Reactive Dyes for Nylon*

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Conventional dyes for nylon have suffered, hitherto, from the disadvantage that those of good fastness properties do not readily cover the chemical and physical irregularities of the fibre, whilst those which are free from these defects have relatively low fastness properties.

A new range of reactive dyes for nylon has now been developed. They are disperse dyes and can be applied in an unreactive form under acid conditions, when they possess the level-dyeing properties of disperse dyes. When the bath is made mildly alkaline, reaction occurs between dye and fibre, and a fast, level dyeing is obtained. It has been found that these dyes react both with the amine end-groups and with the amide groups in the fibre, so difficulties associated with saturation of amine end-groups are not encountered.

Rates of dyeing and fixation of the dyes have been determined both separately and in mixtures and it is shown that the dyes are compatible for dyeing as mixtures. Rate-of-dyeing curves indicate that these dyes behave as medium-to-slow dyeing disperse dyes.

As with Procion dyes when applied to cellulose, a side-reaction occurs in the dyebath, and in this case the deactivated dye remains on the fibre after the soaping treatment. Since, however, the unfixed dye has fastness properties at least equal to those of conventional disperse dyes, this small proportion can be tolerated without undue loss of fastness.

For the first time a range of dyes is available for dyeing nylon to level, attractive colours with good wet fastness properties using a simple technique and conventional dyeing machinery.

Introduction

The basic difficulty confronting any dyer, apart from light fastness and subsidiary requirements, is to obtain attractive level shades having good fastness to laundering. With some fibres— and nylon is a particularly good example— these two requirements are to some extent opposed. Dyes which give level dyeings on nylon have merely moderate fastness properties; those which have good fastness are apt to show barriness— distinct light and dark streaks in weft or warp directions. The reasons for this are well recognised. Barriness arises from the difficulty of manufacturing and preparing nylon fibre in a completely homogeneous condition, both chemically as well as physically.

The chemical variation lies in the proportion of free amino groups to the remainder of the molecule, and is essentially a molecular weight factor [1]. The physical differences arise largely in the spinning and heat setting processes. Although there are indications [2] that chemical differences may eventually be reduced to an innocuous level, it would appear that physical differences (which are not, of course, confined to nylon) are likely to remain a problem. As would be expected, amine end-group differences affect only those dyes with affinity for such groups, e.g. acid dyes, whereas the physical differences influence all types of dyes to a greater or a lesser degree.

Disperse dyes are unaffected by chemical variation and relatively little affected by physical variation. The original problem remains, however: the levelling dyes have only moderate wet fastness properties, whilst dyes with reasonably good fastness properties show barriness. This dilemma is placed in perspective when it is remembered that, although at the present time by far the greater proportion of continuous-filament nylon is dyed with disperse dyes, there is continuous and increasing commercial demand for the use of faster dyes [2].

There have been many attempts to solve this problem by applying acid dyes in a level manner. One obvious approach is to employ a continuous dyeing process, in which the dye is applied by padding and then fixed *in situ*, but little success appears to have attended such efforts [3–7]. An alternative approach has been to apply acid dyes from extremely dilute dyebaths by using drip feed, almost insoluble metal salts of the dyes [8], or insoluble complexes of the dyes with cationic agents [9]. The use of special agents to promote the levelling of acid dyes has also been tried [10, 11]. Finally, the use of swelling agents [12] or high-temperature dyeing to open up the fibre structure and so overcome physical differences has been advocated [2, 13–15]. None of these methods has proved entirely successful, and the need still remains for fast dyes which have the same ability to cover fibre irregularities as have disperse dyes.

The success of reactive dyes applied to cellulose fibres inevitably suggested a further line of attack. Procion dyes do not, of course, provide the answer, since, being anionic they suffer from the same defects as acid dyes, but the high degree of washing fastness shown by Procion dyes on nylon encouraged further investigation.

What was clearly needed was a dye without ionic solubilising groups, capable of dyeing in the same level manner as a disperse dye and capable of becoming reactive when inside the fibre. Insertion of a chemically reactive group into a molecule of a disperse dye is relatively simple. It is highly desirable, however, that the resultant molecule should retain the advantageous properties of a disperse dye, and this, together with the retention of other desirable properties, is by no means easy to achieve. Investigation of these requirements has now resulted in the development of a new range of dyes— the Procinyl dyes— which are disperse dyes containing a group carrying a labile chlorine atom capable of reacting with nylon. These dyes are quite stable in water and in weakly acidic liquors under hot dyebath conditions, and dye in the same level manner as normal disperse dyes. When exhaustion has been achieved, the system is activated by addition of alkali, whereupon chemical reaction occurs between dye and

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TABLE I

Comparative Resistance of Procinyl and Disperse Dyes to Propanol Extraction from Nylon

Dye	Dye on Fibre (%) after—		
	Dyeing	Washing at 85°C.	Propanol Extraction
3·3% Procinyl Orange GS	70	59	48
3·3% Procinyl Scarlet GS	77	72	60
2·5% Procinyl Yellow GS	85	81	49
3·3% Procinyl Blue RS	90	88	77
1·5% Dispersol Fast Orange G 300 (C.I. Disperse Orange 3)	95	60	0
1·5% Dispersol Fast Scarlet B 150 (C.I. Disperse Red 1)	95	44	0
7·5% Duranol Brilliant Blue BN 300 (C.I. Disperse Blue 3)	86	47	0
2·5% Dispersol Fast Yellow G 300 (C.I. Disperse Yellow 3)	93	58	0

fibre, and in this way the dyeing of fast, level, attractive shades on nylon has at last become a reality.

Evidence of Reaction with Nylon

Before discussing dyeing properties, the evidence which indicates that Procinyl dyes do react with nylon under alkaline conditions will be reviewed. The evidence is of three kinds—

(1) Nylon dyed with conventional disperse, azoic, or acid dyes can be stripped by boiling with solvents such as chlorobenzene, propanol, or aqueous pyridine. These, although excellent solvents for Procinyl dyes, do not extract them from nylon, which suggests that some force other than adsorption, mechanical retention, or salt linkage is holding the dye on the fibre.

(2) If nylon fibre, dyed with disperse dyes, is dissolved in *o*-chlorophenol and the resulting solution poured into propanol so that the nylon is precipitated, the dye appears in the liquid phase. If, however, nylon dyed with Procinyl dyes is treated in the same way, the dye remains associated with the precipitated nylon, even though it is normally quite readily soluble in both *o*-chlorophenol and propanol. If the unreactive analogue of Procinyl Scarlet G is treated in a similar manner the colour is removed from the nylon and is dissolved in the liquid phase.

(3) The colour of Procinyl Scarlet G is due to the presence of an azo group. Consequently the dye can be reduced on the fibre with sodium sulphoxylate formaldehyde and formic acid to two amine-containing end-products. If the dye has reacted with the fibre, one of the products should remain firmly anchored to the fibre and should resist extraction with hydrochloric acid. Such a "discharged" fibre can, in fact, be diazotised and coupled with a phenol to produce a new dye. If nylon is dyed with the unreactive analogue of Procinyl Scarlet G and treated in a similar manner, no colour is developed. Again this is very strong evidence that the Procinyl dye is combined with the fibre.

It is of interest at this point to show quantitatively the resistance of the Procinyl dyes to propanol extraction. Table I shows that, of the dye exhausted on to the fibre, a large proportion remains fixed, whereas with disperse dyes the dye is removed completely. Dyeings of both Procinyl and conventional disperse dyes were also subjected to a severe washing treatment with 5 g. soap per litre at 85°C. for 30 min., and the amounts remaining on the fibre after the treatment determined. The results (Table I) show that not only the fixed, but also the unfixed, Procinyl dye has greater resistance to washing than coventional disperse dyes.

The above observations show fairly conclusively that Procinyl dyes do react in some way with nylon, but do not indicate the precise mode of attachment. This is a matter of considerable interest, since if reaction takes place only on amine end-groups the difficulties associated with saturation may again arise. However, reaction with amide groups along the nylon chain is also possible. These two possibilities have been examined.

If each molecule of dye reacts with one amine end-group, this should be demonstrable by estimating the number of amine ends left unreacted after dyeing. This has been determined by the standard method, which consists in dissolving the fibre in phenol-methanol and titrating conductimetrically with a standard hydrochloric acid solution in methanol. The amounts of dye estimated colorimetrically and the amine end-sites occupied are in good agreement up to the point at which these sites are completely saturated (Table II). Over this range of dye concentration, therefore, reaction appears to occur solely with the amine groups.

However, if the dye reacts only with primary amino groups in the fibre, a point will be reached with increasing dye uptake when no more sites will be available for reaction, and a limit will be imposed to the amount of dye retained after extraction with propanol. For a nylon containing 42·6 m-equiv. of end-groups per kg. of fibre, the maximum theoretical amount of dye which can be retained on this basis is 1·8–2·0 g./100 g. approx., but, as is seen from Table II, much larger quantities can be fixed on the fibre.

There are two possible explanations of this observation—

(*a*) The production of fresh primary amine sites by the hydrolysis of amide links

(*b*) Reaction of the dye with amide groups.

Degradation of nylon under the pH conditions used for dyeing is unlikely, since the fibre is

TABLE II

End-group Analysis of Nylon dyed with Procinyl Dyes

Dye applied (g./100 g. fibre)	Dye "fixed" (g./100 g. fibre)	Dye "fixed" (m-equiv./ kg. fibre) Colorimetric Estimation	Amine End-groups reacted (m-equiv./ kg. fibre) Titrimetric Estimation
	PROCINYL SCARLET GS		
0·5	0·35	7·4	7·6
1·0	0·72	16·5	18·6
1·5	1·23	25·8	24·6
2·5	1·47	30·9	34·6
5·0	2·8	59	42·6
10·0	4·2	88	42·6
20·0	6·1	128	42·6
	PROCINYL BLUE RS		
0·5	0·39	9·3	5·6
1·0	0·78	18·4	22·6
1·5	1·02	24·0	25·6
2·0	1·23	29·0	27·6
2·5	1·44	34·0	38·6
4·0	1·84	43·5	42·6
6·0	2·29	54·1	42·6
8·0	2·37	56·0	42·6

normally stable to alkali other than caustic alkali at elevated temperatures, and the acids required to achieve hydrolysis are either mineral acids or strong organic acids. Since degradation as judged by tensile strength and extensibility does not occur to any significant extent (cf. Table III), it can be inferred that amide hydrolysis plays a negligible part.

TABLE III

Strength of Nylon Yarn dyed with Procinyl Scarlet G

Dye applied (g./100 g. fibre)	Dye absorbed (g./100 g. fibre)	Tensile Strength (g./denier)	Extensibility (%)
0	0	5·2	26·9
0·5	0·3	4·7	23·0
1·0	0·6	4·9	28·9
2·0	1·1	5·1	25·3
5·0	2·8	4·8	26·9
10·0	4·2	4·7	25·2
20·0	6·1	4·5	25·8

Some indication of reaction between Procinyl dye and amide groups in nylon has been obtained by showing that reaction is possible between the dye and a "nylon model" compound—

$$C_4H_9\cdot NHCO(CH_2)_4\cdot CONH(CH_2)_6\cdot NHCONH\cdot C_4H_9$$

containing amides as the only reactive group. This insoluble compound was treated in a normal dyebath of Procinyl Orange G, and the coloured solid obtained was extracted with acetone, recrystallised from propanol, and treated with charcoal. The product was still coloured. When this reaction product was dissolved in propanol and the solution poured into benzene (in which Procinyl Orange G is readily soluble and in which the model compound is insoluble), the coloured solid was again precipitated and the solvent layer was almost colourless. This slight coloration is attributable to the slight solubility of the reaction product in the mixed solvent. When a mechanical mixture of Procinyl Orange G and the model compound was similarly treated, the dye remained dissolved in the solvent and a white precipitate of the model compound was obtained.

Additional evidence for reaction has been obtained by measuring the rate of hydrolysis of the dyes in aqueous liquors—

(*a*) In presence of alkali and hexamethylenediamine at pH 10

(*b*) In presence of alkali and *NN'*-dibenzoylhexamethylenediamine at pH 10

(*c*) In presence of alkali only at pH 10.

For each dye the rate of hydrolysis was slightly greater (10–20%) in presence of *NN'*-dibenzoylhexamethylenediamine than in water, and in presence of hexamethylenediamine itself it was very much greater.

Taking these two types of experiment together, it is inferred that Procinyl dyes do react, under alkaline conditions, with amide groups in nylon, at a rate considerably less than the reaction rate with free amine groups. This accounts both for the stoichiometry of the reaction with amine groups shown in Table II and for the fact that reaction continues to take place after the amine groups are saturated. As the saturation point approaches, the rate of dyeing, now associated chiefly with amide groups, should be reduced from the high rate associated with the amines. Fig. 1 shows that this is so.

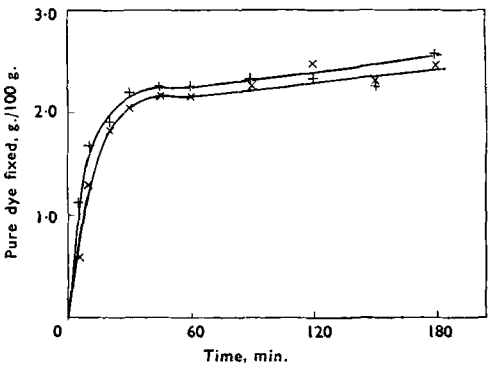

FIG. 1— Rate of Fixation of 50% Shades

Dyeing Properties of Procinyl Dyes

Like other types of reactive dyes, Procinyl dyes undergo a side-reaction with water, and to minimise this it is desirable, as with Procion dyes on cellulose, to absorb the dye on to the fibre initially in an unreactive form. However, the main advantage to be gained in this manner is in terms of levelling rather than degree of fixation. With Procion dyes on cellulose the preliminary absorption may be brought about by adding electrolyte to the neutral dyebath followed by the addition of a suitable alkali. Procinyl dyes, on the other hand, are relatively insensitive to electrolyte concentration. Fortunately, however, adequate absorption takes place from acid suspensions, in which the dyes are relatively inert. This allows an efficient two-stage system to operate, by absorption of the dye in presence of acid followed by reaction in alkali.

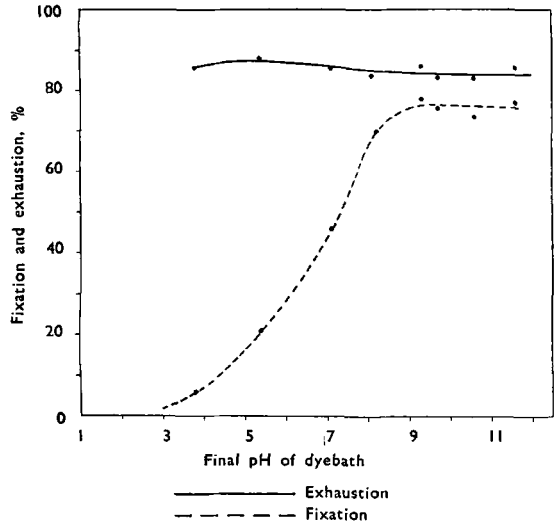

FIG. 2— Procinyl Blue RS: Variation of Exhaustion and Fixation with Dyebath pH (1% Shade (Pure Dye), Dyed for 1 hr. at 95°C., 40:1 Liquor Ratio)

Fig. 2 illustrates the behaviour of Procinyl Blue R applied by a one-stage process from dyebaths of different pH values. Whilst the exhaustion of dye varies little with change of pH, the percentage fixation—

$$\frac{\text{Dye on fibre after extraction with propanol}}{\text{Dye in dyebath}} \times 100$$

increases sharply from about zero at pH 4 to a high figure between pH 9 and 10, and a very high proportion of the dye actually absorbed on the fibre becomes fixed at these higher pH values.

The other Procinyl dyes behave similarly, although the fixation of Procinyl Orange G and Procinyl Scarlet G (Fig. 3) starts to rise at a lower pH, does not reach so high a maximum fixation, and decreases more markedly at pH >10. This difference appears to be due to the different degrees of reactivity of the dyes with water at the higher pH values.

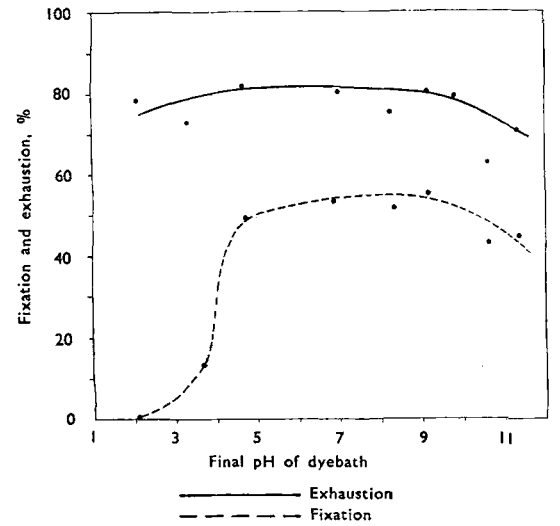

FIG. 3— Procinyl Scarlet GS: Variation of Exhaustion and Fixation with Dyebath pH (1% Shade (Pure Dye), Dyed for 1 hr. at 95°C., 40:1 Liquor Ratio)

The rate of fixation and the percentage fixation finally achieved are affected by temperature. Fig. 4 illustrates the temperature-range properties of Procinyl Blue R, the dye most sensitive to temperature. The exhaustion after dyeing for 1 hr. changes little between 70° and 95°c. The fixation at pH 9, however, rises with increasing temperature, and clearly, to achieve maximum fixation, the temperature of the dyebath should be as high as possible.

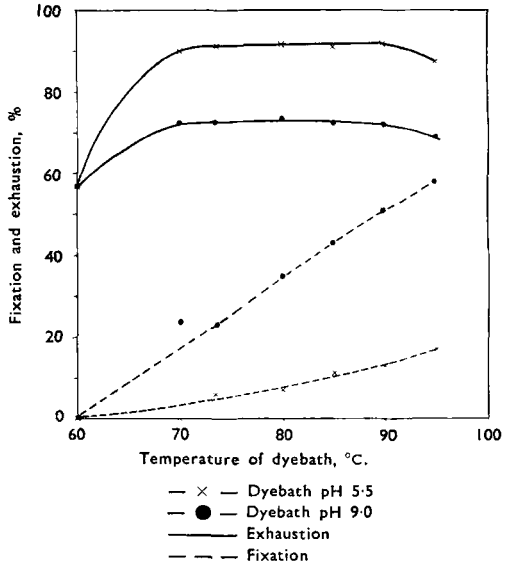

FIG. 4— Procinyl Blue RS: Effect of Temperature of Dyeing on Exhaustion and Fixation (1% Shade (Pure Dye), Dyed for 1 hr., 40:1 Liquor Ratio)

The choice of precise dyeing conditions involving a preliminary absorption under acid conditions must depend largely on the rate of decomposition of the dye in acid. It has been found that very little hydrolysis of dye occurs at pH 4 at a temperature as high as 95°c., and this, therefore, is chosen as the pH of the bath in the first stage of the dyeing process.

The advantages to be expected from the two-stage dyeing process are twofold. The first is enhanced levelling, since in the acid dyebath little fixation takes place: and the second is a higher percentage fixation. The levelling action is achieved in all cases; the increased fixation is expected only for those dyes which are relatively unstable at pH 10, and this latter effect is significant only with Procinyl Scarlet G.

RATES OF DYEING OF PROCINYL DYES IN ACID DYEBATHS

Under the conditions used in the first stage of the application of the reactive disperse dyes, they appear to act as typical disperse dyes. Rate-of-dyeing curves have been determined, using 3·3% shades, by dyeing in a buffer solution of 2 g. acetic acid, 0·25 g. ammonium acetate, and 1 g. Dispersol VL per litre. The results are illustrated in Fig. 5 and are compared with the rate-of-dyeing curves for three typical disperse dyes.

Diffusion coefficients have been determined directly by application of the Hill equation to the

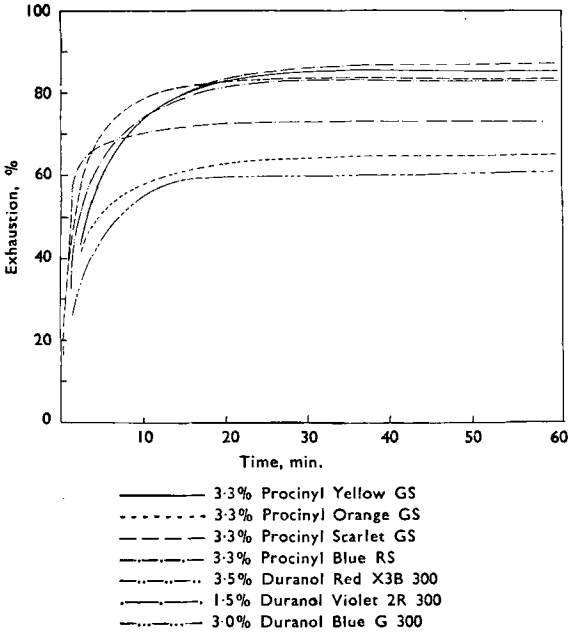

FIG. 5— Rate-of-dyeing Curves for Procinyl and Disperse Dyes

dyeing of nylon yarn from an infinite dyebath at 95°c. The yarn used was bright 120-denier, 40-filament having a density of 1·13, so the radius was $9{\cdot}7 \times 10^{-4}$ cm. Figures for the diffusion coefficients (Table IV) were obtained from dyeings which had been carried out for 5, 10, and 20 min., saturation values being taken as the amount of dye on the fibre after 6 hr.

The velocity coefficient k in Table IV has been derived from the equation of the hyperbola—

$$kt = \frac{1}{A - x} - \frac{1}{A}$$

where A is the equilibrium exhaustion and x the exhaustion after time t. Application of this equation to the rate of dyeing of disperse dyes on nylon gives fairly close agreement with experimental curves [16], and the same is true in this instance. The value of the velocity coefficient gives an indication of the rate at which the dyeing takes place, and, as is seen in Table IV, the values of diffusion coefficient and velocity coefficient agree well with the observed times of half-dyeing. If the values of the velocity coefficients are compared with those for disperse dyes on nylon at 95°c., it is seen that the Procinyl dyes have rate properties similar to the medium-slow dyeing disperse dyes.

It would be expected that the diffusion coefficients so far determined should be related to levelling power, so that the Blue should level to a greater extent than the Scarlet, for example. Levelling tests have been carried out in the manner described by Hadfield and Seaman [14]. The percentage levelling is expressed as—

$$\frac{\text{Dye on levelled hank}}{\text{Dye on initially dyed hank}} \times 100$$

The results are given in Table V, the grading of the controls being taken from the ICI manual [17].

Procinyl Blue R and Orange G, which have almost identical percentage levelling values, have similar diffusion coefficients; Procinyl Scarlet G has a lower percentage levelling, and this is accompanied by a lower diffusion coefficient. Procinyl Yellow G, which levels to the least extent, would be expected to have the lowest diffusion coefficient, and this is indeed the case.

RATES OF FIXATION IN ALKALINE DYEBATHS

These were determined by first dyeing a number of hanks to equilibrium under acid conditions and

TABLE IV

Rates of Dyeing and Diffusion Coefficients of Procinyl and Disperse Dyes

Dye	$t_{\frac{1}{2}}$ (min.)	$k \times 10^5$	$D \times 10^{11}$ (cm.²/sec.)
3·3% Procinyl Yellow G	2	750	8
3·3% Procinyl Orange G	1·7	1010	20
3·3% Procinyl Scarlet G	1	1600	16
3·3% Procinyl Blue R	2	650	21
3·5% Duranol Red X3B 300 (C.I. Disperse Red 11)	1·7	720	—
1·5% Duranol Violet 2B 300	1	2900	--
3% Duranol Blue G 300 (C.I. Disperse Blue 26)	3·5	350	—

TABLE V

Levelling Properties of Procinyl and Disperse Dyes

Dye	Levelling (%)	$D \times 10^{11}$ (cm.²/sec.)	Grading
Procinyl Yellow G	43	8	—
Procinyl Orange G	88	20	—
Procinyl Scarlet G	75	16	—
Procinyl Blue R	87	21	—
Dispersol Fast Crimson B (C.I. Disperse Red 13)	44	—	Good
Duranol Brilliant Blue BN (C.I. Disperse Blue 3)	82	—	Good
Duranol Blue Green B (C.I. Disperse Blue 7)	60	—	Poor
Duranol Violet 2R (C.I. Disperse Violet 1)	92	--	Very good

then making the baths alkaline by the addition of sodium carbonate solution to give a final pH of 10·5 approx. The hanks were removed at various time intervals, plunged into cold acid buffer to halt reaction, and immediately extracted with propanol to remove unfixed dye. The percentage dye on the fibre was then determined by dissolving a weighed amount of fibre in *o*-chlorophenol. The curves obtained from the application of 3·3% depths are shown in Fig. 6.

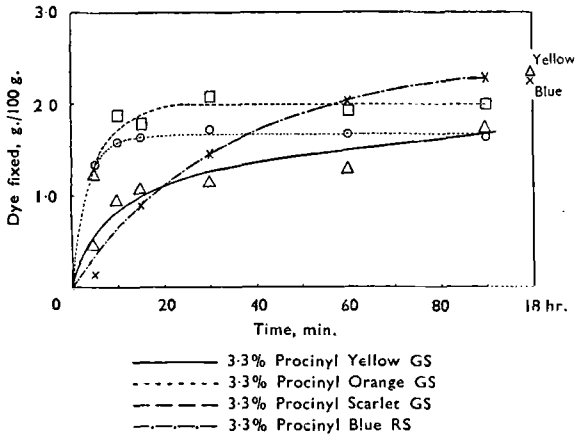

FIG. 6— Rate of Fixation of Procinyl Dyes

The times of half-reaction (Table VI) indicate that Procinyl Blue R and Yellow G are much less reactive than the other two. However, the amount of dye which ultimately reacts with the fibre is governed by the degree to which it exhausts on to the fibre. For example, although Procinyl Blue R reacts much more slowly than either Procinyl Orange G or Procinyl Scarlet G, the ultimate amount of dye which reacts is greater than with the two latter dyes; this is due to its higher equilibrium exhaustion.

TABLE VI

Times of Half-reaction (min.) of Procinyl Dyes

3·3% Procinyl Yellow G	25
3·3% Procinyl Orange G	2·5
3·3% Procinyl Scarlet G	2·5
3·3% Procinyl Blue R	20

RATES OF ADSORPTION AND FIXATION IN MIXTURES

These measurements were carried out in order to determine whether the individual dyes had any mutual effect when dyed together. Two mixtures were applied, consisting of 3·3% each of Procinyl Blue R and Procinyl Orange G or Scarlet G. The results (Table VII) show that the rates of dyeing of the individual dyes are not greatly affected by the presence of a second dye, although the equilibrium exhaustions of the Scarlet G and Orange G in the presence of the Blue R appear to be depressed slightly. It appears, therefore, that the dyes can be applied together in acid without affecting one another to any marked extent.

Rate-of-fixation curves were also determined for the dyes in the mixtures, and the times of half-reaction are summarised in Table VIII.

TABLE VIII

Times of Half-reaction (min.) of Procinyl Dyes

	Alone	In Mixture
Procinyl Orange GS	2·5	6·5
Procinyl Scarlet GS	2·5	4·5
Procinyl Blue RS	20	>25

It is seen that in all cases reaction is slower when a second dye is present. In a system where there are two reacting species of differing reactivities competing for the same site, which is present only in limited quantities, such an increase in the times of half-reaction would be expected.

COVERAGE OF IRREGULARITIES

Before discussing the practical application of Procinyl dyes, it is interesting to examine their behaviour on nylon containing deliberate gross irregularities.

In order to obtain information on the effect of large chemical differences, a sample of nylon was acetylated [1], and the absorption and fixation of Procinyl dyes on this acetylated nylon were compared with those on the control. Information on the proportions of amine end-groups in the two nylons was obtained by measuring the amount of Naphthalene Scarlet 4RS (C.I. Acid Red 18) necessary to saturate the fibre.

The amine end-content of the fibre was reduced to about one-sixth (from 42·6 to 6·9 m-equiv./kg.) by the acetylation. The total amount of dye absorbed, either in an acid dyebath or after an alkaline treatment, showed only a small reduction on the acetylated fibre, from 6·3 to 5·6 g./100 g. for Procinyl Blue RS and from 16·1 to 13·5 g./100 g. for Procinyl Orange GS, which suggests that the dyeing itself is governed by a disperse-dye type of mechanism and is little affected by chemical differences in the fibre. The amount of dye which had combined with the fibre was more markedly reduced, from 3·1 to 1·6 g./100 g. for Procinyl Blue RS and from 10·2 to 6·6 g./100 g. for Procinyl Orange GS, but even this reduction by about one-half is very much less than the difference in amine

TABLE VII

Compatibility of Procinyl Dyes

Time (min.)	Exhaustion (%) of Blue			Exhaustion (%) of Orange		Exhaustion (%) of Scarlet	
	Alone	With 3·3% Orange G	With 3·3% Scarlet G	Alone	With 3·3% Blue R	Alone	With 3·3% Blue R
5	59·8	62·4	66·6	51·6	43·3	71·2	65·2
10	74·1	74·1	72·2	57·0	50·0	78·9	68·1
15	80·0	78·2	82·6	60·1	52·1	81·6	75·3
30	84·7	83·2	84·1	62·8	57·6	82·0	77·9
45	88·0	83·8	84·6	65·2	57·7	83·8	79·1
60	86·7	84·8	85·5	66·0	59·7	84·0	78·0

end-group content. It appears, therefore, that the very much smaller chemical differences which are likely to be encountered in practice will have a negligible effect on the dyeing of Procinyl dyes.

In order to assess the coverage of large structural differences in nylon, two samples of nylon of the same amine end-group content and denier but of different draw ratio were dyed together—

(*a*) In an acidic dyebath
(*b*) In an alkaline dyebath
(*c*) In an acidic dyebath subsequently made alkaline

to medium depths with Procinyl Scarlet GS and Procinyl Blue RS. The results are given in Table IX.

TABLE IX

Distribution of Dyes between Nylons of Different Draw Ratio dyed in the Same Bath

Nylon A — draw ratio 3·08
Nylon B — draw ratio 3·99

Dyed at 95°C., using 40:1 liquor ratio, with Dispersol VL (1 g./litre) and buffer

Buffers— (*a*) Acid bath— acetic acid (30%: 2 g./litre)
(*b*) Alkaline bath— soda ash (2·4 g./litre) added to acid bath

Dyeing Method	(Dye on Nylon A)/(Dye on Nylon B)	
	3·3% Procinyl Scarlet GS	3·3% Procinyl Blue RS
Dyed 1 hr. acid	1·12	1·08
Dyed 1 hr. alkaline	1·43	1·14
Dyed 1 hr. acid, 1 hr. alkaline	1·00	1·00

With such an exaggerated difference in draw ratio some difference in rate of dyeing would be expected; at the end of the 1 hr. dyeing period the hank with the higher draw ratio should be less heavily dyed, giving a ratio of (dye on Nylon A)/(dye on Nylon B) greater than unity. Table IX shows results in the expected direction. In an alkaline bath the ratios are greater than in acid, whereas using the acid–alkali method both hanks are dyed equally. These results show the advantage of using the correct method of application.

The acid bath should, of course, produce less differentiation than the alkaline bath, since migration and levelling can occur more readily in acid. It is significant that the ratio in the alkaline bath is greater with Procinyl Scarlet GS, which has the higher rate of fixation, than with Procinyl Blue RS. The longer total dyeing time (2 hr.) for the acid–alkali method allows the two hanks to reach equality, since the fixation is not immediate, and some migration can occur in alkali.

Again, the difference in draw ratio in these experiments is very much greater than would be encountered in practice, and these experiments therefore give assurance that coverage of barriness will be achieved in practice through the application of Procinyl dyes by the acid–alkali technique.

Practical Application of Procinyl Dyes

The practical application of Procinyl dyes to continuous-filament nylon and nylon staple may be accomplished both by batchwise dyeing and by printing. They may also be applied usefully to a number of other fibres.

6,6-NYLON

Batchwise Dyeing

The dyes are first applied at 95°C. from an acidic bath containing 2 parts acetic acid (30%) and 1 part of Dispersol VL per 1,000 parts of dye liquor. The pH should lie in the range 3·5–4·0. Under these conditions the dye is least reactive, so that its fixation to the fibre is low, and maximum levelling and coverage of fibre irregularities can occur. Dyeing is carried out at 95°C. for 30–60 min., the longer time being required only for highly irregular yarn.

The bath is then made alkaline by adding 2·5–3·0 parts of soda ash per 1,000 parts of dye liquor. The pH of the bath should be 10–10·5. Fixation of the dye then takes place, and a further dyeing period of 60 min. at 95°C. is sufficient to develop the high wet fastness. For heavy dyeings it is advisable to complete the process by "soaping" the dyed fibre in a solution containing 2 parts of Lissapol ND and 2 parts of soda ash per 1,000 parts of water at 65°C. for 15–30 min.

For the production of dyeings of the highest standard, the dyeing temperature should be 95°C. If the temperature is reduced to 85°C. the levelling properties of the Procinyl dyes during the initial stage of dyeing will be impaired in the same way as in the case of disperse dyes. Also, the degree of fixation and washing fastness developed during the second stage of dyeing will be a little lower. Dyeing at temperatures below 80°C. results in a more marked reduction in the degree of fixation and washing fastness. However, dry-heat setting of the nylon, after dyeing, stimulates reaction between dye and fibre, and can be used to obtain the full washing fastness of dyeings which have been dyed at too low a temperature.

This general process can be used to apply Procinyl dyes to nylon fibres in most types of dyeing machinery, e.g. the winch, the paddle dyeing machine, and the jig; if the jig is used, it is best enclosed in order that a temperature as near the boil as possible may be attained. Application

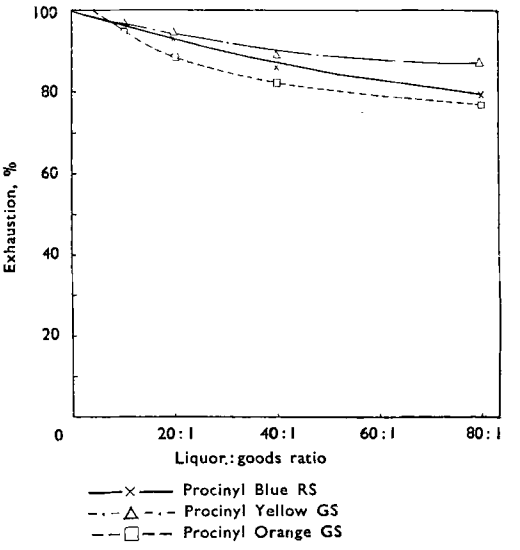

FIG. 7— Effect of Liquor: Goods Ratio on Exhaustion

to yarn packages in circulating machines has also proved quite satisfactory.

The reduction in absorption with increasing liquor ratio is more noticeable with Procinyl dyes than with conventional disperse dyes, but, as Fig. 7 shows, the effect will not be large in practice. Procinyl Orange GS is affected most, and here the exhaustion falls from 95 to 75% as the liquor ratio is increased from 10 to 50:1. Due allowance should therefore be made for this variation when setting the bath with dye, in order to avoid excessive shading additions.

Printing

In the printing of nylon, Procinyl dyes offer the user of disperse dyes a means of obtaining improved wet fastness properties. In general their wet fastness is of the same order as that of the best acid dyes of the level-dyeing type, e.g.—

Lissamine Fast Yellow 2G (C.I. Acid Yellow 17)
Croceine Scarlet 3B (C.I. Acid Red 73)
Solway Blue RN (C.I. Acid Blue 47)

but whereas there is a tendency for "flushing" of the outline and occasional "displacement" effects to occur when using acid dyes, Procinyl dyes, like conventional disperse dyes, are free from these defects.

The Procinyl dyes may be printed on nylon using a printing paste containing acetic acid and sodium acetate, which, during the steaming process, develops slight alkalinity, thus providing conditions for reaction to take place. The procedure is to print, dry, steam for 30 min., and soap for 5 min. at 50°C.

Fastness Properties

Examples of fastness properties of the Procinyl dyes on nylon are compared with those of disperse dyes in Table X. As would be expected, the washing and heat fastness properties of Procinyl dyes are excellent and much better than those of conventional disperse dyes, whereas the light fastness is of the same order.

A close parallel with the properties of reactive dyes on cellulose cannot be drawn. Unfixed Procion dyes are removed during washing off, and the properties of the finished dyeing are due solely to the fixed dye which remains. With Procinyl dyes, on the other hand, a proportion of unfixed dye remains on the fibre after washing off. This causes only a minor reduction in fastness to subsequent washing, because in this case the unfixed dye itself has a moderate wash fastness, and being present only as a minor constituent has little effect on the overall fastness. A useful and unexplained property of Procinyl dyes is their high fastness to heat sublimation. This could be considered to be associated with their reaction with the fibre, were it not for the fact that on cellulose triacetate, where there is strong evidence against reaction, the heat sublimation properties are markedly superior to those of conventional dyes. On nylon the heat sublimation fastness is excellent.

6-NYLON

6-Nylon fibres such as Perlon, Enkalon, and Amilan may be dyed with Procinyl dyes by the methods already described for 6,6-nylon. The properties of the dyes on 6-nylon are very similar to those on 6,6-nylon; the rate of dyeing is higher, and the temperature-range properties are a little better.

SECONDARY CELLULOSE ACETATE AND CELLULOSE TRIACETATE

Procinyl dyes may be applied to secondary cellulose acetate and cellulose triacetate in the same way as normal disperse dyes. Although there is no evidence of reaction with these fibres, fastness to wet treatments is generally somewhat higher than with normal disperse dyes. The temperature-range properties are generally poor, however, and the Procinyl dyes are of limited interest for dyeing these fibres.

Procinyl dyes are of more interest when applied by printing; on secondary cellulose acetate they offer the advantages over conventional disperse dyes of a reduced steaming time (15 min. as against 30 min.) and superior washing fastness. When applied to cellulose triacetate by printing, their wet fastness is comparable with that of vat dyes, and their superior sublimation fastness and brightness of colour make them particularly suitable for application to pleated styles. In addition, they are simpler to apply than are vat dyes, a conventional recipe for disperse dyes being used, with the addition of urea and steaming for 30 min. For full colours it is necessary to steam at 10 lb./sq.in., however.

POLYACRYLONITRILE FIBRES

On polyacrylonitrile fibres such as Orlon and Courtelle the build-up of Procinyl dyes is limited; there is strong evidence that no reaction with the fibre occurs, and they have no advantages over disperse dyes.

However, on the modified polyacrylonitrile fibre Acrilan, the Procinyl dyes build up well and, if

TABLE X

Fastness Properties of Procinyl and Disperse Dyes on 6,6-Nylon

Dye	Washing Fastness: 1 Wash at 85°C. Effect on Dyeing	Staining of Nylon	Staining of Cotton	5 Washes at 100°C. Effect on Dyeing	Staining of Nylon	Staining of Cotton	Perspiration: Effect on Dyeing	Staining of Nylon	Staining of Wool	Heat Setting: Effect on Dyeing	Staining of Nylon	Light Fastness (Daylight)
Procinyl Yellow G	5	4–5	5	4	3	5	5	5	5	5	5	6
Procinyl Orange G	4	4–5	5	3–4	4–5	5	5	4	4	5	5	5
Procinyl Scarlet G	5	4–5	5	4	4–5	5	5	4–5	4–5	5	5	5
Procinyl Blue R	5	4–5	5	4	5	5	5	5	5	5	5	4–5 (redder)
Dispersol Fast Yellow G	3	2	4–5	–	–	–	5	3	4	4–5	5	6–7
Dispersol Fast Orange G	1	1	3	–	–	–	4	2	3	4	2	4–5
Dispersol Fast Scarlet B	2	2	4–5	–	–	–	5	3	4	4	3–4	3–4
Duranol Brilliant Blue BN	2	2	4	–	–	–	5	2	3–4	4	2	4 (redder)

applied by a method similar to that used for nylon, give dyeings of very high wet fastness. There is some evidence that the dyes react with this fibre, as might be expected in view of its basic nature. A mixture of dimethylformamide and chlorobenzene will not remove the dyes completely from the fibre, and Acrilan fibre dyed with Procinyl Blue RS is much more difficult to dissolve in dimethylformamide than is undyed Acrilan. However, most Procinyl dyes are of minor importance on Acrilan because of their poor light fastness on this fibre.

POLYESTER FIBRES

In general the Procinyl dyes are not useful for dyeing Terylene and other polyester fibres because of their unsatisfactory light fastness and uptake.

Procinyl Yellow G is an important exception, however. It possesses very good light fastness in heavy depths and outstanding fastness to heat treatment, giving faster results in the latter respect than have hitherto been possible. In spite of this excellent heat fastness, there is strong evidence that there is no chemical reaction between dye and fibre, as the dye is extracted from the fibre by organic solvents, and moreover it is applied by the normal method for conventional disperse dyes, and can be used in mixtures with selected members of the latter range.

Conclusions

The introduction of Procinyl dyes represents a further development in the field of reactive dyes for textiles. This application of the principle of reaction between dye and fibre makes it possible to combine good levelling properties with high wet fastness, by dyeing first in an acid dyebath, in which levelling takes place, and then in an alkaline dyebath, in which reaction with the fibre occurs. This process is simple, may be carried out in conventional machinery, and does not entail the use of abnormal dyeing conditions or special reagents. By the use of Procinyl dyes it is now possible to dye nylon textiles to fast, bright colours with excellent coverage of fibre irregularities.

* * *

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Discussion

Prof. E. ELÖD: I should like to congratulate the lecturer and his co-workers on these new and important developments in nylon dyeing. From the theoretical point of view it might be expected, in view of the analogies in the chemical and X-ray structures between polyamide fibres and silk, that the latter fibre would also be dyed by Procinyl dyes under the same conditions. According to the lecturer, a chemical reaction takes place between the Procinyl dyes and the amino groups in the fibres. Therefore, it must be expected that, by deamination of nylon, the amount of dye absorbed should decrease according to the reduction in the content of amino groups. From the theoretical point of view of estimating the true chemical reaction between Procinyl dyes and polyamide fibres, this would undoubtedly be of interest. The "alkali shock" process used here for the fixation of Procinyl dyes shows some analogy to the "acid shock" process for dyeing wool.

Dr. VICKERSTAFF: As Professor Elöd suggests, the Procinyl dyes can be used for dyeing silk, but they show no advantage in dyeing properties over Procion dyes, and since the latter are generally of higher light fastness and in addition cover a much wider shade range, the Procinyl dyes are at present of little interest on this fibre. As regards deamination of nylon, this experiment would certainly be of interest, but has not so far been undertaken.

Mr. E. J. KOLLER: What is the reactive system in the new Procinyl dyes, and in what respect does it differ from that of the earlier Procion dyes?

Dr. VICKERSTAFF: The essential difference between the Procion and Procinyl dyes is that the former are water-soluble dyes containing sulphonic groups, whereas the latter are insoluble disperse dyes containing no ionisable groups. Procion dyes, therefore, behave in the first place as acid dyes and tend to accentuate any small chemical differences between different nylon fibres. In addition, the reactive group in Procion dyes is of a relatively high reactivity and will combine with amino groups in nylon under both acid and alkaline conditions. It is, therefore, impossible to apply Procion dyes under any conditions which prevent chemical reaction, so that little or no levelling can take place. In consequence, any physical differences between fibres which allow these dyes to penetrate more or less easily are shown up in the initial dyeing stages and cannot be eliminated by the levelling treatment. In searching for suitable dyes for nylon, it was necessary to employ a much less reactive group. In the first place the dyeing of nylon must

be carried out at temperatures near 100°C. in order to speed up the diffusion process into this compact fibre and so shorten the dyeing time to a reasonable length. Because of this increase in temperature a reactive grouping of much lower activity is required, as compared with the Procion dyes which are applied to cellulose in the cold. In the second place a less reactive grouping is required in order that the reactivity may be controlled by pH. In the chosen system, the reactivity is so low that no significant reaction takes place at temperatures around 100°C. at a pH below 4. The chemical nature of the reactive group cannot be disclosed at this stage, but it does contain a chlorine atom which combines with the amino groups in the nylon.

Mr. J. T. MARSH: Is there any likelihood of the recent methods of making polyamides by interfacial condensation giving a product which will be easier to dye?

Dr. VICKERSTAFF: It is difficult to say at this stage whether fibres produced in this way will be more consistent and reproducible in their chemical constitution than fibres produced by bulk reaction followed by melt spinning. However, it is unlikely that the difference will disappear entirely. The physical differences between fibres arise mainly in the drawing stage, due to the difficulty of controlling this process with 100% accuracy, and since a drawing process will almost certainly be involved, even with new methods of making polyamides, it is probable that this source of irregularity will remain; the chemical differences between fibres are essentially differences of molecular weight. Presumably fibres made by this new process will also have a definite molecular weight, and I should expect small differences in molecular weight to arise, which will result in slightly different amino end-group contents, so that chemical differences may also persist.

Dr. H. ZOLLINGER: A graduate student in the Institute of Dye Chemistry, University of Basle, who is investigating adsorption isotherms of disperse dyes on polyamides, has studied the fixation of Procinyl-like reactive dyes and their hydrolysed products. We have been able to show that the hydrolysed dye has a considerable affinity for 6,6-nylon in an acidic medium, but practically no affinity in an alkaline dyebath. We think that this explains the contrast with respect to degree of fixation of reactive dyes on nylon and cellulosic fibres, respectively. Hydrolysed reactive dyes for cellulose have a considerable affinity for the substrate, whereas hydrolysed Procinyl dyes have no affinity for nylon under dyebath conditions, i.e. at pH > 8.

Dr. VICKERSTAFF: The results described by Dr. Zollinger are completely at variance with our own observations. It is not clear whether Dr. Zollinger has in fact investigated the Procinyl dyes, or merely some compounds of a reactive type which are considered to be similar in behaviour. With Procinyl dyes, the hydrolysed product has a high affinity for nylon, although admittedly this is lower in an alkaline solution than in acid solution. The high affinity is revealed by the fact that it is difficult to remove the hydrolysed dye by washing, so that an estimate of the chemically combined dye can finally be obtained by extracting the hydrolysed dye with propanol. I am surprised to hear that Dr. Zollinger considers that hydrolysed reactive dyes of the Procion type have a considerable affinity for cellulose. As a result of our own experiments, we consider the affinity of these dyes for cellulose in absence of electrolyte is very low indeed. It is obvious that a further comparison of Dr. Zollinger's results with our own will be necessary in order to resolve this matter.

Prof. R. H. PETERS: The authors have brought strong evidence to show that combination of dye with the fibre occurs. However, combination with the hydrogen atom of the amide group usually requires rather stringent conditions, so I should like to ask the following questions—

(*a*) Is it possible that the dye may combine with itself to form dimers or trimers, or even polymers in the fibre? These may not be leached out easily with propanol.

(*b*) The model compound mentioned (p. 106) is a substituted urea (as well as being an amide). May not the dye have combined with the urea portion rather than the amide group?

(*c*) The combination of the dye with the primary amine end-group may produce a compound with the properties of a secondary amine (constitution of the dye being unknown); if this is so, could this then react with a second molecule of dye? This would make the possible uptake of dye equal to twice that of the amine end-content.

Dr. VICKERSTAFF: In reply to the first question, certain of the Procinyl dyes might conceivably react with themselves, and this possibility was carefully considered. It was for this reason that the experiment was carried out whereby dyed nylon fibre was dissolved in *o*-chlorophenol and the nylon precipitated by propanol. Under these conditions any mechanical retention of dye by the fibre is eliminated, and we consider that this possibility may be ignored. Furthermore, certain of the dyes are not capable of reaction with themselves.

It is possible that the dye may have reacted with the urea portion of the first compound, but evidence of reaction was also obtained with dibenzoylhexamethylenediamine.

The possibility that two molecules of dye may react with the amino end-groups in nylon has not so far been examined and cannot be eliminated as a possibility from the results of the experiments to date.

Dr. J. WEGMANN: Since about 10–20% of the Procinyl dye remains in the fibre in an inactivated state, but without affecting the fastness properties, the question arises as to whether it is necessary for the Procinyl dye to react with the fibre at all.

Dr. VICKERSTAFF: It is true that the uncombined reactive dye appears to have a high affinity for nylon and has relatively high wet fastness

properties. Nevertheless, if conditions in processing are such as to give incomplete reaction, then a deterioration in wet fastness properties can be observed. In such cases, however, it is possible to improve the wet fastness properties by a further alkaline heat-treatment, which suggests that the uncombined dye in the original dyeing is still capable of reaction.

CORRESPONDENCE

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Vapour-phase Dyeing with Disperse Dyes

The investigations of Majury [1] on the system solid dye–dye vapour–substrate have been extended by us, with emphasis on the kinetic aspects. Majury has studied the rate of absorption of unsaturated *p*-nitroaniline vapour by secondary cellulose acetate. We have calculated from Majury's results that the diffusion coefficient of this substance, for a temperature of 150°C. and a relative vapour pressure of 0·063, is $1{\cdot}3 \times 10^{-10}$ cm.^{2}/sec. approx.

Apparent diffusion coefficients for larger molecules, including some disperse dyes, may be calculated from our measurements on the rate of absorption of saturated vapour by secondary acetate. The rate was measured by suspending a known amount of anhydrous film from a previously calibrated helical spring of silica in an evacuated glass envelope containing solid dye. The envelope was totally enclosed in a metal-block thermostat and the deflection of the spring was observed through a mica window of 1 cm. diameter by means of a cathetometer.

The results (Table I) are not complete and it is hoped to submit more complete results later. The values of D have been calculated from the equation used by McBain [2] for non-steady-state diffusion and refer to a total concentration of 0·75 g. dye per 100 g. anhydrous acetate. Owing to the small rate of absorption from the vapour phase, especially of the larger dye molecules, it has not yet been possible to obtain sufficient results to compare the activation energies of vapour-phase diffusion with those obtained by conventional dyeing.

These values of D are very much smaller than those obtained from experiments on the rate of dyeing using aqueous dyebaths [3–5], possibly owing to the unswollen state of the anhydrous cellulose acetate film. It may not be necessary to postulate the existence of gross pores and capillaries in anhydrous diffusion since, according to Barrer [6], fluctuation in thermal energy would ensure the presence of a number of "holes" sufficient for diffusion to occur.

We have also shown, in experiments similar to those of Jensen [7], that an apparent second-order transition temperature of 125°C. in cellulose acetate film is lowered to 117°C. in the presence of the saturated vapour of 1-methylaminoanthraquinone. The shrinkage temperature is also lowered from 184° to 174°C., indicating that the dye may be acting as a plasticiser at high temperatures. Such action probably accounts for the high saturation values obtained in vapour-phase dyeing. The dyed films remain transparent, but on standing for several weeks under atmospheric conditions develop a surface layer of needle-like dye crystals which are easily visible under the microscope. This phenomenon has previously been observed [8] in the migration of dyes in cellulose acetate mouldings, but not so far as is known in film dyed from the vapour.

TABLE I

Dye	Temperature (°C.)	Saturation Value (g./100 g. dry cellulose acetate)	Diffusion Coefficient D (cm.^{2}/sec. $\times 10^{13}$)
Azobenzene	100	14·19	5·05
p-Aminoazobenzene	100	32·29	1·59
NN-Dimethyl-*p*-aminoazobenzene	133	10·08	8·42
1-Methylaminoanthraquinone	150	9·54	22·03
1-β-Hydroxyethylaminoanthraquinone	150	10·80	0·853

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