Aftertreatment of 1:2 metal complex acid dyes on conventional and microfibre nylon 6.6 with a commercial syntan/cation system

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Dyeings (2% owf) were produced on conventional and microfibre nylon 6.6 fabrics using unsulphonated, monosulphonated and disulphonated 1:2 metal complex acid dyes. When subjected to the ISO 105:C06/C2 wash test, the wash fastness behaviour of the dyeings was related to the degree of sulphonation of the dyes. Aftertreatment of the dyeings using a commercial syntan improved the wash fastness of the dyeings whereas the sequential application of a cationic compound to the syntanned dyeings caused a further improvement in wash fastness.

INTRODUCTION

Metal complex acid dyes remain one of the most popular types of dye for polyamide fibres, owing to their generally very good light and wash fastness properties on such fibres [1,2]. Commonly, only selected 1:1 metal complex acid dyes are used on nylon because of the generally low saturation values secured; in addition, the dyes display poor coverage of fibre irregularities and poor compatibility in admixture [1]. In contrast, 1:2 metal complex acid dyes exhibit high build-up on polyamide fibres and good compatibility in admixture, although they tend to accentuate physical irregularities in the fibre [1]. Three types of 1:2 metal complex acid dyes are commercially available, namely, weakly polar, monosulphonated strongly polar and disulphonated strongly polar [1–3], each of which yield typically dull shades on nylon fibres [1].

Despite the generally very good wash fastness properties of 1:2 metal complex acid dyes on nylon fibres, an aftertreatment with a syntan or the full back tan can be used to improve wash fastness [1]. It is considered that syntans (synthetic tanning agents) are adsorbed at the periphery of the dyed fibre and their ability to impart improved wash fastness is due to this peripheral 'layer' of syntan molecules reducing the propensity of the dye to diffuse out of the fibre during washing [1,4]. Generally syntans marketed for the aftertreatment of dyed nylon are anionic, formaldehyde polycondensates of sulphonated dihydroxydiphenylsulphones [1]. Indeed, the particular commercial syntan used in this work, Fixogene AXF (ICI), is described as an anionic sulphonated high molecular weight product based on phenol sulphone [5].

Recently it was demonstrated that the effectiveness of a commercial syntan in improving the wash fastness of various unmetallised acid dyes on nylon 6.6 could be enhanced by the subsequent application of selected cationic compounds to the syntanned, dyed substrate [4,6]. It was proposed that in this sequential aftertreatment process, a large molecular size, low aqueous solubility, complex was formed between the anionic syntan and the cationic compound within the fibre [4,6]. The enhanced effectiveness of the syntan achieved using the sequential application technique was attributed to a lowering of the syntan's aqueous solubility and an increase in its effective molecular size, by means of which the propensity of the syntan to desorb from the dyed fibre during washing was reduced [1,4].

The technique of sequentially applying a cationic agent to syntanned, dyed nylon now enjoys commercial usage in the form of the Fixogene AC system [7]. This particular system comprises the sequential use of Fixogene AXF, a syntan, and Fixogene CXF (ICI), a cationic agent. However, although the use of this syntan/cation system in improving the wash fastness of unmetallised acid dyes on polyamide fibres has been discussed [1,4], an account of its applicability to the aftertreatment of metal complex acid dyes on nylon has not been published. The purpose of the work described here is to describe the effectiveness of the above mentioned commercial syntan/cation system in improving the wash fastness of 1:2 metal complex acid dyes on both conventional and microfibre nylon 6.6 fabrics.

EXPERIMENTAL

Materials

Two types of scoured, knitted nylon 6.6 fabrics, namely conventional (78f68; 1.15 dtex per filament) and microfibre (60f68; 0.88 dtex per filament), were used, each kindly supplied by DuPont Nylon (UK).

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The following commercial dyes were used, all of which were generously supplied by Crompton & Knowles (France):
Neutrilan Yellow K-3R (CI Acid Yellow 137)
Neutrilan Black K-BL (CI Acid Black 107)
Neutrilan Rubine S-2R
Neutrilan Bordeaux M-B (CI Acid Violet 90)
Neutrilan Black M-RC (CI Acid Black 194)
Neutrilan Bordeaux K-RL (CI Acid Red 182)
Neutrilan Orange S-R (CI Acid Orange 144)
Neutrilan Navy S-B (CI Acid Blue 284)
Neutrilan Navy M-BR (CI Acid Blue 193).

Commercial samples of Fixogene AXF and Fixogene CXF aftertreatment agents were kindly provided by ICI Surfactants.

Procedures

Samples of fabric (4.0 g) were dyed in sealed, stainless steel dye pots, of 300 ml capacity, housed in a Zeltex Polycolor laboratory dyeing machine, using a liquor ratio of 50:1. The dyeing procedure is given in Figure 1. At the end of dyeing the samples were rinsed thoroughly in tap water and dried in the open air.

Samples of dyed fabric (2.0 g) were syntanned using Fixogene AXF in sealed, stainless steel dye pots, of 300 ml capacity, housed in a Zeltex Polycolor laboratory scale dyeing machine, using a liquor ratio of 20:1. The aftertreatment procedure is given in Figure 2. At the end of aftertreatment the samples were rinsed thoroughly in tap water and dried in the open air.

Samples of dyed, syntanned fabric (1.0 g) were aftertreated with Fixogene CXF in sealed, stainless steel dye pots, of 300 ml capacity, housed in a Zeltex Polycolor laboratory scale dyeing machine, using a liquor ratio of 20:1. The treatment procedure is given in Figure 3. At the end of aftertreatment the samples were rinsed thoroughly in tap water and dried in the open air.

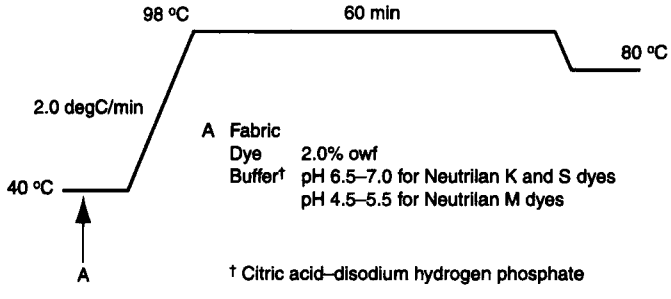

Figure 1 Dyeing of nylon 6.6 with 1:2 metal complex acid dyes

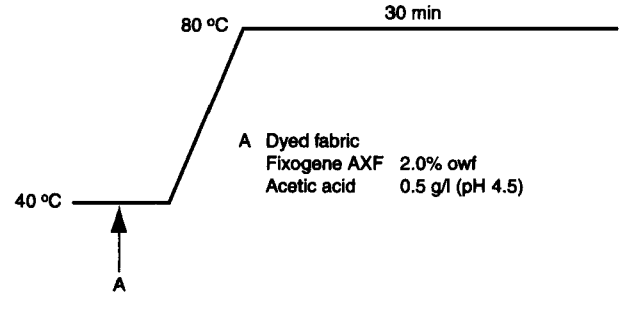

Figure 2 Aftertreatment of dyed nylon 6.6 with syntan

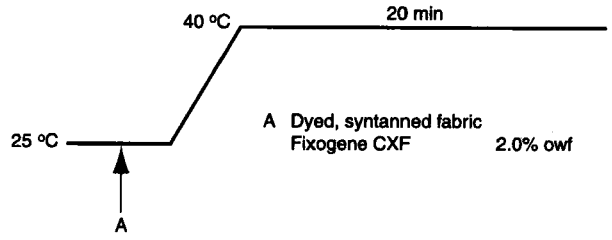

Figure 3 Aftertreatment of dyed, syntanned nylon 6.6 with cationic agent

Samples were washed according to the ISO 105:C06/C2 wash test using SDC multifibre strip fabric as adjacent [8]. Any reduction in depth of shade that occurred as a result of washing was calculated using Eqn 1 for the percentage colour loss (L_c):

$$L_c = \left(1 - \frac{(K/S)_t}{(K/S)_s}\right) \times 100 \qquad (1)$$

where $(K/S)_t$ and $(K/S)_s$ are the colour strengths of the washed, untreated/treated dyeings and the unwashed, untreated dyeings respectively.

RESULTS AND DISCUSSION

Table 1 shows the colorimetric data obtained for both the unwashed and washed Neutrilan K (unsulphonated) dyeings on conventional and microfibre fabrics. In the case of dyeings which had been subjected to the ISO 105:C06/C2 wash test, data are shown for dyeings which had received no aftertreatment before washing (nil), for dyeings which had been treated with the syntan only prior to washing (AXF) and also for dyeings which had been treated with the commercial syntan/cation system before washing (AXF + CXF). In the case of the unwashed dyeings, it is evident that for each of the three dyes used the colour strength (K/S) of the dyed conventional fabric was greater than the corresponding dyeing on its microfibre counterpart. The lower colour strength observed for dyeings on microfibre is attributable to the greater extent of surface reflection that results from the greater surface area of the polyamide microfibres [1,9].

Table 1 also shows that for the three dyes used, the ISO 105:C06/C2 wash test removed dye from both the dyed microfibre and conventional fabrics, as revealed by the lower K/S values of the washed dyeings. The extent of dye loss that occurred as a result of washing varied for the three dyes used.

It is clear from Table 1 that aftertreatment using 2% owf syntan alone reduced the amount of dye that was removed during washing, for each of the three dyes used. However, the use of the syntan in conjunction with the

Table 1 Colorimetric data for 2% owf Neutrilan K (unsulphonated) dyeings

Treatment	Fibre[a]	L^*	a^*	b^*	C^*	$h°$	K/S
CI Acid Yellow 137							
Unwashed	C	57.0	27.9	48.0	55.5	59.9	9.6
Nil	C	57.3	27.8	48.4	55.8	60.1	9.0
AXF	C	56.4	28.1	48.5	56.0	59.9	9.4
AXF + CXF	C	55.9	27.4	47.8	55.1	60.2	9.5
Unwashed	M	58.4	27.3	47.5	54.7	60.1	8.5
Nil	M	59.6	26.9	47.5	54.5	60.5	8.0
AXF	M	58.8	27.1	47.9	55.1	60.5	8.2
AXF + CXF	M	58.9	27.0	47.9	55.1	60.6	8.3
CI Acid Red 182							
Unwashed	C	28.2	34.0	−2.5	34.1	355.8	18.8
Nil	C	28.3	34.0	−2.5	34.1	355.8	18.3
AXF	C	27.9	33.9	−2.7	34.0	355.5	18.5
AXF + CXF	C	28.3	34.1	−2.7	34.2	355.5	18.6
Unwashed	M	30.8	34.8	−3.4	35.0	354.4	15.4
Nil	M	31.3	35.2	−3.4	35.3	354.5	13.9
AXF	M	31.2	34.9	−3.3	35.0	354.5	14.8
AXF + CXF	M	30.3	34.6	−3.2	34.7	354.7	15.0
CI Acid Black 107							
Unwashed	C	19.8	−1.0	−4.5	4.6	257.0	21.1
Nil	C	19.8	−0.9	−4.5	4.6	258.8	19.4
AXF	C	20.7	−1.0	−4.7	4.8	257.5	19.9
AXF + CXF	C	19.9	−0.9	−4.4	4.5	258.1	20.5
Unwashed	M	22.5	−1.1	−4.8	4.9	256.9	16.7
Nil	M	23.5	−1.2	−4.9	5.1	256.5	15.0
AXF	M	22.3	−1.1	−4.7	4.8	256.7	15.7
AXF + CXF	M	22.8	−1.3	−4.6	4.8	254.3	16.4

a C – conventional, M – microfibre

Table 2 Colorimetric data for 2% owf Neutrilan S (monosulphonated) dyeings[a]

Treatment	Fibre	L^*	a^*	b^*	C^*	$h°$	K/S
CI Acid Orange 144							
Unwashed	C	48.8	45.7	42.3	62.2	42.8	14.6
Nil	C	50.3	44.9	42.7	62.0	43.6	13.2
AXF	C	49.7	45.2	43.2	62.5	43.7	13.7
AXF + CXF	C	49.9	45.1	43.0	62.3	43.7	14.0
Unwashed	M	50.9	44.8	41.7	61.2	42.9	11.7
Nil	M	52.7	44.0	41.8	60.7	43.5	10.5
AXF	M	51.3	44.2	42.4	61.3	43.8	10.8
AXF + CXF	M	50.9	44.4	42.5	61.5	43.8	11.2
Neutrilan Rubine S-2R							
Unwashed	C	31.1	42.7	5.4	43.1	7.2	18.4
Nil	C	32.7	43.5	5.4	43.8	7.1	16.7
AXF	C	32.1	43.2	5.6	43.6	7.4	17.3
AXF + CXF	C	32.1	43.2	5.5	43.6	7.3	17.7
Unwashed	M	33.2	43.2	4.5	43.5	6.0	15.4
Nil	M	35.2	43.6	4.2	43.8	5.6	13.7
AXF	M	33.6	43.7	5.0	44.0	6.5	14.3
AXF + CXF	M	33.4	43.6	5.0	43.9	6.5	14.6
CI Acid Black 284							
Unwashed	C	23.2	1.9	−19.6	19.6	275.5	18.9
Nil	C	24.0	2.0	−20.0	20.1	275.6	17.4
AXF	C	23.5	2.1	−20.0	20.1	276.0	17.9
AXF + CXF	C	23.8	1.9	−19.9	20.0	275.6	18.2
Unwashed	M	25.6	1.8	−20.3	20.4	275.2	15.6
Nil	M	26.1	2.2	−20.4	20.5	276.2	14.1
AXF	M	25.4	2.0	−20.4	20.5	275.5	14.7
AXF + CXF	M	25.5	1.9	−20.4	20.5	275.5	14.9

a For key see Table 1

cationic agent was far more effective in reducing the extent of dye loss that occurred during washing.

The aftertreatments employed had very little or no effect upon the shade of the dyeings. This can be seen from the colorimetric parameters given in Table 1 which show variation only within a small range. The only great difference noted was between the lightness (L^*) values, which increase with washing, but this was expected as colour strength was reduced following the ISO 105:C06/C2 wash test, thus the dyeings became lighter.

The same trend was shown with the Neutrilan S and Neutrilan M dyes, shown in Tables 2 and 3 respectively, the shade of the dyeings being unaffected by aftertreatment.

Tables 2 and 3 show the colorimetric data secured for the unwashed and washed dyeings using the monosulphonated Neutrilan S dyes and the disulphonated Neutrilan M dyes respectively. In the case of the samples which had been subjected to the ISO 105:C06/C2 wash test, results are presented for dyeings which had been untreated before washing, treated with the syntan only before washing as well as treated with the syntan/cationic system prior to washing. The results obtained using these two types of 1:2 metal complex acid dyes were identical to those secured for the Neutrilan K dyes (Table 1), in that while aftertreatment with the syntan reduced the extent of dye loss that occurred during washing, aftertreatment with the commercial syntan/cation system was far more

Table 3 Colorimetric data for 2% owf Neutrilan M (disulphonated) dyeings[a]

Treatment	Fibre	L^*	a^*	b^*	C^*	$h°$	K/S
CI Acid Violet 90							
Unwashed	C	29.1	39.8	−3.9	40.0	354.4	19.8
Nil	C	30.3	40.3	−3.5	40.4	355.1	17.6
AXF	C	29.9	40.2	−3.5	40.3	355.1	17.9
AXF + CXF	C	30.0	40.1	−3.4	40.2	355.1	18.6
Unwashed	M	31.7	40.4	−4.9	40.7	353.1	16.0
Nil	M	32.9	40.8	−4.3	41.0	354.0	14.2
AXF	M	32.1	40.8	−4.3	41.0	354.0	14.4
AXF + CXF	M	32.0	40.7	−4.2	41.0	354.1	15.0
CI Acid Blue 193							
Unwashed	C	25.7	1.0	−17.4	17.5	273.3	15.8
Nil	C	25.9	0.9	−17.3	17.3	273.1	13.7
AXF	C	24.7	1.0	−17.0	17.0	273.3	14.7
AXF + CXF	C	24.4	1.0	−16.9	17.0	273.3	15.1
Unwashed	M	27.1	1.0	−17.7	17.8	273.2	14.0
Nil	M	27.6	0.8	−17.5	17.5	272.6	12.1
AXF	M	26.7	0.8	−17.4	17.4	272.7	12.9
AXF + CXF	M	27.6	0.9	−17.8	17.8	273.0	13.3
CI Acid Black 194							
Unwashed	C	20.2	0.1	−5.3	5.3	271.2	20.6
Nil	C	20.2	0.3	−5.3	5.3	273.6	18.9
AXF	C	20.1	0.1	−5.0	5.0	271.3	19.3
AXF + CXF	C	20.3	0.2	−5.1	5.1	271.8	19.6
Unwashed	M	21.8	0.1	−5.4	5.4	271.1	17.9
Nil	M	22.7	0.0	−5.3	5.3	270.4	15.7
AXF	M	22.1	0.1	−5.4	5.4	270.9	16.4
AXF + CXF	M	21.6	0.2	−5.2	5.2	271.9	17.0

a For key see Table 1

effective in reducing dye loss. Also, Tables 2 and 3 show that the extent of dye loss that occurred as a result of washing varied for the six dyes used. This latter finding can be attributed to the greater surface area of the dyed microfibre from which dye desorption could occur.

The findings presented in Tables 1–3 are depicted graphically in Figure 4 which shows the extent of dye loss, calculated using Eqn 1, that occurred during wash testing for each of the nine dyes used on both microfibre and conventional fabrics. From Figure 4 it is apparent that although aftertreatment using 2% owf syntan alone reduced the extent of dye loss during washing, for each of the nine dyes used, the use of the syntan/cationic system was far more effective in reducing the amount of dye removed during wash testing. Figure 4 shows that the percentage dye loss that occurred during washing was greater in the case of the dyed microfibre for each dye used. This finding can be attributed to the greater surface area of the microfibre from which dye loss can occur [1,4].

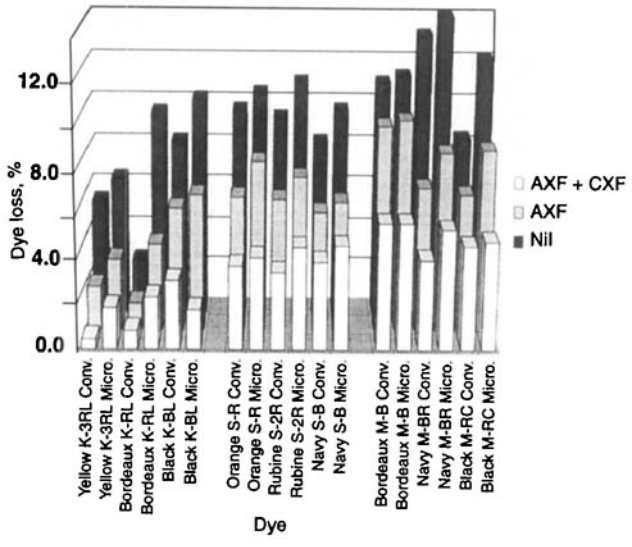

Figure 4 Percentage dye loss of washed, dyed conventional and microfibre nylon 6.6

Figure 4 also reveals that, for the nine dyes used, the extent of colour loss occurring during washing increased in the order: unsulphonated dyes < monosulphonated dyes < disulphonated dyes. This finding implies that the propensity of the dye to be removed during washing is related to the degree of sulphonation or aqueous solubility of the dye, if it is assumed that the disulphonated dyes are the most water soluble and the unsulphonated dyes are the least water soluble.

Additional evidence in support of this suggestion that the desorptive behaviour of the dyes is related to the aqueous solubility of the dye accrues from the wash fastness results obtained for the nine dyes (Tables 4–6).

The results presented in Tables 4–6 clearly show that each of the three types of 1:2 metal complex acid displayed identical wash fastness behaviour in the six adjacent fibres present in the SDC multifibre strip fabric used, the dyes stained mainly the adjacent nylon 6.6. However, in the context of the staining of adjacent nylon 6.6, the three dye types clearly differed in that fastness of the 2% owf dyeings decreased in the order: disulphonated dyes > monosulphonated dyes > unsulphonated dyes. However,

Table 4 Grey scale assessment of aftertreated Neutrilan K (unsulphonated) dyed nylon 6.6 samples compared with untreated, unwashed dyeing[a]

Aftertreatment	Fibre[b]	Shade	D	C	N	P	A	W
CI Acid Yellow 137								
Nil	C	5	5	5	2–3	5	5	5
AXF	C	5	5	5	4	5	5	5
AXF + CXF	C	5	5	5	4–5	5	5	5
Nil	M	5	5	5	2	5	5	5
AXF	M	5	5	5	3–4	5	5	5
AXF + CXF	M	5	5	5	4	5	5	5
CI Acid Red 182								
Nil	C	5	5	5	2–3	5	5	5
AXF	C	5	5	5	3–4	5	5	5
AXF + CXF	C	5	5	5	3–4	5	5	5
Nil	M	4–5	5	5	2	5	5	5
AXF	M	5	5	5	3	5	5	5
AXF + CXF	M	5	5	5	3	5	5	5
CI Acid Black 107								
Nil	C	4–5	5	5	1–2	5	5	5
AXF	C	4–5	5	5	3	5	5	5
AXF + CXF	C	5	5	5	3–4	5	5	5
Nil	M	4–5	5	5	1–2	5	5	5
AXF	M	4–5	5	5	2–3	5	5	5
AXF + CXF	M	5	5	5	3–4	5	5	5

a D – secondary acetate, C – cotton, N – nylon 6.6, P – polyester, A – acrylic, W – wool
b For key see Table 1

Table 5 Grey scale assessment of aftertreated Neutrilan S (monosulphonated) dyed nylon 6.6 samples compared with untreated, unwashed dyeing[a]

Aftertreatment	Fibre	Shade	D	C	N	P	A	W
CI Acid Orange 144								
Nil	C	4	5	5	3–4	5	5	4–5
AXF	C	4–5	5	5	4–5	5	5	5
AXF + CXF	C	5	5	5	5	5	5	5
Nil	M	4	5	5	3	5	5	4
AXF	M	4–5	5	5	4	5	5	5
AXF + CXF	M	4–5	5	5	4–5	5	5	5
Neutrilan Rubine S-2R								
Nil	C	4	5	5	3	5	5	4–5
AXF	C	4–5	5	5	4	5	5	5
AXF + CXF	C	4–5	5	5	4–5	5	5	5
Nil	M	4	5	5	3	5	5	4–5
AXF	M	4–5	5	5	4	5	5	5
AXF + CXF	M	4–5	5	5	4	5	5	5
CI Acid Blue 284								
Nil	C	4–5	5	5	2–3	5	5	5
AXF	C	4–5	5	5	3–4	5	5	5
AXF + CXF	C	5	5	5	4	5	5	5
Nil	M	4–5	5	5	2	5	5	4–5
AXF	M	4–5	5	5	3–4	5	5	5
AXF + CXF	M	5	5	5	4	5	5	5

a For key see Tables 1 and 4

Table 6 Grey scale assessment of aftertreated Neutrilan M (disulphonated) dyed nylon 6.6 samples compared to untreated, unwashed dyeing[a]

Aftertreatment	Fibre[b]	Shade	D	C	N	P	A	W
CI Acid Violet 90								
Nil	C	4	5	5	4	5	5	5
AXF	C	4	5	5	4–5	5	5	5
AXF + CXF	C	4–5	5	5	5	5	5	5
Nil	M	4	5	5	4	5	5	5
AXF	M	4	5	5	4–5	5	5	5
AXF + CXF	M	4–5	5	5	5	5	5	5
CI Acid Blue 193								
Nil	C	3–4	5	5	4	5	5	5
AXF	C	4–5	5	5	5	5	5	5
AXF + CXF	C	4–5	5	5	5	5	5	5
Nil	M	3–4	5	5	3–4	5	5	5
AXF	M	4	5	5	4–5	5	5	5
AXF + CXF	M	4–5	5	5	5	5	5	5
CI Acid Black 194								
Nil	C	4	5	5	3–4	5	5	5
AXF	C	4–5	5	5	4–5	5	5	5
AXF + CXF	C	4–5	5	5	5	5	5	5
Nil	M	3–4	5	5	3	5	5	5
AXF	M	4	5	5	4	5	5	5
AXF + CXF	M	4–5	5	5	4–5	5	5	5

a For key see Tables 1 and 4

in terms of the change in shade that occurred during washing, the opposite was observed, in that the fastness of the 2% owf dyeings increased in the order: disulphonated dyes < monosulphonated dyes < unsulphonated dyes.

These observations can be explained in terms of the differing water solubility (or hydrophobicity) of the three types of dye. Accordingly, it is suggested that the unsulphonated (Neutrilan K) dyes displayed smallest shade change because of their lower aqueous solubility (and thus greater hydrophobicity), while the disulphonated (Neutrilan M) dyes exhibited the greatest shade change because of their greater aqueous solubility. In contrast, the hydrophobicity of the unsulphonated dyes was responsible for their high staining of the relatively hydrophobic nylon 6.6 fibre, while the high aqueous solubility of the hydrophilic disulphonated dyes was responsible for them having imparted little staining to adjacent nylon 6.6 material.

Tables 4–6 also show that, for all of the dyes used, although aftertreatment with the syntan alone enhanced the fastness of the dyeings to the ISO 105:C06/C2 wash test, aftertreatment with the syntan/cation system was more effective. In the case of most of the unsulphonated dyes, the syntan/cation aftertreatment resulted in a half point improvement in shade change and a two point improvement in staining of adjacent nylon 6.6, while a half point improvement in shade change and a 1.5 point improvement in nylon staining in the case of the disulphonated dyes were sometimes achieved.

It is also evident from Tables 4–6 that dyeings on microfibre displayed slightly lower wash fastness than identical depth dyeings on its conventional counterpart. This finding was expected and can be attributed to the greater surface area of the microfibre [1,4].

CONCLUSIONS

The differences observed in the wash fastness behaviour of the three types of dye on the conventional and microfibre nylon 6.6 fabrics can be attributed to the difference in sulphonation of the dyes.

Although aftertreatment of the dyeings using the commercial syntan alone improved the wash fastness of each of the nine dyes on both types of fibre, the sequential application of a cationic compound to the syntanned dyeings enhanced the effectiveness of the syntan in improving wash fastness.

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