

FAST DYES ON CELLULOSIC FIBERS*

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INTRODUCTION

ONE of the main preoccupations of the dyer always has been the achievement of fast dyeings, but the present paper is concerned mainly with the problem of wetfastness on cellulosic fibers. From the theoretical point of view, wetfastness can be obtained in two ways, namely:

1) The introduction into the fiber of insoluble coloring matters. Wetfastness is then attained by the mechanical retention of the pigment particles within the fiber, coupled with the insolubility of the pigment in soap solutions. Typical examples of this method are the mass pigmentation of rayons and the use of vat, azoic, phthalogen and Alcian dyes.

2) The use of soluble dyes, which are designed to have an appreciable affinity for the fiber. The classical example of this method is the direct dyes, where the molecular structure of the dye is selected so that physical absorption forces of considerable strength are built up between dye and fiber.

The simplicity of application of water-soluble dyes has always been attractive, but in order to achieve any significant wetfastness, the soluble dyes must have a high affinity for cellulose. Simple acid wool dyes have negligible affinity and are completely removed by washing, and the higher affinity of direct dyes is obtained by building up long, flat molecules. These molecules must be linear and must be large, which means in effect that polyazo structures must be used. Consequently, many attractive chromophoric systems, such as anthraquinone dyes and triphenyl methane dyes, are ruled out, while the complexity of a polyazo system almost inevitably introduces dullness. Direct dyes are therefore somewhat limited

in their brightness and range of shades. Furthermore, large molecules diffuse into cellulose very slowly so that if a direct dye molecule is made larger to increase its affinity and wetfastness, it becomes increasingly difficult to level, and dyeing temperatures near the boil must be used in order to obtain penetration of the fiber in a reasonable time. Finally, direct dyeing must remain fundamentally a reversible adsorption process, and since the adsorbed dye remains unchanged and water-soluble, the highest degree of wetfastness must remain unattainable.

APPLICATION OF REACTIVE DYES

The recent introduction of chemically reactive dyes opens an entirely new approach to this problem. The principle involved is very simple and consists merely of attaching to a water-soluble dye molecule a reactive group which is capable of entering into chemical combination with cellulose. With such a system it is possible to use dyes which have little or no affinity for cellulose. Consequently, simple dye molecules can be employed and theoretically any shape of chromophoric system. The dye molecule can be small and thus able to diffuse within the fiber quickly to give rapid penetration and good leveling. Once within the fiber, however, the reactive group will combine with cellulose and will anchor the dyestuff to give a high degree of wetfastness.

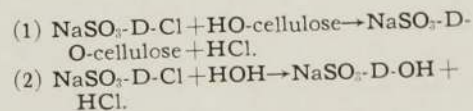
These principles are employed in the Procion dyes. The dyes at present available are simple mono-azo, anthraquinone, or phthalocyanine derivatives, which are polysulfonated to give high solubility. With the exception of the phthalocyanine derivative, they are of small molecular size, diffuse very rapidly within the

fiber, and are therefore suitable for cold dyeing and continuous processing. To the dye molecule is attached the reactive group, which contains one or two reactive chlorine atoms. In alkaline solution, reaction between the dye and the hydroxyl groups in cellulose can occur to link the dye to the fiber by a definite chemical bond. These dyes do therefore combine the simplicity of application of water-soluble dyes with high wetfastness properties to an extent which has not hitherto been attainable.

THEORY OF DYEING WITH REACTIVE DYES

The evidence for the existence of chemical linkages within Procion-dyed fibers has been reviewed elsewhere (1) and the practical methods of dyeing have also been described (2). Consequently attention will be directed in this paper towards the theoretical aspects of the application of reactive dyes and the implications in terms of practical dyeing methods.

In the first place, the use of reactive dyes introduces a new characteristic into the dyeing operation. Dyeing behavior is no longer controlled solely by rate of diffusion and affinity but also involves reaction rates. Any dye which will react with cellulose will almost certainly react with water so that in any dyeing operation two competing reactions must be taking place, namely:-



Reaction (1) is the desired reaction with the fiber. Reaction (2) is a side reaction leading to inactivation of the dye, since the hydroxyl derivative formed will not react with cellulose. The relative speeds of these

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two reactions are obviously of vital importance, and reaction (1) must be much faster than (2) if the dyes are to be of practical value.

RELATIVE RATES OF REACTION WITH CELLULOSE AND WATER—Attempts to determine quantitatively the rates of reaction of Procion Brilliant Red 2BS with cellulose have so far failed completely, except in so far as they establish that the reaction is very rapid. Pieces of viscose film (Diophane PT 300) were dyed to equilibrium in a neutral solution of Procion Brilliant Red 2BS (0.33 g/l) and common salt (30 g/l) at 30°C. Under these conditions no reaction with the fiber occurred and all the dye could be removed by treatment in boiling Lissapol NC solution. The pieces of dyed film were immersed for short times ranging from 15 seconds to 12 minutes in a cold solution of sodium carbonate (10 g/l) and salt (30 g/l) and then transferred immediately to boiling Lissapol NC solution (2 ml/l) and boiled for 10 minutes. The film was then squeezed on to a glass plate and its optical density measured at 538 m μ . The results in Table I show no significant change in density with time so that reaction must be complete in less than 15 seconds.

A similar experiment was carried out by air drying the dyed film and then suspending the film in ammonia vapor for short times before washing off. The results are shown in Table II.

Again the results show no increase in fixation beyond the shortest practicable time of treatment so that again the reaction of the absorbed reactive dye with cellulose when the environment is made alkaline must be extremely rapid.

The rate of reaction of these dyes with water is more easily measured. To stirred solutions of the dyes, alkali was added and samples removed at various times. The samples were

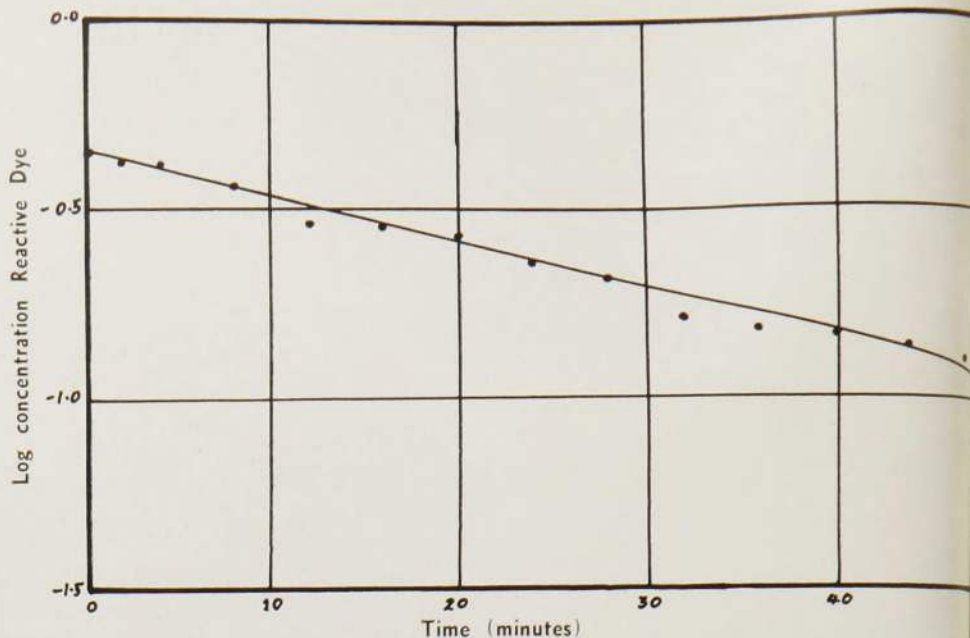


Figure 1
Rate of hydrolysis of Procion Brilliant Red 2BS at 25°C

immediately diluted and buffered to pH 6.4 to stop the reaction, and then measured on a spectrophotometer without delay. It was found that the absorption spectra of the initial reactive dye and the inactivated hydroxy derivative differed sufficiently to enable the proportions of the two forms to be measured, although the accuracy is not high owing to the small differences in optical density which are involved. In all the experiments it was found that the kinetics of decomposition were those of a first order reaction in that a straight line was obtained by plotting the logarithm of the concentration of reactive dye remaining in solution at any time against the time. An example is shown in Figure 1. From the slope of the line, the velocity constant K of this hydrolysis reaction may be calculated. Results obtained at different hydrogen ion concentrations, electrolyte concentrations, and temperatures are summarized in Tables III, IV and V.

TABLE I
Rate of reaction of Procion Brilliant Red 2BS with cellulose in soda ash solution

Time of Treatment	15 secs	30 secs	45 secs	1 min	4 min	12 min
Optical Density	0.175	0.169	0.165	0.169	0.174	0.174

TABLE II
Rate of reaction of Procion Brilliant Red 2BS with cellulose in ammonia vapor

Time of Treatment	0	5 secs	10 secs	15 secs	1 min	16 min
Optical Density	0.020	0.093	0.090	0.091	0.091	0.084

TABLE III
Effect of pH on hydrolysis of Procion Brilliant Red 2BS in water at 25°C (Dye concentration = 0.33 g/l)

Conditions	Measured pH	Velocity Constant K
4 g/l Na ₂ CO ₃ , 0.91 g/l HCl	10.1	0.005
5 g/l Na ₂ CO ₃	11.1	0.030
4.5 g/l Na ₂ CO ₃ , 0.5 g/l NaOH	11.8	0.054
2 g/l NaOH	12.7	0.175

TABLE IV
Effect of electrolyte concentration on hydrolysis of Procion Brilliant Red 2BS in water (Dye concentration = 0.33 g/l)

Temp	Conditions	Measured pH	Velocity Constant K
25°C	5 g/l Na ₂ CO ₃	11.1	0.030
25°C	10 g/l Na ₂ CO ₃ , 30 g/l NaCl	11.1	0.048
25°C	20 g/l Na ₂ CO ₃ , 60 g/l NaCl	11.1	0.074

TABLE V
Effect of temperature on the hydrolysis of Procions Brilliant Red 2BS and Blue 3GS (Dye concentration = 0.33 g/l; Na₂CO₃ = 10 g/l; NaCl = 30 g/l)

Temp	Procion Brilliant Red 2BS		Procion Blue 3GS	
	pH	K	pH	K
25°C	11.1	0.048	11.1	0.013
30°C	11.1	0.10	10.95	0.021
35°C	11.1	0.14	10.85	0.051

These results show clearly that the rate of hydrolysis increases rapidly with increasing pH and with increasing temperature and to a lesser degree increases with increasing electrolyte concentration. They also show that Procion Brilliant Red 2BS is much more easily hydrolyzed than Procion Blue 3GS.

The importance of decomposition in alkaline solution depends on the method of application. If the Procion dyes are applied by padding in a continuous dyeing process, then the dye and alkali are taken up together by the fibers and when subsequently dried or steamed, reaction takes place so much more rapidly with the fiber than with water that good fixation is obtained. Nevertheless, some portion of the dye does react with the water in the fiber and the unfixed inactive dye must be removed by thorough washing in order that the full wetfastness of the fixed dye can be revealed. The main importance of decomposition in solution in continuous processes is therefore the stability of the padding liquor. One way of increasing this stability is to use sodium bicarbonate as the alkali, solutions being stable for several hours in the cold under such conditions. This mild alkali is sufficient to produce fixation if a subsequent heat treatment is involved or if the goods are allowed to remain in the wet condition for several hours or conveniently, overnight. Where more rapid fixation at room temperature is required, sodium carbonate must be employed and the only method of obtaining solution stability is to keep the dye and alkali in separate solutions until just before they are applied to the cloth. For example, the two solutions may be added separately to the padding trough. Special bazaar dyeing and printing methods have been devised for the Eastern markets based on this principle.

Where decomposition in the dye-bath is of much greater importance, however, is in batch dyeing. The general recommendation is to commence dyeing in a cold neutral solution of the Procion dyes containing some salt, and then after about 30 minutes, to add a mild alkali, such as sodium carbonate, trisodium phosphate or sodium silicate, sufficient to produce a pH of about 11, and continue dyeing for a further hour. It is apparent that some dyeing takes place in neutral solution but the absorbed dye is not fixed and can be washed out of the fiber by water at this stage. It is also clear that the affinity of the dyes is low, as shown by the poor exhaustion in a neutral solution, which means that very good leveling is shown through-

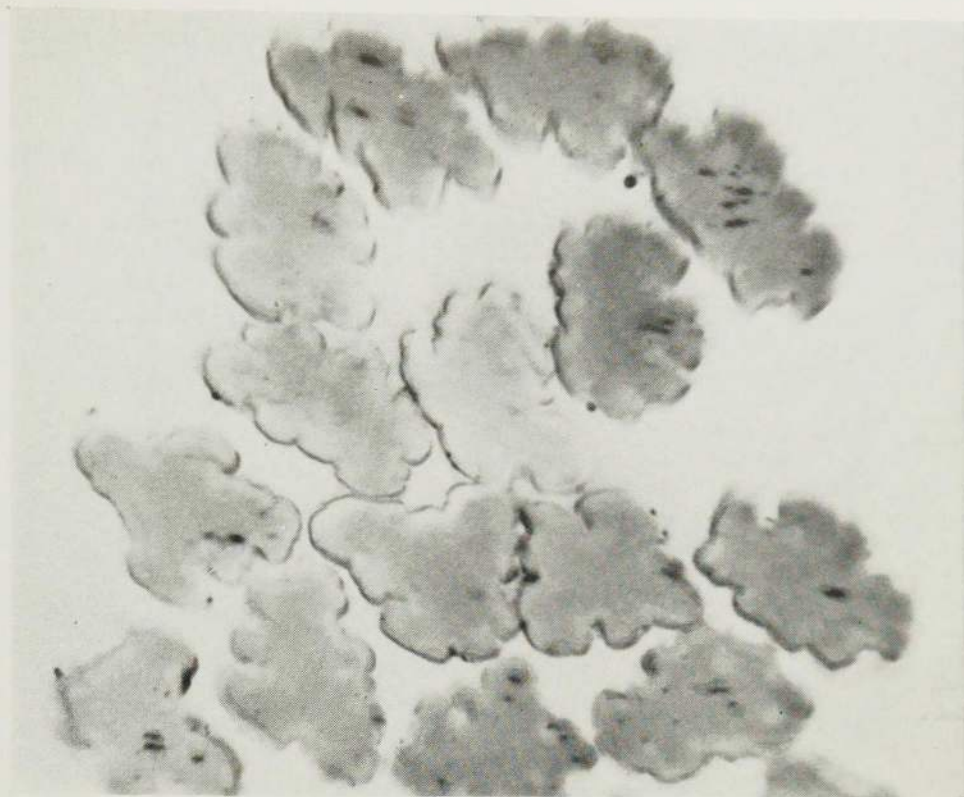


Figure 2a

Viscose fiber dyed with Procion Brilliant Orange G by impregnation and cold fixation

out this stage of the process. Such a low exhaustion would be uneconomic. When the alkali is added, all the dye already on the fiber is very rapidly fixed. This upsets the equilibrium which existed between the dye in the fiber and in the bath, and further diffusion of dye into the fiber begins. The new reactive dye entering the fiber may be expected to be fixed as soon as it enters so that the additional dyeing should take place almost entirely in a thin layer of fiber near the surface. The real existence of this phenomenon can be seen by examination of cross-sections of fibers dyed under appropriate conditions. To exaggerate the effect for illustration, viscose yarn was impregnated with a solution of Procion Brilliant Orange G containing sodium bicarbonate and allowed to stand in a wet condition in a closed bottle for 24 hours at room temperature, and then washed thoroughly. Under these conditions, the dye can penetrate the whole of the fiber before reaction occurs and is then fixed in situ to give a uniformly dyed fiber. This corresponds fairly closely to the conditions of most continuous dyeing processes and to the pad-roll process. In the second place, the yarn was immersed in a cold dye-bath containing dye and sodium carbonate and dyed for 3 hours at room temperature before washing. Since the alkali was present at the beginning of the dyeing process, fixation should occur as soon as the dye enters the fiber and severe ring dyeing should be obtained. The photomicro-

graphs in Figure 2 confirm these expectations.

It should be emphasized that, in the recommended practical batch dyeing methods, alkali is not present in the initial stages, so that the dye absorbed from neutral solution will penetrate the fiber and fix in situ on addition of alkali. Under such conditions, therefore, distribution of dye through the fiber will be intermediate between that shown in the two illustrations and will approach more closely to uniform distribution the better the degree of exhaustion obtained before alkali addition.

It should be noted also that, since the dye is chemically combined with the fiber, it cannot diffuse out again and therefore the existence of ring dyeing will not adversely affect the wetfastness properties of the dyed fiber as it would with a direct dye. This has been confirmed by washing tests on the samples used for the preparation of the photomicrographs. It is obvious also that no leveling can occur after alkali has been added to the bath in batch dyeing.

Returning to the more theoretical aspects of the dyeing process, it is clear that, in the second phase of the batch dyeing process, the reactive dye in the alkaline bath will also be reacting with water, so that the extent to which dyeing by fixation occurs will depend on the relative rates of diffusion into the fiber and decomposition in the bath. In other words, in this stage it is a question of probability as to whether a reactive dye mole-

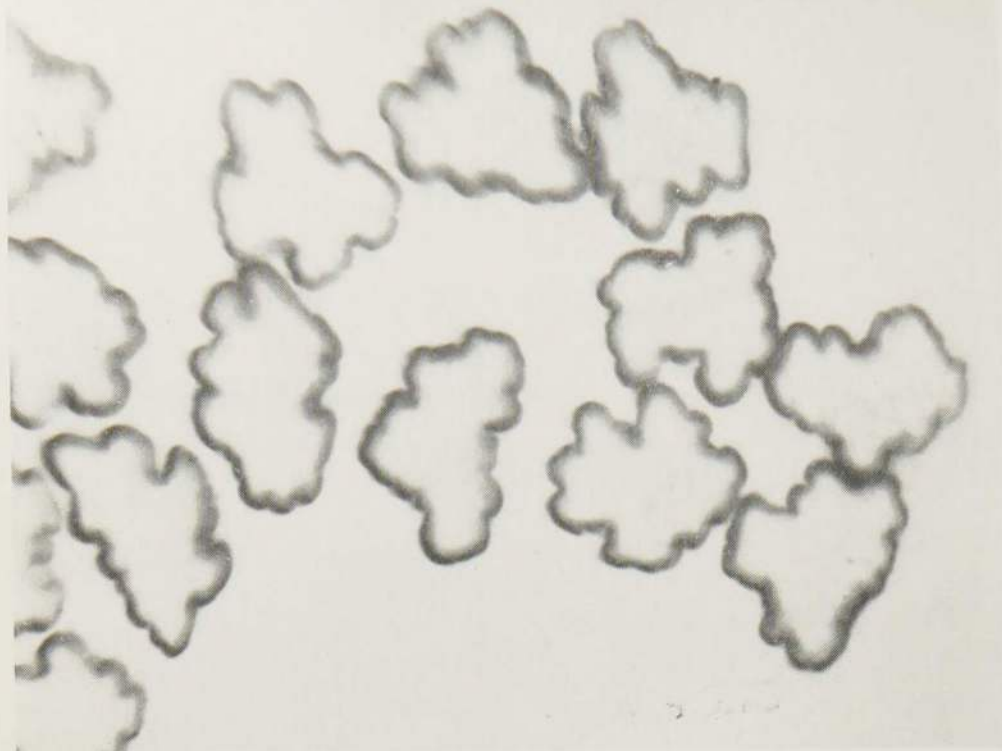


Figure 2b
Viscose fiber dyed with Procion Brilliant Orange G from an alkaline dyebath

cule can diffuse to and into the fiber before it collides with an active hydroxyl ion and is destroyed.

The importance of decomposition in batch dyeing can only be assessed from a knowledge of the rates of diffusion and decomposition. The measurement of the latter has already been described. The rate of diffusion was studied in viscose film. The film was squeezed on to a glass plate which formed one wall of a cell filled with dye solution. Inlet and outlet tubes were fitted to the cell and a pump arranged to circulate dye liquor through the cell continuously from a large reservoir. The volume of the reservoir was such that the total dyebath concentration of reactive and inactive dye could be regarded as constant. The total optical density of the cell containing dye solution and viscose film was measured at intervals at the isosbestic wavelength. Any increase in density was attributed to uptake of dye by the film, and the process was treated as diffusion from one side into an infinite slab. Applying the usual diffusion equations based on Fick's Law, diffusion coefficients were calculated for the intermediate times of the experiments. Data obtained at very short times or at long times gave unsatisfactory results owing to the experimental inaccuracy in determining small amounts of dye uptake or small changes in the uptake.

These experiments were carried out in neutral solution to determine the diffusion of the reactive dye in absence of complicating reaction with the fiber. In addition, similar experi-

ments were carried out with completely inactivated dye, ie, the hydroxyl instead of the chloro derivative. The results are shown in Table VI. It will be seen that the diffusion coefficients of both the reactive and inactive forms of Procion Brilliant Red 2BS are very similar, as would be expected since the molecular size and shape of the two forms are nearly the same, although the reactive dye is more sensitive to temperature.

TABLE VI
Diffusion of Procions Brilliant Red 2BS and Blue 3GS into viscose film
(0.33 g/l dye; 30 g/l salt; wet thickness of film 3.3×10^{-3} cm)

Dye	Diffusion Coefficient ($\text{cm}^2/\text{min} \times 10^7$)		
	25°C	30°C	35°C
Procion Brilliant Red 2BS	1.7	2.4	3.5
Inactive form of Red 2BS	1.4	1.6	2.0
Procion Blue 3GS	1.0	1.2	1.5

TABLE VII
Comparison of calculated and observed dye fixation from an alkaline dyebath

Dye	Temp (°C)	Dye absorbed	Dye combined	Dye in fiber which is chemically combined (%)	
				Actual	Calculated
Procion Brilliant Red 2BS	25	0.31 g	0.21 g	68	73
	30	0.25 g	0.15 g	60	64
	35	0.24 g	0.15 g	63	65
Procion Blue 3GS	25	0.39 g	0.27 g	69	76
	30	0.36 g	0.25 g	69	73
	35	0.34 g	0.23 g	68	68

In order to assess the practical significance of diffusion and hydrolysis, a preliminary attempt has been made to develop a simple theory of the dyeing process. It is assumed that diffusion of dye into the fiber takes place according to Fick's Law, the reactive and inactive species being indistinguishable in this process. The fate of the reactive dye entering the fiber is governed by the relative rates of the hydrolysis and fixation reactions within the fiber. If the two reaction constants are designated by K and F respectively, it can be shown that, at an infinite time later, the proportion of reactive dye which is fixed to the

fiber will be $\frac{F}{F+K}$. From the preceding

data it is obvious that, in sodium carbonate solution about pH 10, F must be very much greater than K so that this fraction reduces to unity. In other words, under these conditions all the reactive dye which enters the fiber will be fixed. This simplification may not apply under less alkaline conditions, as will be seen later.

Diffusion into the fiber, however, is a much slower process and comparable in speed with the rate of hydrolysis. Hence diffusion into the fiber takes place from a dyebath in which the concentration of reactive dye is steadily decreasing even in the case of an infinite dyebath. The proportion of reactive dye remaining at any time (t) will be given by $C_0 e^{-Kt}$ where C_0 is the initial concentration. Hence the amount of dye fixed at equilibrium may be calculated from Hill's equation for diffusion into cylindrical fibers modified by the decrease in external concentration. Using the diffusion coefficients and hydrolysis constants already determined, the amount of dye fixed at 25, 30 and 35°C has been calculated under the conditions described below and is shown in Table VII. In the same table are the experimental results obtained by dyeing to equilibrium viscose rayon yarn (50 g) in a dyebath (1,500 cc) containing Procion Brilliant Red 2BS or Blue 3GS (0.5 g), sodium carbonate (15 g) and salt (45 g). After dyeing, the fiber

was removed, squeezed and weighed to determine the amount of entrained liquor. The concentration of dye in the dyebath was determined optically. The dyed fiber was extracted with boiling Lissapol NC solution (2 g/l) and the amount of dye removed determined optically. In this way the content of fixed and unfixed dye in the fiber was found.

Considering the approximations introduced into the theory, the agreement is good and the theory does explain why a finite equilibrium is reached rather than the complete reaction and 100% fixation which would be expected if no hydrolysis took place.

This theory has an important bearing on practical dyeing. Considering first the effect of temperature, it will be seen from Table VII that, as the temperature is raised, the total amount of dye absorbed by the fiber decreases. In other words, the affinity of the reactive and inactive dye decreases with increasing temperature as with all other systems. The percentage of dye absorbed which is fixed, however, is only slightly affected by temperature. The reason for this is that, although an increase of temperature increases hydrolysis (Table V), it also increases the rate of diffusion into the fiber (Table VI) and the two effects almost cancel out.

From the practical point of view, therefore, in the two-stage batch dyeing process the temperature of the alkaline phase is relatively uncritical between 20 and 60°C. As noted earlier, however, the exhaustion obtained during the first phase of neutral dyeing decreases considerably with increasing temperature, and when alkalis added, the dye already on the fibers fixed almost instantaneously and efficiently. Hydrolysis of active dye takes place mainly in the dyebath. Thus the overall process will be most efficient when the maximum amount of dye is induced to go on the fiber in the first neutral-dyeing phase. Consequently in practice the highest degree of fixation will be produced by carrying out the first phase as cold as is conveniently possible, i.e., room temperature. There is then no advantage in yield to be obtained by raising the temperature after addition of alkali. It is theoretically possible that an increase of temperature at this point might permit a reduction in the time of dyeing in the second phase, but the success of this maneuver would depend on whether liquor circulation is adequate to give level adsorption of dye at the increased rate of dyeing (reduced by the higher temperature since no migration can take place). Success is also likely to depend on the properties of the particular dyes in-

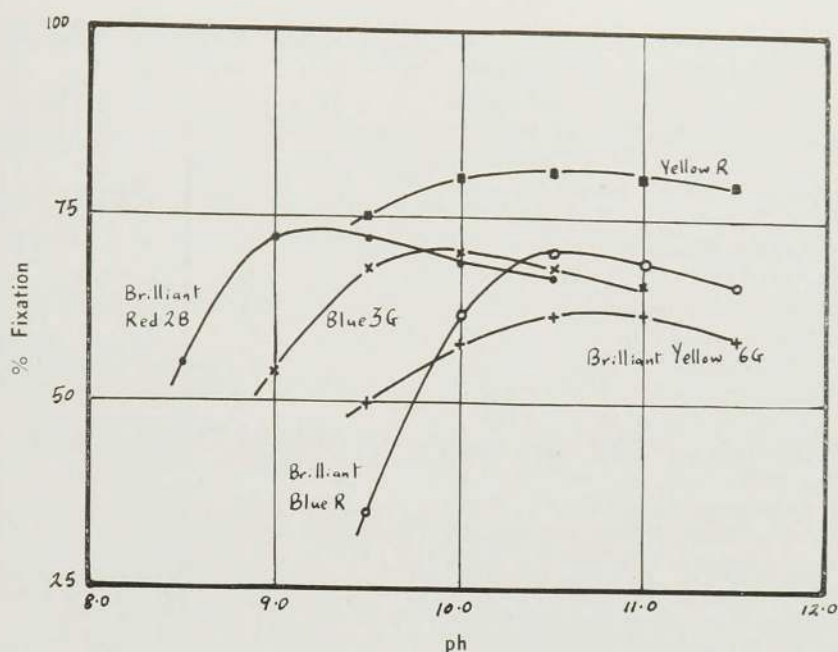


Figure 3

Effect of pH on the fixation of several Procion Dyes

involved and, moreover, the saving in time may be offset by the increased steam usage. These considerations might well repay investigation by dyers under their own conditions, but as a general recommendation the safest policy is to carry out the whole dyeing at or near room temperature.

Considering next the effect of alkalinity, at any one temperature, diffusion into the fiber is only slightly affected but the hydrolysis rate is increased with increasing pH. The percentage of dye fixed should, there-

fore, decrease with increasing pH. Measurements of percentage fixation against pH determined on dyeings carried out by the standard batch dyeing process on viscose rayon and bleached cotton yarns are shown in Tables VIII and IX, and in Figure 3.

It will be seen that in all cases the fixation passes through a maximum. The effect is more noticeable on cotton than on viscose rayon and in all cases the optimum pH of fixation is lower on the latter fiber. The decrease in fixation with increasing pH

TABLE VIII

Fixation of Procion Dyes on viscose rayon at different pH values

(1.5% dye, 30:1 liquor, 50 g/l salt, dyed 30 min without alkali, then 90 min at indicated pH, all at 20°C)

Dye	% Fixation at							
	pH 8.5	pH 9.0	pH 9.5	pH 10.0	pH 10.5	pH 11.0	pH 11.5	pH 12.0
Procion Brilliant Yellow 6G	—	—	50	58	62	62	59	—
Procion Yellow R	—	—	75	80	81	80	80	79
Procion Brilliant Orange G	—	—	68	76	78	78	76	—
Procion Brilliant Red 2B	55	72	72	69	67	—	—	—
Procion Brilliant Blue R	—	—	35	62	70	69	66	—
Procion Blue 3G	—	54	68	70	68	66	—	—

TABLE IX

Fixation of Procion Dyes on bleached cotton at different pH values

(Data as in Table VIII)

Dye	% Fixation at						
	pH 9.0	pH 9.5	pH 10.0	pH 10.5	pH 11.0	pH 11.5	pH 12.0
Procion Brilliant Yellow 6G	—	17	27	34	35	31	—
Procion Yellow R	—	—	65	76	79	75	—
Procion Brilliant Orange G	—	—	61	72	75	72	—
Procion Brilliant Red 2B	35	52	59	58	54	—	—
Procion Brilliant Blue R	—	—	—	55	61	56	48
Procion Blue 3G	—	36	54	63	63	56	—

at the upper end of the range is in accord with the theory outlined above, but the initial increase with increasing pH is not. The explanation of this effect may be found in a more detailed examination of the rate of reaction with the fiber, which has not so far been examined over a range of pH. Clearly, however, the rate of the fixation reaction must be extremely slow in neutral solution, since most of the dye can be washed out of the fiber if no alkali treatment is involved, but on the other hand is very rapid at pH 10 as shown in Table I. Around pH 8, therefore, both the rate of fixation and the rate of hydrolysis must be slow, and in dyeings for a limited time, such as those forming the basis of Tables VIII and IX, it may be that a considerable proportion of the dye still remains in the reactive form at the end of the dyeing operation. As the pH increases, more and more of the dye is either fixed or hydrolyzed, and the optimum pH is the point at which all the reactive dye has been used up in one way or the other at the end of the dyeing period. Further increase of pH then merely accelerates hydrolysis before the dye can get into the fiber. This view is supported by experiments in which the time of dyeing was prolonged up to 6 hours after addition of alkali. The results are shown in Table X and Figure 4.

The results show that, at lower pH, the percentage fixation improves with increasing time of dyeing, but the effect is negligible above pH 10.5. Given infinite time, the fixation would presumably increase continuously with decreasing pH as predicted by theory.

In theory, therefore, the pH of the alkaline stage of batch dyeing should be adjusted according to the dyeing time, the temperature, and the particular dye being used, the alkalinity being such that at the end of the dyeing operation the last part of reactive dye has just been destroyed or has combined with the fiber. The use of strong alkalis giving a much higher pH than the optimum is detrimental in batch dyeing. Again this situation leaves scope for investigation by dyers under their own particular conditions but is unsatisfactory as a general

recommendation. Fortunately the change of fixation with increasing pH is not great once the optimum has been passed, while most of the normal Procion dyes show optimum fixation in the same pH range. Consequently, it is possible to arrive at a satisfactory compromise and recommend one general set of conditions for batch dyeing. In the case of viscose rayon, the use of sodium carbonate as the alkali is satisfactory, but on cotton the pH of optimum fixation is higher and a stronger alkali, such as trisodium phosphate, is necessary to obtain maximum yield. Sodium carbonate can be used in cotton dyeing if some loss in yield is accepted. Procion Brilliant Red 2B is somewhat anomalous in that it is more reactive than the other members of the range and can be fixed satisfactorily at a lower pH.

It must be noted that all the work described in the present paper has been concerned with the original highly reactive Procion dyes. A further range of dyes known as the Procion "H" dyes has now been marketed, which are of a similar type but which are less reactive. These "H" dyes have greater stability in aqueous alkaline solution and in alkaline print

pastes but in general require heating in order to make them react with cellulose. Consequently, the discussion in this paper cannot be extended to cover the Procion "H" dyes.

CONCLUSION

Clearly much remains to be done in this field and the possibilities of further development are great. Although the theory of dyeing with reactive dyes is still in a somewhat elementary state, the basic principles have been uncovered and have resulted in the development of a wide range of novel and practical dyeing methods. Reactive dyes go a long way towards meeting the target of dyes for cellulose which combine simplicity in application with high wetfastness.

ACKNOWLEDGMENT

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LITERATURE CITED

- (1) Vickerstaff T, *J Soc Dyers Col* 73, 1 (1957).
 - (2) Fowler, JA, and Preston, C, Society of Dyers and Colourists Symposium, Buxton, 1957 (forthcoming publication).
- See also pattern cards and technical literature issued by Imperial Chemical Industries Ltd.

A list of papers accepted for future publication in the American Dyestuff Reporter will appear in the February 10th issue.

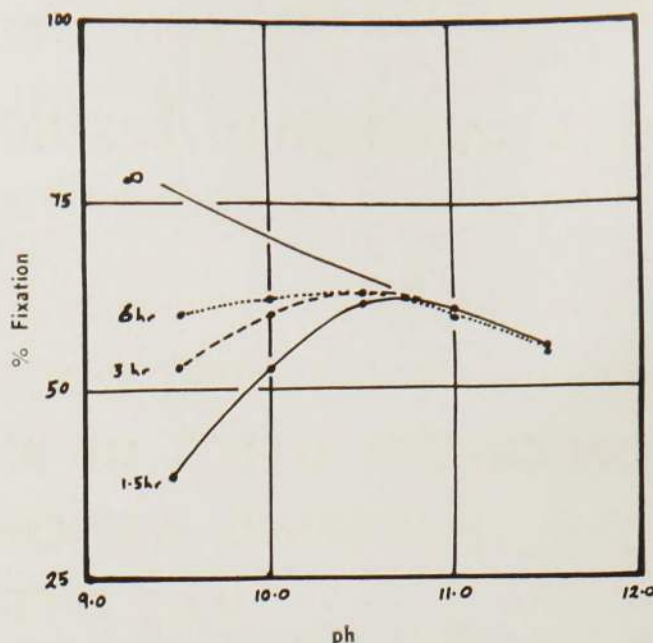


Figure 4
Effect of time on the fixation of Procion Blue 3GS

TABLE X
Effect of Prolonging Dyeing Time on the Fixation of Procion Blue 3G at Different pH Values
(Data as in Table VIII)

Time of dyeing after addition of alkali	% Fixation at				
	pH 9.5	pH 10.0	pH 10.5	pH 11.0	pH 11.5
1.5 hours	40	53	62	61	56
3 hours	53	60	63	61	56
6 hours	60	62	62	60	55