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The Dyeing of Conventional and Microfibre Nylon 6.6 with Reactive Disperse Dyes

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ABSTRACT

The dyeing and wash-fastness characteristics of three monoazo reactive disperse dyes and one monoazo disperse dye on both conventional and microfibre Nylon 6.6 have been examined. Application at 95°C and pH 8 yielded optimum colour strength for the reactive disperse dyes on both types of fibre. The presence of a commercial dispersing agent in the dyebath enhanced the levelness, but did not markedly reduce the colour strength of dyeings achieved using each of the three reactive disperse dyes on both conventional and microfibre Nylon 6.6. The excellent build-up profiles obtained for the three reactive disperse dyes were in sharp contrast to the poor build-up profile secured for the disperse dye on both substrates; this was attributed to the covalent reaction of the reactive disperse dyes having promoted dye uptake. The three reactive disperse dyes exhibited excellent wash-fastness on both conventional and microfibre Nylon 6.6, the level of fastness achieved being identical on both types of fibre.

1 INTRODUCTION

Nylon 6.6 can be dyed using a variety of dye classes; although both non-metallised acid and direct dyes provide a wide range of bright shades on nylon, the wet-fastness properties of these dyes on the substrate leave much to be desired. Pre-metallised acid and especially mordant dyes display superior wet-fastness characteristics on Nylon 6.6, but the hues obtained are generally dull, and, in the case of mordant dyes, the application method is both time-consuming and attended by environmental concern. Although reactive dyes furnish a wide range of bright dyeings of excellent wet-fastness on such fibres, this dye type, together with each of the other four previously mentioned types of anionic dye, are sensitive to fibre variations (barréness). Although disperse dyes provide excellent coverage of fibre irregularities, this class of dye exhibits poor to moderate build-up on Nylon and generally low wash-fastness properties on the substrate.

Microfibres are a relatively recent introduction, finding increasing use in functional and fashion clothing as a result of their superior drape, handle and feel.[1,2] Although the polymer used in microfibre is often the same as that employed in conventional fibres and, therefore, the microfibre can be dyed in a similar manner to its conventional counterpart, owing to their smaller decitex and consequently higher surface area, more dye has to be applied to microfibres than conventional decitex fibres in order to achieve the same visual depth of shade, with the result that microfibre dyeings generally exhibit lower wet-fastness properties than comparative-depth dyeings on conventional fibres.

The aim of this work was to synthesise a series of reactive disperse dyes which, potentially at least, would combine the favourable properties of both disperse dyes (excellent coverage of fibre irregularities) and reactive dyes (excellent wet-fastness) on Nylon 6.6 and also to determine whether the wash-fastness of the reactive disperse dyes on microfibre Nylon 6.6 fibres was similar to that on their conventional decitex counterparts.

2 EXPERIMENTAL

2.1 Materials

2.1.1 Fibres

Commercially available, scoured conventional (78f46, 1·7 decitex per filament) and microfibre (85f92, 0·9 decitex per filament) knitted Nylon 6.6 fabrics of amino end group content 66·4 g equiv. $g10^{-6}$,[3] kindly supplied by DuPont Fibres, were used.

2.1.2 Chemicals and auxiliaries

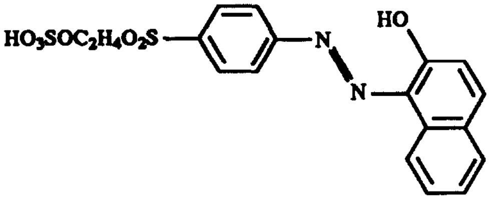
Aminophenyl-4-(β-sulphatoethylsulphone) (98% purity) was kindly supplied by Zeneca Specialties and aminophenyl-4-ethylsulphone was obtained from a personal source.[4] *N*,*N*-dimethylaniline (98% purity) *N*,*N*-diethylaniline (98% purity), 2-naphthol (98% purity) and HPLC grade acetonitrile were obtained from Aldrich; Sandozin NIE was supplied by Sandoz and Ufoxane 2 by Yorkshire Chemicals (YCL). All other reagents were of general-purpose grade.

2.2 Procedures

2.2.1 Synthesis of reactive disperse dyes[5]

2.2.1.1 Dye I

Preparation of diazo component. Aminophenyl-4-(β-sulphatoethylsulphone) (5·6 g; 0·02 M) was stirred in 300 cm^3 of distilled water to which was added 2·4 cm^3 of 35% hydrochloric acid (0·03 M); the suspension was cooled to below 5°C and 37 cm^3 of a 0·5 M aqueous sodium nitrite solution added over 20 min. Excess nitrous acid was destroyed by the addition of 10% aqueous sulphamic acid.

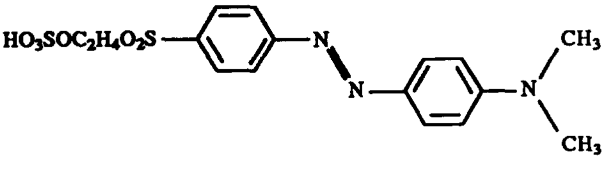


(I)

Aminophenyl-4-(β-sulphatoethylsulphone) → 2-naphthol. 2-Naphthol (2·65 g; 0·18 M) was dissolved in 50 cm^3 of 0·2 M aqueous sodium hydroxide solution. The ensuing solution was added to the pale orange-coloured solution of the diazo component prepared as described above, the temperature being maintained between 0 and 5°C. The pH of the dispersion was adjusted to 7 by the addition of dilute (0·1 M) aqueous hydrochloric acid and stirring continued for 1 h at 0 to 5°C. After this time, the temperature of the ensuing solution was allowed to reach ambient and 40 g of solid sodium chloride added; the mixture was then stirred for 45 min at room temperature. The precipitated dye was isolated by filtration under vacuum and dried overnight at room temperature.

2.2.1.2 Dye II

*Aminophenyl-4-(β-sulphatoethyl sulphone) →*N,N*-dimethylaniline.* *N,N*-Dimethylaniline (2·25 g; 0·018 M) was added to the solution of the diazo component described in the preparation of dye I above, the temperature being maintained between 0 and 5°C. Aqueous (2 M) sodium acetate (25 cm^3) was then added and the pH of the dispersion raised to 5·8 by the addition of 0·1 M aqueous sodium carbonate. Stirring was continued

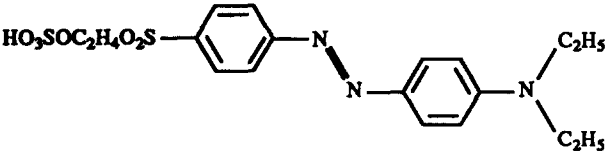


(II)

for 1 h between 0 and 5°C, after which time the pH of the solution was adjusted to 7 using 0·1 M aqueous sodium carbonate solution. The temperature of the solution was allowed to reach ambient and 30 g of solid sodium chloride was added; the mixture was stirred for 30 min at room temperature. The precipitated dye was isolated by filtration under vacuum and dried overnight at room temperature.

2.2.1.3 Dye III

Aminophenyl-4-(β-sulphatoethylsulphone) → N,N-*diethylaniline.* *N,N*-Diethylaniline (2·25 g, 0·018 M) was added to the diazonium component described in the preparation of dye I above with the temperature being maintained between 0 and 5°C. Aqueous (2 M) sodium acetate (25 cm^3) was then added and the pH of the dispersion raised to 5·8 by the addition of 0·1 M aqueous sodium carbonate. Stirring was continued for 90 min between 0 and 5°C, after which time the pH of the solution was adjusted to 7 using 0·1 M aqueous sodium carbonate solution. The temperature of the solution was allowed to reach ambient and 45 g of solid sodium chloride added; the mixture was stirred for 30 min at room temperature. The precipitated dye was isolated by filtration under vacuum and dried overnight at room temperature.



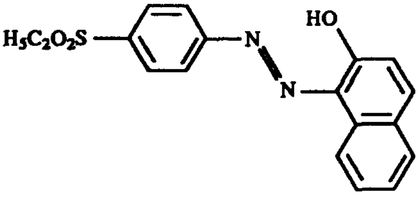
(III)

2.2.1.4 Purification of reactive disperse dyes

A sample (2·0 g) of each of the dyes I–III was slurried using a mortar and pestle with ethanol (25 cm^3) and the precipitate recollected and washed with ethanol. The product was dried under vacuum at room temperature overnight.

2.2.2 Synthesis of disperse dye (dye IV)

One gram (4 × 10^{-3} M) of aminophenyl-4-ethylsulphone was stirred in 50 cm^3 of distilled water at 0 to 5°C; 1·5 cm^3 of 0·1 M aqueous hydro-



(IV)

chloric acid solution ($5{\cdot}5 \times 10^{-3}$ M) was added, followed by 10 cm^3 of 0·5 M aqueous sodium nitrite solution over 10 min.

2-Naphthol (0·71 g; $4{\cdot}8 \times 10^{-3}$ M) was dissolved in 50 cm^3 of 0·2 M aqueous sodium hydroxide solution. To this was added, over 15 min, the above prepared diazo solution, the temperature being maintained between 0 and 5°C. Stirring was continued at this temperature for 15 min, after which time the pH of the solution was adjusted to 7 by the addition of dilute (0·1 M) aqueous hydrochloric acid and stirring continued for 30 min at 0 to 5°C. The ensuing orange dye was isolated by filtration under vacuum and dried overnight at room temperature.

2.2.3 *HPLC Analysis of dyes I–IV*

This was carried out using a Varian Series 5000 liquid chromatograph (Varian, USA) equipped with an Apex C18 reverse-phase column using a flow rate of 1·5 cm^3/min and a pressure of 50 atm; the ion-pair system used comprised a 0·25% aqueous solution of dicyclohexamine phosphate in distilled water and acetonitrile. The dyes were dissolved in a 50 : 50 acetonitrile : water mixture.

2.2.4 *Milling of disperse dye (dye IV)*

The dye (0·75 g), 1·5 g of Ufoxane 2 and 50 cm^3 of distilled water were placed in a 250 cm^3 capacity glass jar; the jar was then filled to two-thirds capacity with 1-cm diameter ceramic balls. The sealed jar was rotated on a laboratory-scale ball mill for 24 h at room temperature, after which time the ensuing dispersion was dried at 40°C for 24 h.

2.2.5 *Dyeing*

This was carried out in sealed, 100-cm^3 capacity, stainless-steel dyepots housed in a John Jeffries (Jeffries, UK) laboratory-scale Rota Dyer using a liquor-to-goods ratio of 20 : 1. The appropriate mass of dye was placed in the dyepot and 40 cm^3 of appropriate buffer solution (described below) added; the wetted out fabric sample (2·000 g) was then added and the sealed dyepot housed in the rotadyer; dyeing was then carried out using the method shown in Fig. 1.

2.2.5.1 Effect of pH and temperature on dye I

Buffer solutions of pH 7, 8 and 9 were prepared by dissolution of disodium hydrogen phosphate (5 g) and potassium dihydrogen phosphate (1 g) in 1 litre of distilled water; the appropriate pH value was secured by

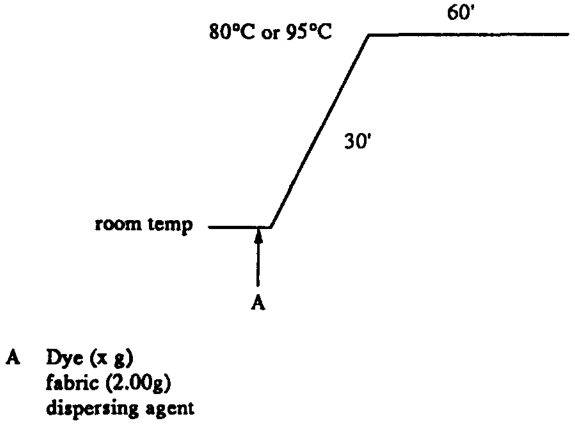


Fig. 1. Dyeing method used.

the addition of either 0·1 M aqueous hydrochloric acid or 0·1 M aqueous sodium hydroxide solution to the mixed phosphate buffer solution. Dyeings (1% omf) of dye I were carried out at pH values 7, 8 and 9 for 1 h at both 80 and 95°C.

2.2.5.2 Effect of dispersing agent on dyes I–III
Samples of 0·1, 0·5 and 1 g of Ufoxane 2 (YCL) were dissolved in 1 litre of pH 8 buffer solution; dyeings (1% omf) of each of the three reactive disperse dyes were then carried out in the presence of 0·1, 0·5 and 1 g/litre dispersing agent at 95°C.

2.2.5.3 Disperse dye (IV)
Buffer solution at pH 6·5 was prepared by the dissolution of sodium hexaphosphate (1 g) in one litre of distilled water; the final pH value was secured by the addition of 0·1 M aqueous hydrochloric acid to the phosphate solution. Using the dyeing procedure described in Section 2.2.5 above, the dye was applied to both conventional and microfibre fabrics at pH 6·5 in the presence of 1 g/litre Ufoxane 2.

2.2.5.4 Dye build-up
Dyeings (0·25, 0·5, 1 and 2% omf) of dyes I–III were carried out at 95°C in the presence of 1 g/litre Ufoxane 2 at pH 8; 0·33, 1, 2 and 3% omf dyeings of dye IV were carried out at 95°C and at pH 6·5 in the presence of 1 g/litre Ufoxane 2.

2.2.5.5 Standard depth dyeings
A series of dyeings of each of the three reactive disperse dyes (I–III) was carried out at 95°C in the presence of 1 g/litre Ufoxane 2 at pH 8 and the

depth of shade of each of the dry, scoured, dye samples visually compared with the appropriately coloured Society of Dyers and Colourists' matt standard depth shades[6] in an ICS/Texicon (ICS, UK) viewing cabinet under illuminant D_{65}. Dyeings were carried out until a 1/1 standard depth of shade was achieved for each of the three dyes on both types of Nylon 6.6 fabric. In a similar manner, a series of dyeings of the disperse dye IV was carried out at 95°C in the presence of 1 g/litre Ufoxane 2 at pH 6·5; dyeings were carried out until a 1/3 standard depth of shade was achieved.

2.2.5.6 Wash-off

At the end of dyeing, the dyed samples were rinsed thoroughly for 2 min in running cold water and then treated in a solution containing 5 g/litre Sandozin NIE for 15 min at the boil using a 50 : 1 liquor-to-goods ratio. The scoured fabrics were then rinsed for 10 min in cold water and allowed to dry in the open air.

2.2.6 Colour measurement

The reflectance data of the dry, washed-off, dyed samples were measured using a Macbeth MS 2020 spectrophotometer (Kollmorgen, USA), interfaced to a Digital Rainbow 100 PC (Digital, USA), under illuminant D_{65} using the 10° standard observer with specular component excluded and UV component included. The dyed samples were folded such that a total of four layers of fabric was presented to the spectrophotometer; an average of four measurements per sample was taken. The corresponding CIE L^*, a^*, b^*, c^* and $h°$ coordinates, as well as the K/S value at the λ_{max} of the dyeing, were calculated from the reflectance values.

2.2.7 Wash-fastness determination

Samples of dry, scoured, 1/1 (dyes I–III) and 1/3 (dye IV) standard-depth dyeings were subjected to an ISO CO6/C2 wash test;[7] the change in shade of the original dyed sample, together with the extent of staining of adjacent fibres, was assessed using the appropriate Grey Scale.[7]

3 RESULTS AND DISCUSSION

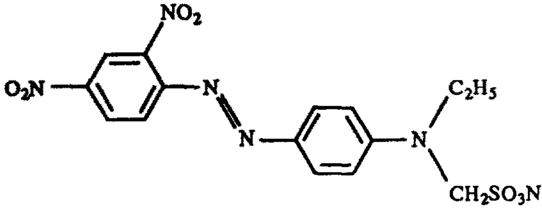
Table 1 shows the results obtained from HPLC analysis of dyes I–IV, from which it is evident that, for the three reactive disperse dyes (I–III), in addition to the desired sulphatoethylsulphone form of the dyes

TABLE 1
HPLC Results for Dyes I–IV

Dye	*Peak*	R_f *(mins)*	*Proportion (%) as peak area*
I	1	9·81	0·18
	2	9·93	0·67
	3	10·18	78·13
	4	10·48	15·06
	5	10·95	5·95
II	1	9·92	0·33
	2	10·19	80·16
	3	10·48	13·01
	4	11·01	6·49
III	1	9·73	0·17
	2	10·18	96·95
	3	10·47	2·88
IV	1	10·29	0·57
	2	10·60	4·00
	3	11·04	95·43

(R_f 10·18/10·19 min), the species of R_f 10·47/10·48 min can be considered to be the hydroxy derivative of dyes I–III, and in the cases of dyes I and II, the R_f values of 10·95 and 11·05 min, respectively, can be attributed to the vinyl form of the two dyes. Since coloured species of R_f values 9·73/9·81/9·92 and 9·93 were found to be present in each of the three reactive disperse dyes, it seems reasonable to propose that these species were dyes obtained from the coupling of impurities present in the diazo component (aminophenyl-4-(β-sulphatoethylsulphone) to the three coupling components used. In the case of the disperse dye IV, in addition to the desired product (R_f 11·04 min), the two species of R_f values 10·29 and 10·60 min can be attributed to dyes obtained from the coupling of impurities present in the diazo component (aminophenyl-4-ethylsulphone) to the coupling component (2-naphthol) used. Table 1 shows that each of the desired dyes were obtained in reasonable purity.

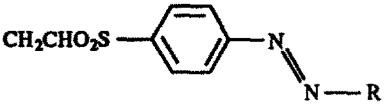
The immediate precursors of disperse dyes were developed by Gardner and Saunders for secondary cellulose acetate fibres and marketed by BDC in the early 1920s.[8,9] These 'temporarily solubilised' methyl sulphonate dyes, such as Ionamine Red KA (V), hydrolysed in the dyebath to yield the corresponding low water-solubility, non-ionic derivative, which was adsorbed on to the hydrophobic cellulose acetate fibre. Practical difficulties associated with varying rates of hydrolysis of the dyes[10] led to the Ionamine range being supplanted by non-hydrolysable,



(V)

low aqueous water-solubility dyes applied from fine aqueous dispersion (i.e. disperse dyes).

The three reactive disperse dyes employed in this work (I–III) resemble the Ionamine dyes in that the use of aminophenyl-4-(β-sulphatoethylsulphone) as diazo component confers ‘temporary solubility’ upon the three reactive disperse dyes, insofar as the sulphuric acid ester group imparts sufficient water solubility to the dyes to facilitate dissolution of the dyes in water, thereby obviating the need to mill the dyes in the presence of a dispersing agent, as is required for conventional disperse dyes: β-elimination of the sulphuric acid ester group during the course of dyeing then yields the non-ionic, sparingly water-soluble, vinyl sulphone form of the dye (VI). It was found that dissolution of dyes I to III was readily achieved in cold (room temperature) water without recourse to the aid of a dispersing agent and, at the end of dyeing, residual dye was present in the dyebath as a fine dispersion.



(VI)

In a study of the dyeing properties of four reactive disperse dyes (which included dyes I–III used in the present work) on conventional Nylon 6.6 fabric, Lo[5] found that dye exhaustion increased with increasing pH of application in the range pH 5–10 and with an increase in temperature over the range 40–95°C; maximum dye fixation occurred at pH 8. These findings concurred with those of Dohmyou *et al.*[11] who observed that maximum fixation of dye II on both polyester and Nylon 6 occurred at pH 8 and that both the exhaustion and fixation of the dye on Nylon 6 increased with increasing temperature of application.

In order to determine the optimum conditions for application of the three reactive disperse dyes (I–III) under consideration to the two types of Nylon 6.6 fabric used in this study, a series of dyeings, using 1% omf of dye I, was undertaken at two temperatures and at three pH values. Table 2 clearly shows that the hue and chroma of the dyeing were little affected by either pH or temperature. It is evident that the colour strength (as given by the K/S values) of the dry, scoured dyeings was

TABLE 2
Effect of pH and Temperature on Uptake of Dye I (1% omf)

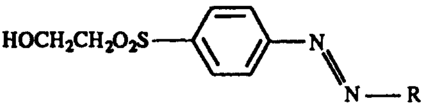
Temperature (°C)	*pH*	*Fibre*[a]	*L**	*a**	*b**	*c**	*h°*	*K/S*
80	7	C	66·3	42·0	70·2	81·8	59·1	16·5
		M	66·6	42·2	71·9	83·4	59·6	15·6
	8	C	65·9	42·4	72·2	83·7	59·6	16·9
		M	67·3	40·8	69·5	80·6	59·6	13·2
	9	C	65·9	41·9	71·2	82·6	59·5	16·0
		M	66·8	40·8	69·3	80·4	59·5	13·7
95	7	C	63·7	43·7	74·7	86·5	59·7	17·2
		M	66·0	42·3	71·9	83·4	59·5	14·7
	8	C	65·0	43·3	73·9	85·7	59·6	17·5
		M	66·6	41·6	71·3	82·6	59·8	14·6
	9	C	65·1	43·7	74·6	86·5	59·7	17·1
		M	66·1	42·0	72·2	83·5	59·8	13·9

[a] C = Conventional Nylon 6.6; M = microfibre Nylon 6.6.

highest, for both conventional and microfibre Nylon 6.6, when the dye had been applied at 95°C, this being attributable to a corresponding increase in diffusion rate of the dyes that accompanied an increase in temperature, and that application at pH 8 gave the highest colour strength for the two temperatures used. These findings concur with those of Lo[5] and Dohmyou *et al.*[11]

In the early stages of dyeing at pH 7, 8 and 9, there will be little, if any, electrostatic interaction operating between the anionic, sulphatoethylsulphone dye and the fibre, since the amino end groups in the substrate will be non-protonated; indeed, at such pH values the fibre can be considered to possess an overall negative potential owing to ionisation of the carboxyl end groups. Thus, in the early stages of dyeing at pH 7, 8 and 9, dye–fibre substantivity will arise by means of, for instance, ion–dipole, ion-induced dipole and dipole–dipole interactions. *β*-Elimination of the sulphuric acid ester group (—OSO_3^-) of the dye will occur as dyeing proceeds to give the non-ionic, vinyl sulphone derivative of the dye (VI). Since this elimination reaction, which is base-catalysed, is considered to commence at a temperature of between 40 and 50°C, then in the later stages, and perhaps for the greater proportion of the dyeing cycle, the dye will be present in the dyebath, at each of the three pH values studied, in the non-ionic, vinyl sulphone form (VI), the adsorption of which can be considered to be pH-independent. However, Table 2 shows that colour strength was pH-dependent, insofar as maximum colour strength was achieved at pH 8. This finding can be explained in terms of the competitive nature of the dye–fibre and dye hydrolysis reactions occurring during dyeing.

As a consequence of the rate of β-elimination of the sulphuric acid ester group of the dye being base-catalysed, the rate of formation of the reactive, vinyl sulphone derivative (VI) is also base-catalysed; thus, the rate and extent of fixation of the dye to the substrate can be expected to increase with increasing pH of application. Hence, the extent of dye fixation, expressed in terms of colour strength (K/S) of the dyeings, should have been greatest when dyeing was carried out at pH 9. However, this was not found to be the case (Table 2) and can be attributed to the rate of hydrolysis of the vinyl form of the dye in the dyebath also being base-catalysed, with the result that the rate of formation of the hydrolysed (VII) form of the dye in the dyebath will increase with increasing pH. Thus, it is suggested that the colour strength obtained at pH 9 was lower than that achieved at pH 8 because of a higher rate and extent of dye hydrolysis at the higher application pH value.



(VII)

Table 2 also demonstrates that at each temperature and pH value used, the colour strength obtained for the corresponding dyeings on conventional fabric was higher than that secured for the dyeings on microfibre Nylon 6.6. This finding, which can be attributed to the greater extent of surface reflection associated with the dyed microfibre, was expected and clearly shows the nature of the problem encountered in the dyeing of such microfibre Nylon 6.6 fibres, namely that more dye must be applied to microfibre in order to achieve the same colour strength of dyed conventional decitex fibre.

Since Table 2 shows that the optimum conditions for application of dye I to both conventional and microfibre Nylon 6.6 were pH 8 at 95°C and, furthermore, that these findings concurred with those of Lo[5] and Dohmyou *et al.*,[11] it was decided that all further application of reactive disperse dyes (I–III) would be carried out under these particular pH and temperature conditions.

In his previous study, Lo[5] had observed that the levelness of the dyeings achieved with reactive disperse dyes on conventional Nylon 6.6 was improved by the presence of a levelling agent in the dyebath; this aspect was investigated for each of the two types of Nylon 6.6 fabrics utilised in this work. As previously discussed, during dyeing, the initially water-soluble sulphatoethylsulphone dyes are converted to the corresponding low water-solubility vinyl form *in situ* in the dyebath. Since it is well known that the quality of a disperse dye dispersion markedly affects the rate, extent and levelness of dyeing achieved on hydrophobic fibres, it is important that an adequate dispersion of the vinyl form of the dye was obtained. It was found that when dyeings (1% omf, pH 8, 95°C) of each of the three reactive disperse dyes under consideration were carried out in the presence of various levels of dispersing agent in the dyebath, the levelness of dyeings was improved. The colorimetric data obtained (Table 3) for the dyeings carried out in the presence of various levels of dispersing agent in the dyebath show, for each of the three dyes used, that the concentration of dispersing agent employed had little effect on the hue (a^*, b^* and $h°$) and chroma (c^*) of the dyeings. It is also evident, for each of the dyes, that the colour strength (K/S) of the dyeings on conventional fibre decreased slightly with increasing concentration of dispersing agent used; this can be attributed to the levelling action of the dispersant. In contrast, the colour strength of the microfibre dyeings increased slightly with increasing concentration of dispersing agent used;

TABLE 3
Effect of Dispersing Agent Concentration on Dyeing (1% omf; pH 8; 95°C)

Dye	*Ufoxane 2 (g/litre)*	*Fibre*[a]	*L**	*a**	*b**	*c**	*h°*	*K/S*
I	0·1	C	65·8	43·9	70·9	83·4	58·3	17·4
		M	66·4	42·1	68·4	80·3	58·4	14·5
	0·5	C	63·6	44·3	68·8	81·8	57·2	17·8
		M	64·9	43·2	68·1	80·7	57·6	15·9
	1·0	C	63·3	42·6	69·9	81·9	58·7	17·4
		M	64·7	40·8	66·9	78·3	58·7	17·4
II	0·1	C	63·3	49·3	74·2	89·1	56·4	22·0
		M	64·4	46·8	73·4	87·1	57·5	18·9
	0·5	C	62·6	49·7	73·3	88·6	55·9	22·5
		M	64·4	46·4	73·3	86·7	57·7	18·6
	1·0	C	63·1	48·1	77·8	91·4	58·3	21·4
		M	64·0	48·5	76·9	89·9	58·9	19·1
III	0·1	C	60·9	49·9	68·7	84·8	53·9	21·3
		M	62·3	47·8	68·2	83·3	54·9	17·9
	0·5	C	60·8	50·2	68·5	84·9	53·8	21·3
		M	61·8	48·2	67·7	83·1	54·5	18·5
	1·0	C	61·4	48·8	72·4	87·3	56·0	20·0
		M	62·3	47·7	71·8	86·2	56·4	18·1

[a] C = Conventional Nylon 6.6; M = microfibre Nylon 6.6.

this may be due to the dispersant having enhanced the extent and quality of dispersion of the dye since, as previously mentioned, the uptake of disperse dyes on to hydrophobic fibres depends markedly upon the quality of the dye dispersion. A comparison of the results displayed in Table 3 for dye I with those presented in Table 2 for dyeings secured at 95°C and at pH 8 in the absence of dispersing agent, clearly shows that while the colour strength (K/S) of the conventional dyeing was not altered by the presence of dispersing agent, that of the microfibre dyeing was enhanced by the presence of 0·5 and 1% omf dispersing agent. It is possible that the enhancement of colour strength observed for the microfibre may, as previously recounted, be due to the dispersant having improved the extent and quality of dispersion of the dye.

Table 3 also shows, for each of the three dyes used, that the colour strength obtained for the dyeings on conventional fabric was higher than that secured for the dyeings on microfibre Nylon 6.6. The difference, in terms of colour strength of dyeings obtained on conventional and microfibre Nylon 6.6, is further illustrated by the lower build-up profiles obtained for each of the three dyes on microfibre (Figs 2–4) and the higher concentration of each of the three dyes required to achieve a 1/1 standard depth on microfibre (Table 4), when dyeing was carried out at 95°C and pH 8 in the presence of 1 g/litre dispersing agent; in the case of the 1/1 standard depth dyeings (Table 4), it is apparent that between 20 and 25% more dye was required to achieve this standard depth on microfibre. As the polymer used in the microfibre was the same as that employed in the conventional fibre,[3] these observed differences in colour strength of dyeings obtained on conventional and microfibre Nylon 6.6

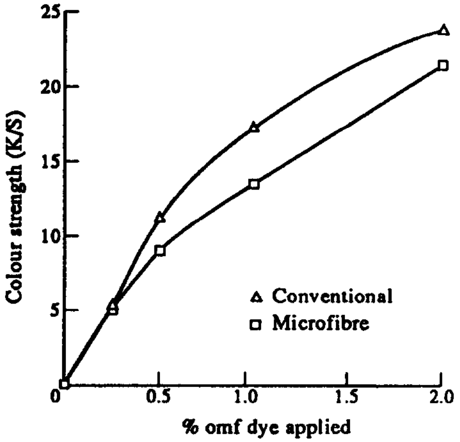


Fig. 2. Build-up of dye I (95°C; pH 8; 1 g/litre dispersing agent).

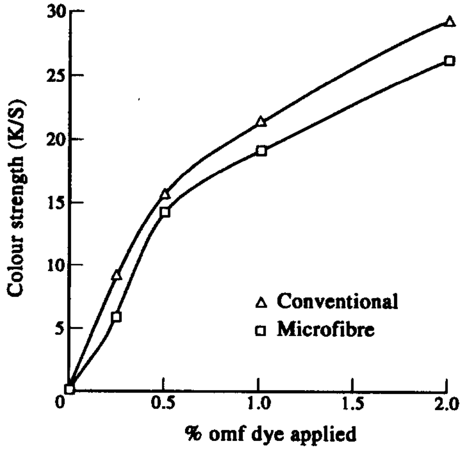


Fig. 3. Build-up of dye II (95°C; pH 8; 1 g/litre dispersing agent).

can, as previously mentioned, be attributed to the greater surface reflection of the dyed microfibre.

Figures 2–4 also reveal that the shape of the build-up curve was similar for both conventional and microfibre Nylon 6.6 for each dye; this finding seems reasonable as both types of fibre comprised the same polymer.[3] Furthermore, each of the three dyes under consideration exhibited very good build-up characteristics on both types of fibre, although Figs 2–4 clearly show that the build-up did not reach a maximum value; indeed, the gradients of the curves obtained imply that dye build-up would continue to markedly increase with further increase in

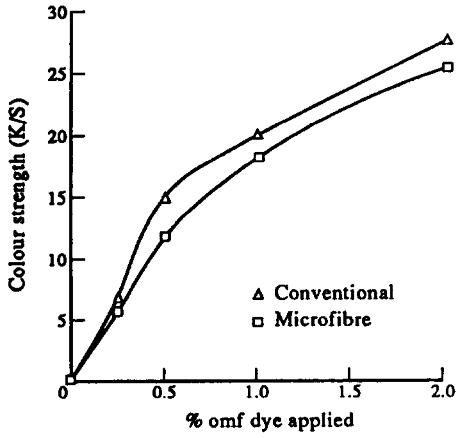


Fig. 4. Build-up of dye III (95°C; pH 8; 1 g/litre dispersing agent).

TABLE 4
Dye Concentration (% omf) Required to Give 1/1 Standard Depth Dyeings (pH 8; 95°C; 1 g/litre dispersing agent)

Dye	*Conventional*	*Microfibre*
I	0·3	0·4
II	0·2	0·25
III	0·25	0·3

concentration of each dye applied to both types of Nylon 6.6 fibre. Work is in hand to investigate further this particular aspect.

It is well known that conventional disperse dyes exhibit poor to moderate build-up on Nylon fibres, this being attributable to the ionic, and thus relatively hydrophilic, nature of the substrate. It was recounted earlier that under the application conditions employed for dyeing (pH 8, 95°C), each of the three reactive dyes may be present in the dyebath in the non-ionic, vinyl sulphone form (VI) for perhaps the greater proportion of the dyeing cycle. If this were the case, adsorption of the non-ionic, disperse form of the reactive dye on to the fibre could be considered to arise by virtue of those forces of interaction that are proposed to be responsible for the adsorption of conventional disperse dyes on to hydrophobic fibres, namely, dipole–dipole forces and hydrogen bonding. However, such dye–fibre forces should, as is the case for conventional disperse dyes, result in the three reactive disperse dyes exhibiting only poor to moderate build-up on both types of fibre, whereas, as Figs 2–4 clearly show, the three dyes displayed excellent build-up characteristics.

It is well known that in the dyeing of cellulosic fibres with conventional reactive dyes, dye-fibre reaction has a meritorious effect on dye uptake; thus it is possible, for dyes I–III, that the reaction of the vinyl sulphone derivative of the dye with the Nylon 6.6 fibre enhanced dye uptake, and therefore that dye–fibre reactions was responsible for the excellent build-up observed for the three dyes. An attempt was made to determine the effect of dye–fibre reaction on the build-up of the reactive disperse dyes; to this end, dye IV was synthesised. Since structurally dye IV closely resembles the vinyl sulphone form of dye I (the two dyes differing by only two units of M_r) but dye I contains the reactive vinyl grouping, it was considered that a comparison of the build-up characteristics of the two dyes on Nylon 6.6 might demonstrate the effect of dye–fibre reaction on dye uptake.

Figure 5 shows the build-up profiles of dyes I and IV on both con-

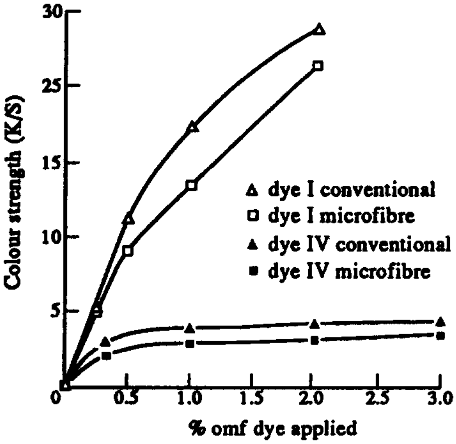


Fig. 5. Build-up of dyes I (95°C; pH 8; 1 g/litre dispersing agent) and IV (95°C; pH 6·5; 1 g/litre dispersing agent).

ventional and microfibre Nylon 6.6, from which it is clear that the build-up of the disperse dye (IV) was markedly lower than that of the reactive disperse dye (I). If it is assumed that for the greater part of dyeing, the reactive disperse dye will exist in its vinyl sulphone form, then both dyes I and IV will be present in their respective dyebaths as disperse dyes; thus, as mentioned previously, since the two dyes differ only by two M_r units, it is proposed that the two dyes possess very similar substantivity towards Nylon 6.6, and therefore their build-up profiles should be similar. However, since dye I contains the reactive vinyl sulphone group, the observed difference in build-up between dyes I and IV (Fig. 5) supports the proposition that, as in the case of dyeing cellulosic fibres with conventional reactive dyes, reaction of dye I with the fibre promoted dye uptake. This proposal in turn implies that at the end of dyeing, whilst dye IV will be bound to the fibre by physical forces of interaction, dye I has reacted with and is covalently attached to the substrate; evidence to support this proposition is provided by the wash-fastness results displayed in Table 5, which clearly show that the wash-fastness of dye I was much higher than that of dye IV. Owing to the poor build-up of dye IV (Fig. 5) it was possible to achieve only a 1/3 standard depth dyeing of both conventional and microfibre Nylon 6.6 rather than the 1/1 standard depth achieved using dye I. Thus, the difference in wash-fastness observed between dyes I and IV (Table 5) is very marked since, in view of the well-known fact that wash-fastness decreases with increasing depth of shade, if it had been possible to obtain 1/1 standard depths using dye IV, it can be anticipated that the fastness to washing of such dyeings

TABLE 5
Colour Fastness to Washing (ISOCO6/C2) of Standard-Depth Dyeings

Dye	*Standard depth*	*Fibre*	*Ch*	*N*	*C*
I	1/1	Conventional	5	4–5	5
	1/1	Microfibre	5	4–5	5
II	1/1	Conventional	5	4	5
	1/1	Microfibre	5	4	5
III	1/1	Conventional	5	4	4–5
	1/1	Microfibre	5	4	4–5
IV	1/3	Conventional	4–5	3–4	4–5
	1/3	Microfibre	4	3	4–5

would have been much lower than that secured for the 1/3 standard depths shown in Table 5. This argument adds further support to the proposal that dye I is covalently attached to the fibre rather than being simply bound to the substrate via physical forces of interaction.

Table 5 also demonstrates that the wash-fastness of the three reactive disperse dyes on microfibre was identical to that on the conventional decitex substrate. This finding is of major significance in the context of microfibre, since despite the presence on the microfibre of between 20 and 25% more dye than on their conventional counterparts (Table 4), the wash-fastness of the dyed microfibres was equivalent to that of the dyed conventional Nylon 6.6

4 CONCLUSIONS

Application at 95°C and pH 8 yielded optimum colour strength for the reactive disperse dye I on both conventional and microfibre Nylon 6.6. The presence of 1 g/litre of a commercial dispersing agent in the dyebath enhanced the levelness, but did not markedly reduce the colour strength of dyeings achieved using each of the three reactive disperse dyes (Schemes I–III) on both types of Nylon 6.6 fibre. The excellent build-up profiles obtained for the three reactive disperse dyes, which contrasted markedly with the poor build-up profile secured for the disperse dye (IV) on both substrates, can be attributed to the covalent reaction of the reactive disperse dyes having promoted dye uptake. The three reactive disperse dyes exhibited excellent wash-fastness on both conventional and microfibre Nylon 6.6, the level of fastness achieved being identical on both types of fibre.

REFERENCES

1. Jacques, M. L., *Textile Asia*, **11** (1992) 50.
2. Anon., *Japanese Textile News*, **5** (1992) 81.
3. Marfell, D., DuPont Fibres, Gloucester, UK.
4. Hinks, D., Department of Colour Chemistry and Dyeing, The University, Leeds, UK.
5. Lo, S. S., The dyeing of Nylon 6,6 with reactive disperse dyes. MSc Thesis, The University, Leeds, UK, 1991.
6. *Standard Depths*. Society of Dyers and Colourists, Bradford, UK.
7. *Standard Methods for the Determination of the Colour Fastness of Textiles and Leather*, 5th edn. Society of Dyers and Colourists, Bradford, UK, 1990.
8. Gardner, W. M., *JSDC*, **38** (1992) 171.
9. Green, A. G. & Saunders, K. H., *JSDC* **39** (1923) 10; **40** (1924) 138.
10. Fourness, R. K., *JSDC*, **69** (1956) 513.
11. Dohmyou, M., Shimizu, Y. & Kimura, M., *JSDC*, **106** (1990) 395.