an equation for such reactions which in a simplified form is expressed as follows:

$$Q = c\sqrt{DK}\left(t + \frac{1}{2K}\right),$$

where: Q = amount of dye diffusing through unit area of solid surface,
c = equilibrium surface concentrations,
D = diffusion coefficient,
K = reaction constant of dye for cellulose,
t = duration of experiment.

This equation has been applied by our colleague Sumner[4] to the case of reactive dyes on cellulose. Since the Danckwerts equation refers to the ideal case of a reactive substance diffusing into a slab of infinite thickness, the rate of dyeing and diffusion measurements were carried out on viscose film rather than on fibre. The quantity Q, which is taken as equivalent to the amount of dye fixed in time t (since the film can be treated as an infinitely thick slab under the experimental conditions) has been measured by means of a flow technique, shown in Figure 4. Freshly mixed dye and alkali flow past the viscose film mounted in the beam of a spectrophotometer. By successive measurements of the optical density through the cell the rate of uptake of dye by the film can be measured. This is possible since the dye solution passing rapidly over the viscose film is itself of constant optical density. A typical plot of optical density against time is shown in Figure 5. The linear nature of the plot shows that fixed dye is wholly responsible for the increasing optical density since normal diffusion of dye would give the usual hyperbolic curve. At the end of the experiment the amount of dye fixed was determined by the normal method.

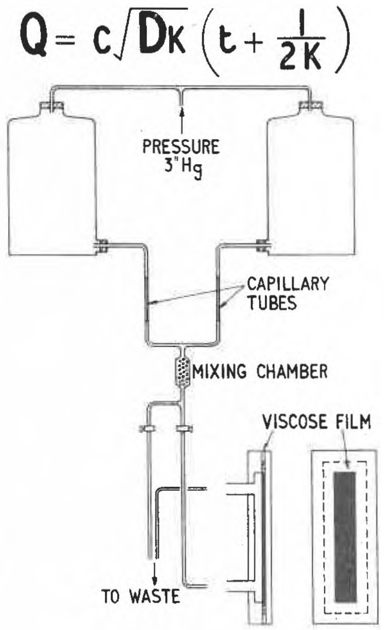


Figure 4

The equilibrium surface concentration c was determined by measuring the affinity of the active dye for

---

[4] Sumner, Communication to Society of Dyers and Colourists.

cellulose. It is, of course, not possible to measure this quantity directly for reactive dyes under alkaline conditions since the equilibrium between dye solution and dye on fibre constantly changes due to fixation. This difficulty has been overcome by using two *inactive* forms of the dye under a range of alkaline conditions and adjusting for differences in intrinsic affinity by comparing these dyes under neutral pH conditions at which no fixation occurs. Figure 6 illustrates the dyes used and the method of interpolation.

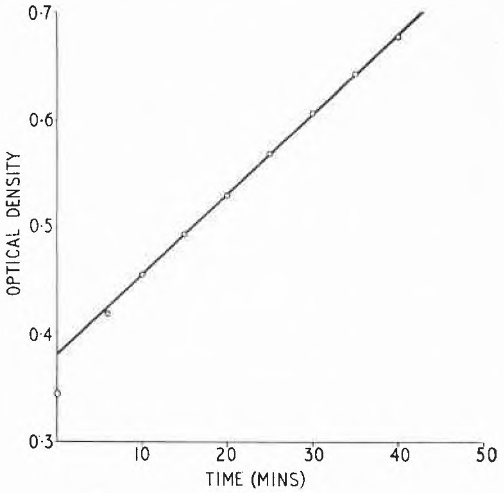


Figure 5

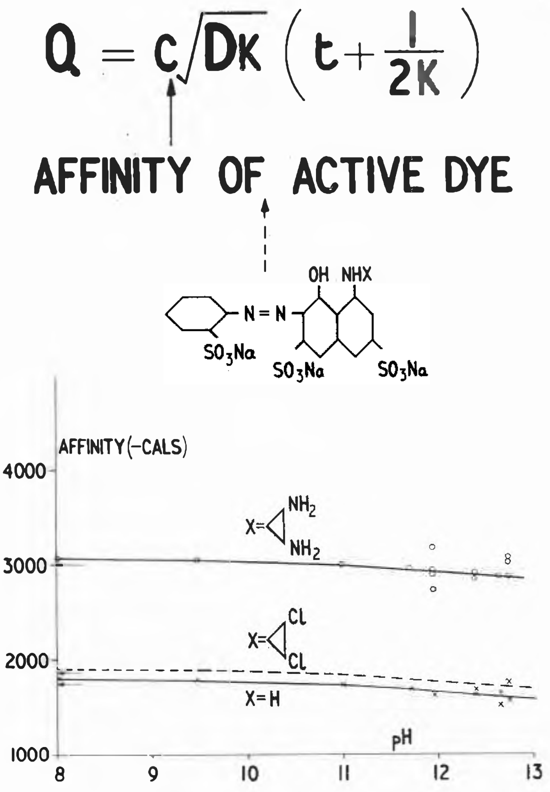


Figure 6

The diffusion coefficient in the Danckwerts equation was measured by the time-lag method due to **Barrer**.[5] In this technique a solution of dye in buffer solution is separated from buffer solution alone by a viscose film. The dye diffusing through the film is progressively determined by optical means. The diffusion cell and the result of plotting amount of dye diffused against time are shown on Figures 7 and 8. The intercept on the

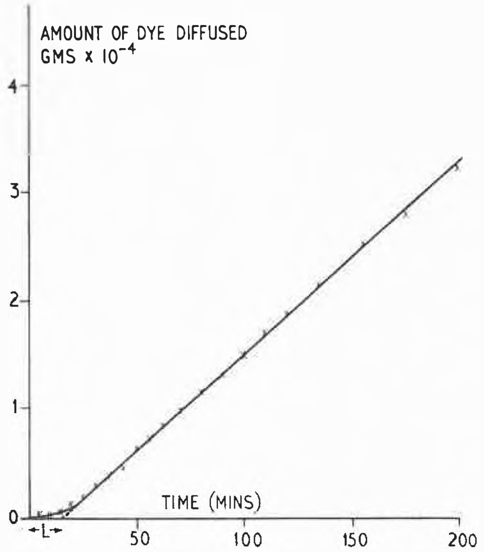


Figure 8

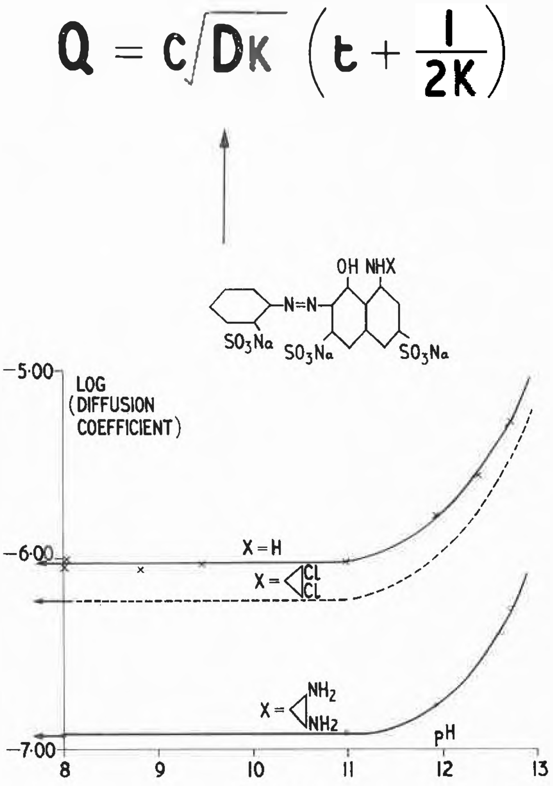


Figure 9

---

[5] **Barrer**, *Diffusion Through Solids*, Cambridge 1941.

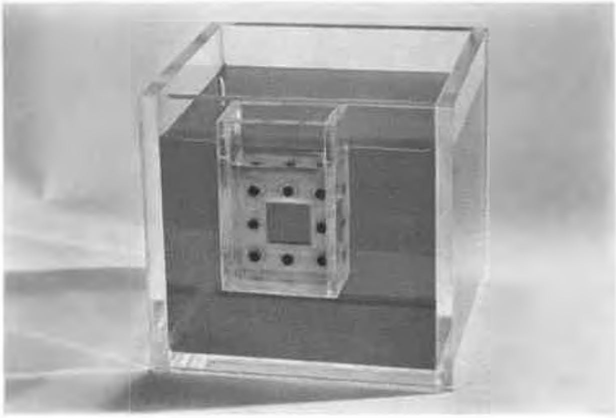


Figure 7

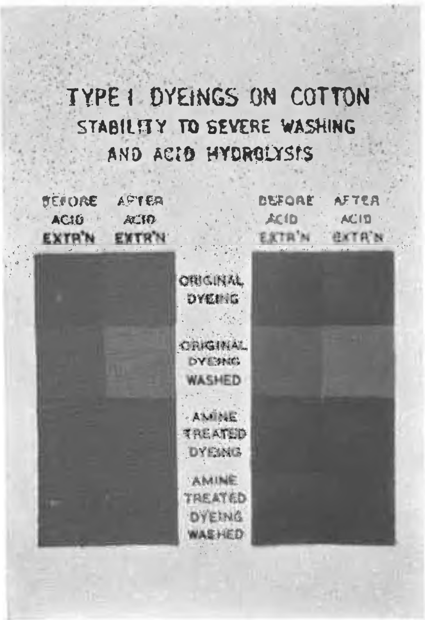


Figure 12

Figure 14

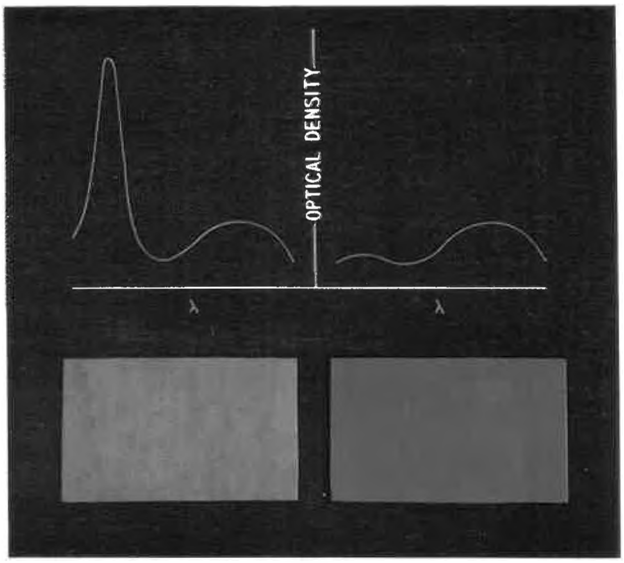


Figure 15

time axis yields the diffusion constant of the dye. Again, the diffusion coefficient of reactive dye cannot be measured under alkaline conditions and, as before, interpolation was made from the behaviour of the inactive variants of the dye, as shown in Figure 9.

Having measured these quantities it is now possible to derive a value for the rate of reaction of dye for cellulose over a wide range of *p*H values and to compare these values with the reaction rates with water. Again the ratio of rate constants with cellulose and water is not a constant, but decreases with *p*H from about 25 down to 10. In this case it is not possible to change the concentration of cellulose to check the effect, but on the basis of the mannitol mechanism, it is reasonable to assume that it should be the bimolecular reaction constants which should be compared, calculated on the number of ionised OH groups in each phase.

For cellulose, controversy has existed for many years on the question of the mechanism by which cellulose absorbs sodium hydroxide. Three mechanisms, chemical combination, physical adsorption and neutralisation have been put forward from time to time. SUMNER[4] has now given strong evidence based on a Donnan equilibrium and Neale's value for the *p*K of cellulose[6] which supports the neutralisation theory. The absorption of sodium hydroxide on cotton over a concentration range, calculated on the assumption of neutralisation and the actual measurements of absorption are compared in Figure 10; the agreement is good. This is clear evidence that cellulose ions exist under the alkaline conditions used for dyeing these dichloro-*s*-triazinyl dyes. When the calculated values for concentration of cellulose-O¯ are used to calculate the true bimolecular constants of reaction with cellulose, it is found, as shown in Table 3, that the ratio of the reaction constant of dye for cellulose and for water is constant at all *p*H values.

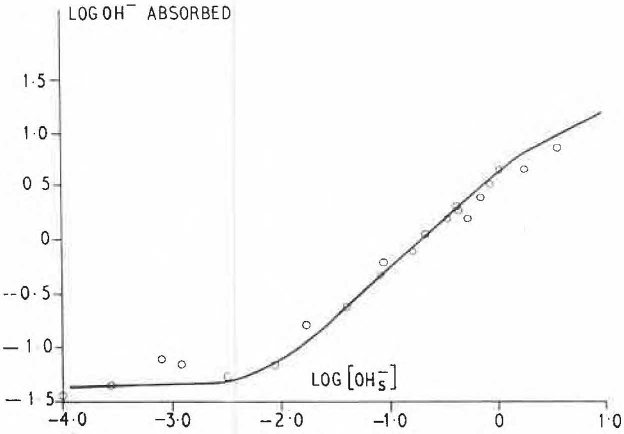


Figure 10

Table 3: $Q = c\sqrt{DK}\left(t + \frac{1}{2K}\right)$ ↓

*p*H	k_{water} min^{-1}	$k_{cellulose}$ min^{-1}	$\frac{k_{cellulose}}{k_{water}}$	$\frac{k_{cellulose\,O^-}}{k_{OH^-}}$
8.00	9.12×10^{-4}	–	–	–
8.81	3.63×10^{-3}	–	–	–
9.14	5.62×10^{-3}	–	–	–
9.46	6.92×10^{3}	1.72×10^{-1}	25	0.95
9.74	1.29×10^{2}	3.30×10^{-1}	26	1.16
10.99	2.82×10^{-2}	7.03×10^{-1}	25	1.16
11.70	6.46×10^{-2}	1.59	25	1.28
11.94	1.00×10^{-1}	1.87	19	1.06
12.63	4.90×10^{-1}	7.71	16	1.37
12.73	6.03×10^{-1}	6.52	11	1.03
			Mean	1.14 ± 0.14

A strikingly simple picture of the Procion reaction has therefore emerged. It seems that the reaction takes place with almost equal facility, both with hydroxyl ions and with ionised cellulose. In the absence of alkali the concentrations of these are negligibly small and reaction with dye is consequently negligible in practical dyeing times. The reactivity both for water and cellulose is increased by addition of alkali and the explanation of the preferential reaction with cellulose rather than with water must reside in factors other than inherent preferential reaction. The first of these is the affinity of the dye for the fibre, causing the concentration of the dye in the cellulose phase to be as much as 500 times greater than in the water. The second factor is the lower dissociation constant of cellulose (*p*K 13.7) compared with water (*p*K 15.7); this is reflected in the greater proportion of cellulose-O¯ ions over water hydroxyl ions at any given dyeing *p*H. These factors completely outweigh the preponderance of water in a practical dyebath. The part played by diffusion of dye through the fibre can also be visualised, qualitatively, since without diffusion surface saturation would limit the amount of fixation. The Danckwerts equation suggests that affinity considerations are more important than diffusion or reactivity which are represented only as a square root and this appears to fit our experience. Since, however, high affinity usually goes hand in hand with low diffusion coefficients some kind of balance is required in a useful dye. Work along the lines outlined above is guiding development research along fruitful channels.

So far, the reaction of only one chlorine atom of the dichloro-*s*-triazinyl group has been discussed. Reaction of the second chlorine is also possible, giving rise to cross-linked cellulose. Evidence of crosslinking has been put forward by a number of workers (VICKERSTAFF,[7] WEGMANN,[8] SCHWERTASSEK,[9] DAWSON[1] *et al.*) and WEGMANN has shown that the cross-link can be broken by

---

[6] NEALE, *J. Textile Inst. Trans. 20* (1929) 373.

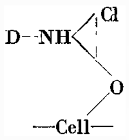
[7] VICKERSTAFF, *Amer. Dyestuff Rep. 47* (1958) 33.

[8] WEGMANN, *Melliand Textilber. 39* (1958) 1006.

[9] SCHWERTASSEK, *Faserforsch. u. Textiltechn. 9* (1958) 321.

alkaline treatment. The properties of the various types of linkage which can be produced from dichlorotriazinyl dyes have been examined in some detail and a number of interesting observations have emerged.

Three main types of dye linkage can be produced.[10] The actual fixation of dye must initially occur through the formation of a monochloro monocellulose derivative:



and it was with the formation of this link that the earlier part of this communication was concerned.

The nomenclature used here is shown in Figure 11. Since the first chlorine in the triazinyl residue is much more reactive than the second chlorine, it is possible to produce dyeings which are almost pure Type 1 dyeings. This is achieved by dyeing at room temperature in mild alkali such as sodium bicarbonate. That the remaining chlorine atom in such dyeings is still reactive can be demonstrated in a number of ways.

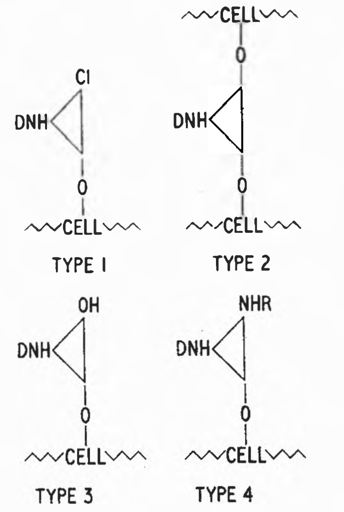


Figure 11

The characteristic absorption spectrum produced by the addition of pyridine/caustic soda reagent to a reactive chloro-*s*-triazinyl group has already been mentioned. When this mixture is applied to a Type 1 dyeing of, for example, Procion Brilliant Blue R, a vivid green coloration appears within a few minutes; this is due to the imposition of the characteristic absorption spectrum at about 450 Å due to complex formation between the monochloro-monocellulose triazinyl compound and the pyridine/caustic soda mixture. This effect is illustrated in Figure 12. When the chlorine of such a Type 1 dyeing is removed by treatment with an amine under suitable conditions and again tested with the pyridine/caustic soda reagent, no characteristic colour change occurs. This process has useful practical consequences which are discussed later. When Type 1 dyeings, which are soluble in cuprammonium hydroxide, are treated for 3 hours at room temperature in a 1% solution of trisodium phosphate they become insoluble in the cuprammonium reagent and are referred to as Type 2 dyeings. By using the sulphuric acid solubility test of SCHWERTASSEK it is possible to judge semi-quantitatively the amount of Type 2 dyeings which has occurred.

When the cross-linked fibres are treated for 3/4 of an hour at 100 °C with 1% caustic soda they become soluble in cuprammonium hydroxide and in the low concentration of sulphuric acid associated with the undyed fibre. Dyeings treated in this way are referred to as Type 3 dyeings.

The behaviour of these three types of dyeing has been investigated in order to throw light on the tendency of some dyeings to give staining on adjacent white material when deep shades are subjected to humid acidic atmospheric conditions for some time and then moistened. A small proportion of the dye is lossened by hydrolysis and this can migrate on to adjacent white material in the presence of water. This stain, since it consists of unreactive low affinity dye can, of course, readily be removed by a mild washing treatment, but it is clearly of interest to determine the factors affecting the quantity of dye removed and to devise ways of minimising it. Dyeings of Types 1, 2 and 3 have been treated with strong acid over a period of time and the rate curves for the hydrolysis are shown in Figure 13.

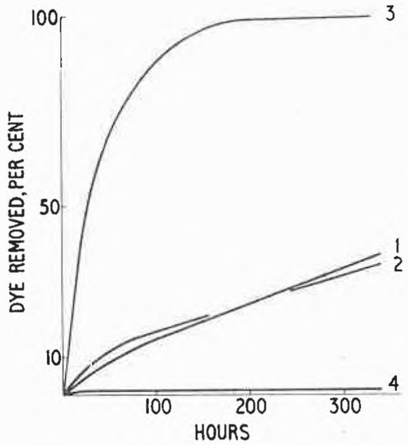


Figure 13. Hydrolysis of Procion Yellow R, on Viscose Rayon, in N/100 HCl

Since Type 1 and Type 2 dyeings, however carefully prepared, must in practice contain some proportion of Type 3, the rate of hydrolysis of these different linkages in acid cannot be very precisely expressed. Nevertheless,

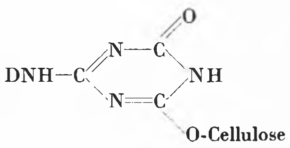
---

[10] After the preparation of this communication an interesting paper by ELÖD appeared which describes the mode of preparation of these three types and discusses their fastness to acid and alkaline hydrolysis (ELÖD and NAKAHARA, *Melliand Textilber. 41* [1960] 567).

the curves reveal clearly that the Type 3 linkage is hydrolysed very much more readily than either the crosslinked dyeing or the monochloro monocellulose dyeing. Very much greater resistance to acid hydrolysis is found, however, if the Type 1 dyeing is first treated with a water-soluble primary amine. Replacement of the reactive chlorine by amine is accomplished within one minute at temperatures near boiling point using a dilute solution of amine. A dyeing treated in this way is referred to as Type 4. Figure 13 shows the reduction in rate of acid hydrolysis when ethylene diamine is used in this way. Practical atmospheric tests have also been made with, of course, very long exposure, and these confirm the results in strong acid.

Similar rate determinations of hydrolysis under alkaline conditions cannot be made since in the presence of alkali a progressive change in the type dyeings takes place in the direction Type 1 → Type 2 → Type 3. However, under the alkaline conditions of a severe washing treatment at the boil, Type 1 linkages are somewhat more readily removed than are Type 3, whilst the cross-linked Type 2 dyeing is noticeably more resistant than either. Type 4 dyeings show the greatest resistance to alkaline hydrolysis under such conditions. This effect with soda ash as alkali is illustrated in Figure 14. In the presence of caustic soda, however, Type 4 dyeings show a disproportionately high loss.

These results are interesting both from the theoretical and practical points of view. The ease of hydrolysis of the ester link with cellulose must be related to the activating influence of the chromophoric part of the dye molecule which is common to the whole series for a particular dye, and also to the influence of the remaining substituent on the triazine ring which differs from one Type dyeing to another. If, as seems likely, the Type 3 dyeing under acid conditions is largely in the keto form



then the series falls into the order of the group dipole moments of the various substituents ranging from C=O (strongly electronegative) to $-NH(CH_2)_2NH_2$ (strongly electropositive).

In more practical terms, the results make it clear that in order to achieve optimum fastness to deleterious storage conditions, particularly for heavy shades of the more highly reactive dyes which may come into contact with white cloth, it is necessary to produce dyeings containing as high a proportion of Type 4 as possible. In the unusual case of a dyeing being required to undergo washing under alkaline conditions followed by long storage in acidic humid atmospheres, the advantage of the Type 4 dyeing can be considerable. Figure 15 shows a Type 1 and a Type 4 dyeing and the result of a prolonged alkaline wash followed by acid hydrolysis. The effect is, of course, exaggerated by the severity of the acid hydrolysis (17 hours in N/100 HCl), but the Figure serves to illustrate the effect.

Since the Type 4 linkage is derived from Type 1 by reaction with amine it is desirable, where optimum fastness properties are required, to produce in the first instance a high proportion of Type 1. It is of interest, therefore, to determine what proportion of Types 1, 2 and 3 exist in dyeings made by different dyeing methods. Fortunately this can be done, to a precision satisfactory for most purposes, by taking advantage of the different fastness properties in acid and alkali, of the various types of linkage.

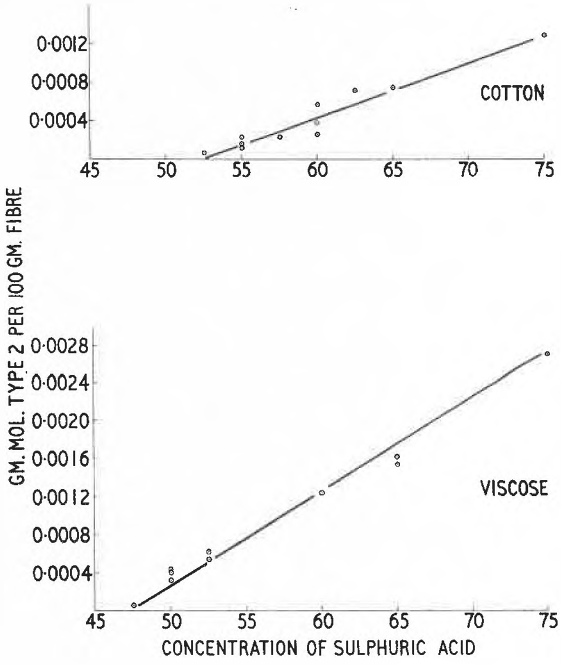


Figure 16

Table 4 shows these proportions for dyeings of Procion Brilliant Orange G prepared by a number of different dyeing procedures. These dyeing methods have been arranged approximately in increasing order of "severity" in terms of temperature and *p*H. The picture that emerges fits well into the pattern outlined above. With mild alkali at room temperature a high proportion of Type 1 linkage is produced, whilst under increasingly severe conditions a build up of Type 2 takes place which is eventually offset by a breakdown to Type 3.

This approximate determination of the proportions of the various types of linkage allows us to examine in more detail the effect of this cross-linking on the solubility of the fibre in sulphuric acid. Using the microscopical method described by SCHWERTASSEK we have determined the critical concentration of sulphuric acid required for solution of dyed cellulose fibres containing various percentages of cross-links. The results are given

Table 4: Procion Brilliant Orange G on Cotton

Dyeing Method	Temp. °C	Time	*p*H	% Types		
				1	2	3
Pad Bicarbonate/Batch, Cold	20	24 hours	7.6	84	8	8
Long Liquor/Soda Ash, Cold	20	1 hour	10.5	75	18	7
Pad Soda Ash/Batch, Cold	20	2 hours	10.6	90	6	4
Long Liquor/Phosphate, Cold	20	1 hour	11.0	67	25	8
Pad Bicarbonate/Bake	105	5 min.	Varies	44	32	24
Pad/Dry/Pad Caustic/Steam	100	1 min.	14	23	25	52

in Figure 16 which shows a linear relationship between amount of cross-linking and critical concentration both for viscose and for cotton. Points derived from the dyeings with five different dichloro-*s*-triazinyl dyes fall reasonably closely along a straight line and this is to be expected since the dimensions and properties of the cross-link are the same in all cases. The proportion of cross-links required to produce insolubility in these relatively high concentrations of acid is surprisingly low. Little is known about the mechanism by which cellulose dissolves in sulphuric acid or the precise way in which cross-linking reduces the tendency to dissolve. However, the method outlined may give insight into these problems and into the topochemical structure of cellulosic fibres.

The authors acknowledge the contribution of Mr. H. H. SUMNER, Dr. R. M. ROBINSON and Mr. G. WILLIAMS to the preparation of the material for this paper.