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The Dyeing of Conventional and Microfibre Nylon 6,6 with Reactive Dyes—3. Vinyl Sulphone and Chlorotriazine Dyes

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ABSTRACT

The dyeing behaviour and wash fastness of three vinyl sulphone and five chlorotriazine dyes on conventional decitex and microfibre Nylon 6,6 fabrics were examined; the extent of dye fixation was determined by stripping unfixed dye from the dyeings using aqueous pyridine. © 1997 Elsevier Science Ltd

Keywords: Nylon 6,6, microfibre, reactive dyes, vinyl sulphone, chlorotriazine.

INTRODUCTION

In the first two parts of this paper the build-up and wash fastness characteristics of commercial chlorodifluoropyrimidinyl[1] and also α-bromoacrylamid[2] reactive dyes on both conventional decitex and microfibre Nylon 6,6 fabrics were examined. It was found that weakly acidic conditions (pH 4) yield good colour strength and that level dyeings were obtained without the need for electrolyte or proprietary levelling agent. Whilst the three chlorodifluoropyrimidinyl dyes examined displayed good build-up on both types of fabric and very good wash fastness[1] only one of the three α-bromoacrylamido dyes studied displayed good build-up on both types of fibre and it was observed that a large proportion of adsorbed dye was unfixed and removed by wash-off.[2] In addition, the fastness of washed-off α-bromoacrylamido dyeings was very good although, in the majority of cases, this was expected in view of the very low colour strengths of the dyeings.[2]

TABLE 1
Dyes Used

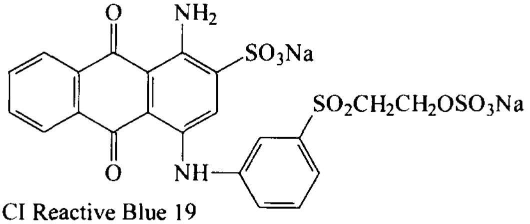
Commercial name	C.I. Generic name
Remazol Brilliant Blue R	Reactive Blue 19
Remazol Red RB	Reactive Red 198
Remazol Yellow 3RS	Reactive Yellow 176
Procion Red HE3B	Reactive Red 120
Procion Yellow MX4G	Reactive Yellow 22
Procion Brilliant Red HEGXL	Reactive Red 231
Procion Navy HEXL	None ascribed
Procion Crimson HEXL	None ascribed

The aim of this work was to examine the exhaustion and fixation characteristics of vinyl sulphone and chlorotriazine reactive dyes on both conventional decitex and microfibre Nylon 6,6.

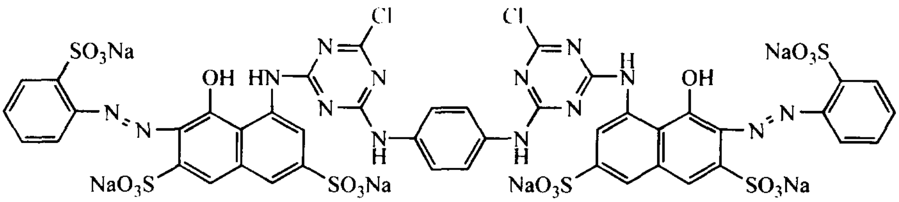
EXPERIMENTAL

Materials

Commercial samples of scoured conventional (78f68, 1.15 dtexpf) and microfibre (60f68, 0.88 dtexpf) knitted Nylon 6,6 fabrics, kindly supplied by Du Pont Nylon (UK), were used. The amino end group (AEG) content of each type of fibre was 45 meq kg^{-1}.[3]

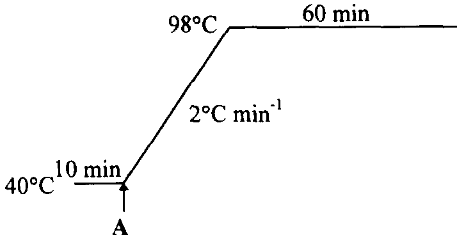


CI Reactive Blue 19
(Remazol Brilliant Blue R)



CI Reactive Red 120
(Procion Red HE3B)

Fig. 1. The chemical structures of two typical reactive dyes.



A Buffer
Fabric (4g)

Fig. 2. Dyeing method used.

Three *Remazol* (Hoechst) dyes and five *Procion* (Zeneca) dyes (Table 1) were used; the dyes were commercial samples that were not purified before use and were generously provided by the respective manufacturers. The structures of only two of the dyes are published in the Colour Index[4] and are given in Fig. 1.

Sodium phosphate, citric acid, sodium perborate and sodium carbonate were each of analytical grade, obtained from Aldrich.

Dyeing

This was carried out in sealed, 100 cm^3 capacity, stainless steel dyepots housed in a John Jeffries laboratory-scale, Rota Dyer machine using a liquor-to-goods ratio of 20:1. Samples of conventional or microfibre nylon 6.6 (4 g) were placed in the dyepot and 80 cm^3 of the appropriate buffer solution (described below) added; the fabric sample was then added and dyeing carried out using the method shown in Fig. 2. At the end of dyeing the samples were removed, squeezed to remove as much excess liquor as possible and dried in air at room temperature overnight.

Buffer solutions

The composition of the McIlvaine[5] buffers used is shown in Table 2.

Wash-fastness determination

Samples of dried dyeings were subjected to the ISOC06/C2 wash fastness test.[6]

TABLE 2

Composition of McIlvaine Buffers[4]

pH	cm^3 required in a total volume of 80 cm^3 0.2 M Na_2HPO_4	 0.1 M citric acid
2	1.6	78.4
3	16.4	63.6
4	30.9	49.1
5	41.2	38.8
6	50.6	29.4
7	65.9	14.1
8	77.8	2.2

TABLE 3

Wash Fastness (ISO CO6/C2) Results

pH	Shade change		Staining of adjacent Nylon		 Cotton		Shade change		Staining of adjacent Nylon		 Cotton	
C.I. Reactive Yellow 176							C.I. Reactive Red 198					
2	5	5*	4/5	5*	5	4/5*	5	5*	5	5*	4/5	4/5*
3	5	5*	5	5*	5	4/5*	5	5*	5	5*	4/5	4/5*
4	5	5*	5	4/5*	5	5*	5	5*	5	5*	4/5	4/5*
5	5	5*	5	5*	5	5*	5	5*	5	5	4/5	5*
6	5	5*	5	5*	5	5*	5	5*	5	5	5	5*
7	5	5*	5	5*	5	5*	5	5*	5	5*	5	5*
8	5	5*	5	5*	5	5*	5	5*	5	5*	5	5*
C.I. Reactive Blue 19							C.I. Reactive Yellow 22					
2	3	3*	2	2*	2/3	2/3*	5	4/5*	5	5*	5	5*
3	3	3*	2	2*	2/3	3*	4/5	4/5*	5	4/5*	5	5*
4	3	3*	2	2*	2/3	3*	4/5	4/5*	5	5*	5	5*
5	3/4	3/4*	2/3	2/3*	3	3*	5	5*	5	5*	5	5*
6	5	5*	5	5*	5	5*	5	5*	5	5*	5	5*
7	5	5*	5	5*	5	5*	5	5*	5	5*	5	5*
8	5	5*	5	5*	5	5*	5	5*	5	5*	5	5*
C.I. Reactive Red 120							C.I. Reactive Red 231					
2	5	5*	5	5*	3/4	3/4*	5	5*	5	5*	4/5	4*
3	5	5*	5	5*	2/3	3*	5	5*	5	5*	4/5	4*
4	5	5*	5	5*	3	3*	5	5*	5	4/5	4/5	4*
5	5	5*	5	5*	3	3*	5	5*	5	5*	4/5	4/5*
6	5	5*	5	5*	3/4	3/4*	5	5*	5	5*	5	4/5*
7	-	-	-	-	-	-	5	5*	5	5*	5	5*
8	-	-	-	-	-	-	4/5	4/5*	4/5	5*	5	5*
Procion Navy HE-XL							Procion Crimson HE-XL					
2	4	4*	5	5*	4/5	4/5*	5	5*	5	5*	4/5	5*
3	4	4*	5	5*	4/5	4/5*	5	5*	5	5*	4/5	4/5*
4	3/4	4*	5	5*	4/5	4/5*	5	5*	5	5*	4/5	4/5*
5	5	4/5	5	5*	4/5	4/5*	5	5*	5	5*	4/5	5*
6	5	4/5*	5	5*	4/5	5*	5	5*	5	5*	5	5*
7	5	4*	5	5*	5	5*	5	5*	5	5*	5	5*
8	-	-	-	-	-	-	5	4*	5	5*	5	5*

*Microfibre.

\- Results not included owing to low K/S.

Colour measurement

The reflectance values of the dyeings were measured using a Colorgen spectrophotometer linked to a PC running Colorgen QC Version 6.70 colour measurement software. The fabric samples were folded four times and an average of four readings per sample taken under illuminant D_{65}, using a 10° standard observer, with specular component excluded and UV component included. The colour strength (K/S values) at the λ_{max} of the dyeing, was calculated from the reflectance data.

Determination of dye fixation

Samples of the dyeings were subjected to a stripping process using 20% aqueous pyridine in order to remove unfixed dye. The dyed sample (1g) was placed in a Soxhlet extraction apparatus filled with 250 cm^3 of 20% aqueous pyridine solution and extraction carried out under reflux until no further colour loss from the dyed sample occurred (approximately 3–5 h). The percentage dye fixation (%F) was calculated using equation (1).

$$\%F = \frac{K/S_{before\ pyridine\ extraction}}{K/S_{after\ pyridine\ extraction}} x100 \tag{1}$$

RESULTS AND DISCUSSION

In Figs 3–11 the left-hand plot shows the colour strength (K/S) of the dyeings and the right hand plot the extent of dye fixation, both as a function of dyebath pH, for each dye, on both types of substrate.

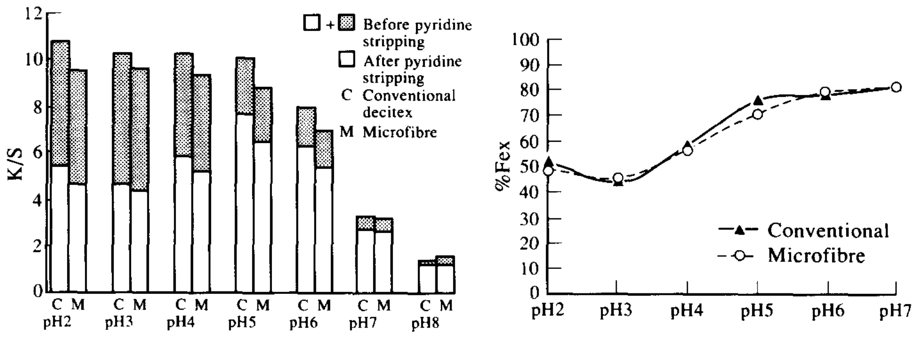


Fig. 3. C.I. Reactive Yellow 176 2% omf.

It was found that, with the exception of C.I. Reactive Blue 19 (Fig. 5), colour strength (K/S) prior to pyridine extraction increased with decreasing pH of application. The structures of only two of the dyes are in the public domain (Fig. 1); however, if it assumed that all of the dyes used in this study

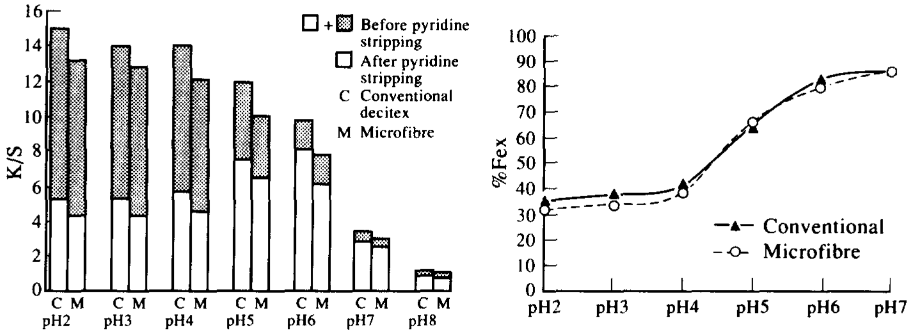


Fig. 4. C.I. Reactive Red 198 2% omf.

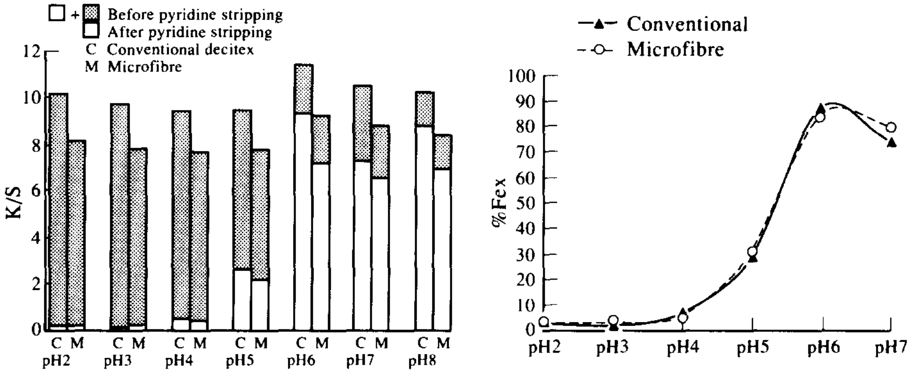


Fig. 5. C.I. Reactive Blue 19 2% omf.

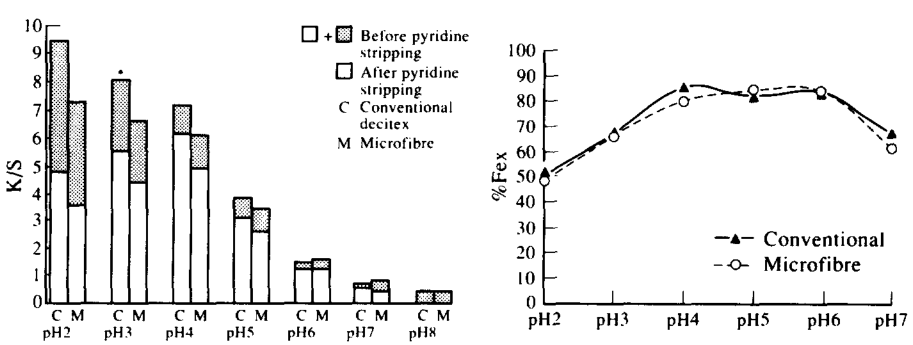


Fig. 6. C.I. Reactive Yellow 22 2% omf.

carried sulphonate groups, the observed increase in dye uptake that accompanied a decrease in application pH (Figs 3, 5–10) can be attributed to a corresponding increase in ion–ion interaction operating between sulphonate

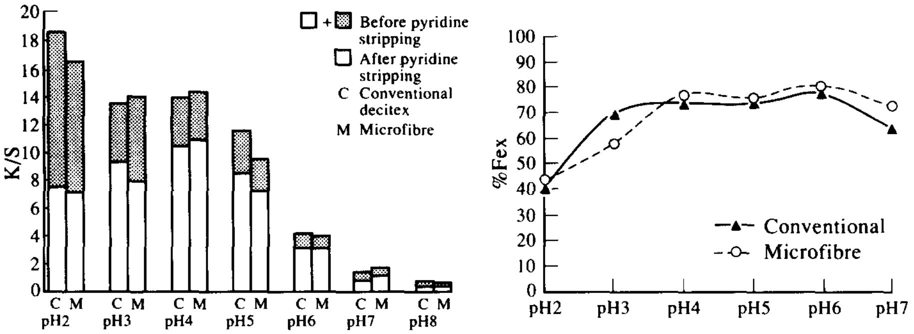


Fig. 7. C.I. Reactive Red 120 2% omf.

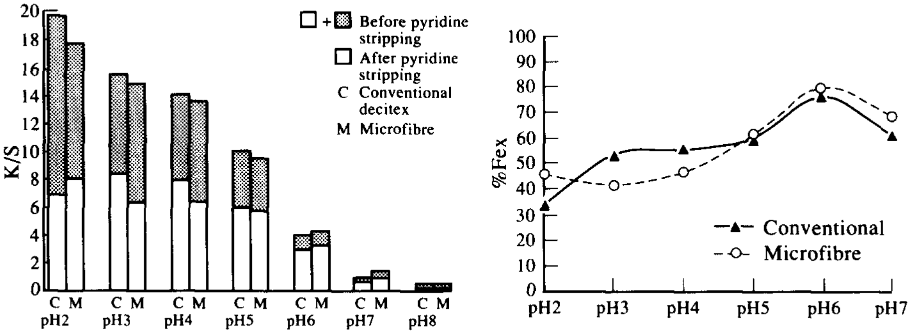


Fig. 8. C.I. Reactive Red 231 2% omf.

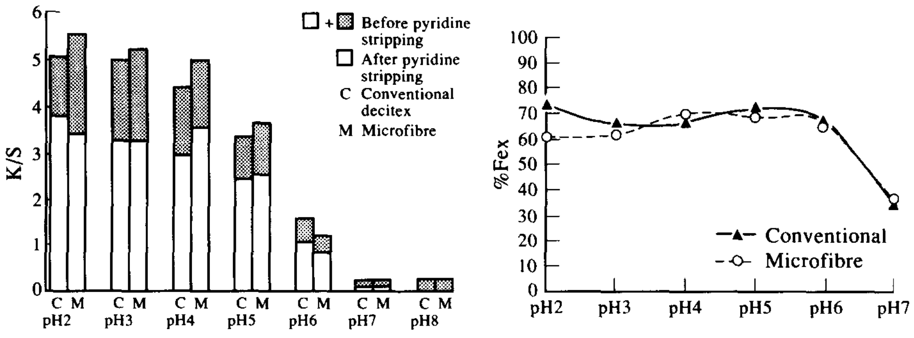


Fig. 9. *Procion* Navy HEXL 2% omf.

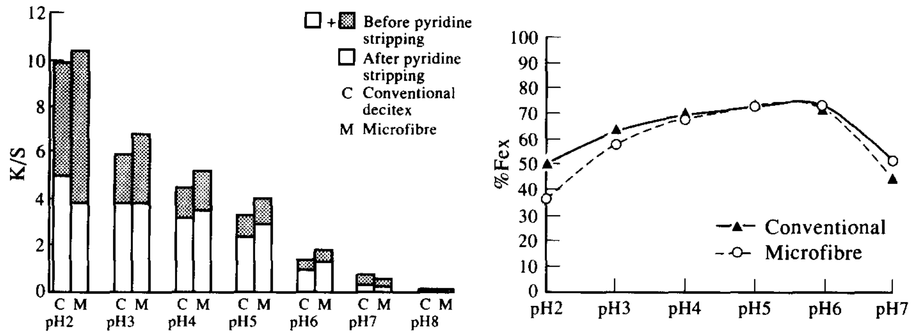


Fig. 10. *Procion* Crimson HEXL 2% omf.

groups in the dye molecule and protonated amino end groups in the fibre. In essence, the anionic reactive dyes can be considered to have behaved as acid dyes in terms of their uptake, insofar as uptake increased with decreasing dyebath pH owing to a corresponding increase in protonation of the terminal amino groups. However, as Figs 3–10 show, the colour strength before pyridine extraction obtained at each of the pH values studied, varied markedly for the eight dyes.

In the case of C.I. Reactive Blue 19 (Fig. 5), the colour strength of the dyeings prior to pyridine extraction did not increase with decreasing pH, as was found for the seven other dyes used. Clearly, for C.I. Reactive Blue 19, dye uptake can be divided into two distinct regions, namely that which occurred at pH values below 6 and that which occurred above pH 6. In each of these two regions, the colour strength of the unextracted dyeings was virtually independent of pH. In order to explain this finding, it is necessary to discuss the fixation (90, F) profiles obtained for the dye.

The fixation profiles (Fig. 5) obtained for the dye are consistent with those expected of a β-sulphatoethyl sulphone dye in view of the well known, marked pH-dependency of activation to the vinyl form of the dye. Osterloh[7] showed that for such dyes, maximum activation occurred about pH 6.5 and, below this pH value, the extent of activation decreased markedly with decreasing pH. Figure 5 reveals that this behaviour was secured for C.I. Reactive Blue 19 on Nylon 6,6, insofar as maximum fixation occurred at about pH 6–6.5 and, below this pH, the extent of fixation decreased markedly with decreasing pH. In turn, the fixation behaviour of the dye can be considered to be responsible for the observed colour strength profiles of the

Fig. 11. The amino end group protonation equilibrium.

unextracted dyeings. Thus, it is proposed that the colour strength (K/S) of the unextracted dyeings of C.I. Reactive Blue 19 at pH values of 6, 7 and 8 were higher than those at pH values below 6 because of the combination of two factors:

1. considerable dye fixation occurred at pH 6, 7 and 8 whereas little fixation occurred at pH values below 6;
2. the well known fact that, in the case of reactive dyes on cellulosic fibres, dye fixation increases dye exhaustion.

A comparison of Figs 4–6 shows that the colour strength and fixation profiles obtained for the other two *Remazol* dyes differed to those obtained for CI Reactive Blue 19. Clearly, in the cases of C.I. Reactive Red 198 and C.I. Reactive Yellow 176, significant fixation occurred in the pH range of 2.2–5; this is contrary to that observed in the case of C.I. Reactive Blue 19 and is not typical of that expected of β-sulphatoethyl sulphone dyes. Although the structures of the two dyes in question are not disclosed, it seems reasonable to propose in view of the fixation profiles obtained (Figs 4 and 6) that the reactive groups in C.I. Reactive Red 198 and C.I. Reactive Yellow 176 are modified vinyl sulphones.

In the case of the five chlorotriazine (Procion) dyes used, the effect of pH on fixation was similar to that secured using the yellow and red vinyl sulphone dyes in that dye fixation gradually decreased as dyebath pH was lowered. A notable exception was *Procion Navy HEXL* (Fig. 9), for which a fixation level of 60–70% was maintained over the pH range 2–6. Generally, the chlorotriazine dyes achieved fixation values of 40–50% at pH 2, showing that dye fibre reaction still occurred under low pH conditions, as was observed for C.I. Reactive Yellow 176 and C.I. Reactive Red 198 (Figs 3 and 4).

Theoretically, reaction between the reactive dyes used in this study and the fibre will occur by the nucleophilic amino end group attacking the electrophilic reactive group of the dye. The protonation of the terminal amino end groups is an equilibrium process; under low pH conditions, the equilibrium (Fig. 11) can be expected to be largely towards the protonated side. However, even under low pH conditions it can be proffered that at a given instant of time, a nucleophilic (unprotonated) amino group can exist. Consequently, under low pH conditions the anionic dye can be considered to be attracted strongly to the protonated amino end group in the fibre and, within this relatively enclosed micro-environment, an unprotonated amino end group attacks the reactive group of the adsorbed dye molecule resulting in dye–fibre reaction. Such a mechanism would account for the observation that dye–fibre fixation was observed at low pH values (i.e. pH 2–4) for all the dyes except C.I. Reactive Blue 19, for which, as discussed above, reaction with the substrate would not occur at low pH values due to inactivation of the β-sulphatoethyl sulphone to the vinyl form of the dye.

It is well known that the colour strength of a given depth of dyeing decreases with decreasing decitex owing to the corresponding increase in surface reflection that accompanies a decrease in linear fibre density.[8] Thus, it was expected that the colour strength of the dyed microfibre Nylon 6.6 would be lower than that of the dyed conventional decitex fibre before extraction with pyridine; however, inspection of Figs 3–10 reveals that this situation was not obtained for all the eight dyes used. Whilst the colour strength of the microfibre dyeings was lower than that of their conventional fibre counterparts in the cases of the three *Remazol* dyes (Figs 3–5), this was achieved only for three of the five *Procion* dyes (Figs 6– 8). In the case of the two remaining *Procion* dyes (Figs 9 and 10) colour strength was generally higher on dyed microfibre. A possible explanation of these findings will be given. In the case of *Procion Navy HEXL*, the difference in colour strength between the microfibre and conventional Nylon was of the order of 0.2–0.5 K/S units, which is well within the limits of experimental error for measuring colour strengths of value less than 5 K/S units. However, in the case of *Procion Crimson HEXL* (Fig. 10) the difference in K/S between the dyed microfibre and conventional fibres was much greater than experimental error and an alternative explanation is offered. Although the structure of *Procion Crimson HEXL* has not been published, it is possible that the dye possessed low diffusional power within the fibre owing to structural characteristics such as large molecular size and/or a high tendency to aggregate. If this were the case, the dye would tend to 'ring dye'. As it has been shown[8] that microfibre Nylon 6.6 has a greater propensity to 'ring dyeing' than conventional decitex Nylon 6.6 with acid dyes, it follows that any ring dyeing that occurred with *Procion Crimson HEXL* would be more pronounced in the case of microfibre. In turn, this would result in dyed microfibre being of higher colour strength, as indeed was found (Fig. 10).

Figures 3–10 show that fixation of the dyes over the pH range examined on microfibre Nylon 6.6 was very similar to that achieved on conventional decitex fibre. This was not surprising since, although the two types of fibre used differed in their decitex per filament, the amino end group content of the two fibre types was identical.[3]

It is generally accepted that in order to achieve a satisfactory level of wash fastness, reactive dyeings should be washed-off, so as to remove unfixed dye. In this study the dyeings were not washed-off as it was considered that this would artificially increase the wash fastness ratings, when a comparison of fixation and wash fastness rating was made. Table 3 shows that, as expected, the fastness of the dyeings to the ISO CO6/C2 wash test mirrored the fixation results (Figs 3–10) obtained in that wash fastness generally increased as the extent of dye fixation increased. Indeed, Table 3 clearly reveals that, in general, a satisfactory level of wash fastness was obtained for dyeings carried out at pH 5, 6, 7 and 8.

It must be borne in mind that the wash fastness results for the eight dyes used are not directly comparable in that the colour strength of the dyeings varied.

CONCLUSIONS

The optimum pH value for dyeing Nylon 6.6 with the two types of reactive dye examined lay between pH 5 and pH 6 where good exhaustion and high fixation were achieved. However, the results imply that the dyeing behaviour of the dyes is pH-dependent and also varies between dyes.

REFERENCES

1. Burkinshaw, S. M. & Gandhi, K., *Dyes and Pigments*, **32** (1996) 101.
2. Burkinshaw, S. M. & Gandhi, K., *Dyes and Pigments*, **34** (1997 63.
3. Marfell, D. J., Du Pont Fibres (UK), personal communication.
4. Colour Index, 3rd edn. Society of Dyers and Colourists, Bradford, 1975.
5. Vogel, A., *A Textbook of Quantitative Inorganic Analysis*. Longmans, London, 1944.
6. Standard Methods for the Determination of the Colour Fastness of Textiles and Leather, 5th edn. Society of Dyers and Colourists, Bradford, 1990.
7. Osterloh, F.. *Mell. Textil.*, **49** (1968) 1444.
8. Burkinshaw, S. M., *Chemical Principles of Synthetic Fibre Dyeing*. Blackie Academic and Professional, Glasgow, 1995.