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The Dyeing of an Experimental Nylon 4.6 Fibre

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ABSTRACT

The dyeing behaviour of an experimental nylon 4.6 fibre towards typical commercial nonmetallised acid and 2:1 premetallized acid dyes was investigated. In terms of dyebath exhaustion, build-up and wash fastness, the results obtained imply that the experimental fibre behaved in a manner that was to be expected of its conventional nylon 6 and 6.6 counterparts; however, the light fastness of 1/1 standard depth dyeings on the experimental fibre was found to be higher than is typically encountered for such dyes on conventional polyamide fibres.

INTRODUCTION

Since the commercial introduction of nylon fibres over 50 years ago, a considerable amount of knowledge has accrued concerning the dyeability of the two major textile representatives, nylons 6.6 and 6. Although other types of nylon are available, such as nylons 6.10 and 11, these enjoy relatively limited, mostly speciality usage. Recently, DSM developed the high temperature resistant polyamide 4.6; polytetra-methylene-adipamide (nylon 4.6) is an aliphatic polyamide that is prepared by polycondensation of 1,4-diaminobutane and adipic acid and marketed exclusively by DSM under the trade name Stanyl. Table 1 displays some typical physical characteristics of the experimental nylon 4.6 fibre used in this work and those of nylons 6 and 6.6. Although nylon 4.6 is more hydrophilic than either nylon 6.6 or 6, the fibre displays greater hydrothermal stability (Table 1) owing to its greater crystallinity.

Polyamide 4.6 is currently commercially used in many engineering plastics applications such as airbags, abrasion resistant fabrics, sewing

TABLE 1
Typical Physical Properties of Nylon Fibres[1]

	Nylon 4.6	*Nylon 6.6*	*Nylon 6*
Melting point (°C)	283	258	216
Moisture content (%) at 65% RH	4·5–5·0	3·5–4·0	4·0–4·5
T_g at 65% RH (°C)	82	74	60
Boiling water shrinkage (%) (15 min; 100°C)	3·4	5·3	10
Hot air shrinkage (%) (15 min; 160°C)	0·9	3·0	7·0
Density (g dm^{-3})	1·17	1·14	1·13

thread, tyre cord and mechanical rubber goods. For the commercialisation of Stanyl fibres and yarns, DSM is working closely with yarn spinners; carpet and hosiery applications are being evaluated. The purpose of the work described was to examine the dyeing behaviour of an experimental form of nylon 4.6 fibre using both nonmetallised acid and premetallised acid dyes.

EXPERIMENTAL

Materials

Fibre
Knitted experimental nylon 4.6 fabric (7.75 dTex per filament) was used; the fibre had an amino end group content of 29 meq kg^{-1} and a carboxyl end group content of 33 meq kg^{-1}.

Dyes
Each of the six nonmetallised acid dyes and three premetallised acid dyes used (Table 2) was generously supplied by Crompton and Knowles Ltd; the dyes were commercial samples that were not purified prior to use.

Chemicals and auxiliaries
Both Asta Agent B and Intrasol CLW, which were used as levelling agents for the Tertroxyl and the Neutrilan S dyes, respectively, were kindly provided by Crompton and Knowles. Lenetol B Conc., which was used to scour the dyeings, and Matexil FA-SNX, which was used to aftertreat the dyed nylon samples, were each generously supplied by ICI Surfactants. All other reagents were of general purpose grade, obtained from either Aldrich or BDH.

TABLE 2
Dyes Used

Commercial name	*CI generic name*	λ_{max} *(nm)*
Tertroxyl Light Blue R	CI Acid Blue 41	598
Tertroxyl Fast Yellow 2R	CI Acid Yellow 42	410
Tertroxyl Fast Red GN	CI Acid Red 337	489
Nylanthrene Blue RNL	CI Acid Blue 129	622
Nylanthrene Yellow FLW	CI Acid Yellow 159	355
Nylanthrene Rubine 5BLF	CI Acid Red 299	518
Neutrilan Navy S-NL	CI Acid Blue 348	591
Neutrilan Yellow S-2G	None ascribed	433
Neutrilan Red S-GN	CI Acid Red 359	492

Procedures

Scouring of knitted fabric

The nylon 4.6 fabric was scoured and bleached, using conditions which, owing to commercial confidentiality, cannot be disclosed at this time.

Dyeing

All dyeings were carried out in sealed stainless steel dyepots of 300 cm^3 capacity housed in a Zeltex Polycolor laboratory dyeing machine. Each of the nine dyes (Table 2) was applied to a wetted out (distilled water) nylon sample (3 g) at concentrations of 1, 2 and 4% omf at 98, 115 and 120°C using a 50:1 liquor-to-goods ratio; also, 1/1 standard depth dyeings of each of the nine dyes were carried out at 98°C. The dyeing methods employed for the three types of acid dye are shown in Fig. 1. At the end of dyeing, the dyed fabric was removed from the exhausted dyebath and scoured in a solution containing 2 dm^{-3} Lenetol B Conc. for 15 min at 80°C; the scoured sample was then rinsed thoroughly in running tap water and allowed to dry in the open air.

Measurement of dyebath exhaustion

At the end of dyeing, the dyed sample was removed from the exhausted dyebath and the dyebath allowed to cool to room temperature. A sample of the cool, exhausted dyebath was removed and diluted using distilled water; the absorbance of the cold, diluted dye solution was then measured at the λ_{max} of the dye (Table 2) using a Pye-Unicam SP800 UV/visible spectrophotometer, employing 1 cm pathlength cells and water as reference solvent. By reference to the appropriate extinction coefficient of

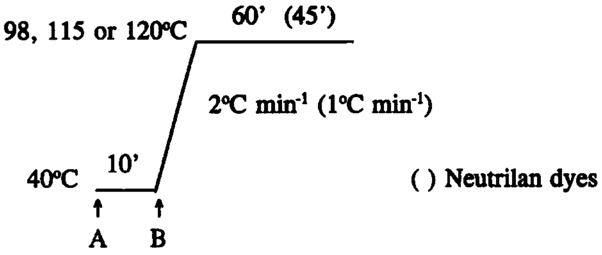

Fig. 1. Dyeing methods used.

Tertroxyl dyes		
A	$(NH_4)_2SO_4$	2% omf for 1% and 2% omf dye
	CH_3COOH	to pH 5·5 for 4% omf dye
	Asta Agent B	1% omf (used in preliminary trials only)
B	Dye	
Nylanthrene dyes		
A	$(NH_4)_2SO_4$	2 gl^{-1} for 1% and 2% omf dye
	monosodium phosphate	1 gl^{-1} for 4% omf dye
	Asta Agent B	1·5% omf (used in preliminary trials only)
B	Dye	
Neutrilan dyes		
A	CH_3COONH_4	4% omf
	CH_3COOH	to pH 6·5 for 1% omf dye, pH 6 for 2% omf dye and pH 5 for 4% omf dye
	Intrasol CLW	1% omf
B	Dye	

the dye, which was obtained from a separate calibration plot, the concentration of the dye in the exhausted dyebath was calculated, from which the corresponding percentage dyebath exhaustion was determined.

Aftertreatment of dyeings

Aftertreatment was carried out in sealed stainless steel dyepots of 300 cm^3 capacity housed in a Zeltex Polycolor laboratory dyeing machine. A sample of nylon 4.6, which had been dyed to 1/1 standard depth and then scoured and rinsed, was treated in an aqueous solution containing 2% omf Matexil FA-SNX at pH 5 (adjusted using acetic acid) for 30 min at 80°C using a 50:1 liquor-to-goods ratio; the aftertreated sample was then rinsed thoroughly in tap water and allowed to dry in the open air.

Wash fastness assessment

Samples of nylon 4.6 fabric, which had been dyed to 1/1 standard depth and then scoured and rinsed, as well as 1/1 standard depth samples which had been aftertreated with Matexil FA-SNX, were subjected to the ISO CO6/C2 wash fastness test; the extent of colour loss from the original dyed sample, as well as the degree of staining of adjacent fabrics, was assessed using the appropriate grey scales.[2]

Light fastness assessment

Samples of nylon 4.6 fabric, which had been dyed to 1/1 standard depth and then scoured and rinsed, as well as 1/1 standard depth samples which had been aftertreated with Matexil FA-SNX, were submitted to the BO2 light fastness test.[2]

Colour measurement

The reflectance values of the dyeings were measured using a Macbeth MS 2020 spectrophotometer interfaced to a Digital PC100 personal computer, under illuminant D_{65} using a 10° standard observer with specular component excluded and UV component included, from which the corresponding CIE$L^*a^*b^*$ and h° coordinates were calculated at the appropriate λ_{max} for each dye. Each fabric sample was folded twice so as to realise a total of four thicknesses of fabric.

RESULTS AND DISCUSSION

In order to obtain fundamental knowledge of the dyeability of Stanyl polyamide 4.6, the work described was carried out using types of dye that are typically used on polyamide fibres. In this context, as acid dyes are the most widely used dyes on polyamide fibres, it was decided to employ three types of commercially available acid dye. Consequently, the Tertroxyl, Nylanthrene and Neutrilan ranges of dyes were chosen as typical representatives of the Groups 2 and 3 nonmetallised acid dyes[3] and 1:2 monosulphonated metal–complex dyes, respectively; the three examples of each dye range used were arbitrarily selected. The dyeing methods employed for each range of dye were as recommended for the application of the dyes to conventional (i.e. nylon 6 and 6.6) polyamide fibres.[4–6]

In order to improve the ability of acid dyes to overcome physical irregularities in polyamide fibres, elevated dyeing temperatures and/or proprietary levelling agents are commonly employed;[7] as the nylon 4.6 fabric had not previously been dyed using acid dyes, an initial investigation was made of the propensity of the fabric to barré dyeing. In the context of the three dye ranges used in the work, the use of Asta Agent B is recommended for improving the migration characteristics of dyes within both the Tertroxyl[4] and Nylanthrene[5] ranges, whilst Intrasol CLW is recommended for use with the Neutrilan range of dyes.[6] A series of dyeings (1, 2 and 4% omf) was carried out at 98, 115 and 120°C, using each of the nine dyes under consideration, in both the absence and presence of the two respective levelling agents, and the extent of barriness of the dyeings was visually assessed. It was found that all dyeings were level and, also, that those secured using the Tertroxyl and Nylanthrene dyes were devoid of barriness when dyeing had been carried out in both the absence and the presence of levelling agents, the addition of Asta Agent B having served only to reduce the colour strength of the dyeings; consequently, all further dyeings involving both the Tertroxyl and Nylanthrene dyes were undertaken in the absence of levelling agent. In the case of the Neutrilan dyes, no evidence of barriness was observed for dyeings which had been carried out in either the presence or absence of the levelling agent; however, as the presence of Intrasol CLW was found to improve slightly the colour yield of the dyeings, all further dyeings using the Neutrilan dyes were carried out in the presence of Intrasol CLW. These preliminary dyeings also revealed that temperature had no effect on the levelness of dyeing, insofar as barriness was not observed for any of the dyeings at each of the three temperatures used.

Although the purpose of this work was to evaluate the dyeing behaviour of the experimental nylon 4.6 substrate towards typical commercial acid dyes, rather than to study the dyeing and fastness characteristics of the individual dyes used, an investigation was made of the exhaustion and build-up characteristics of the nine dyes under consideration on the substrate. It is emphasised that, as the nine dyes used were arbitrarily selected, the results obtained in this context can be interpreted as reflecting only the dyeing behaviour of the fibre towards typical acid dyes, and cannot be considered to represent the relative compatibility of the dyes within each of the three commercial dye ranges employed.

Figures 2 to 4 show that, as expected, for each of the three Tertroxyl dyes used, dyebath exhaustion decreased with increasing concentration of dye applied from 1 to 4% omf. Also, it is evident that the three dyes varied slightly in their temperature dependence insofar as, whilst the degree of dyebath exhaustion achieved for CI Acid Blue 41 was lower at 120°C than at both 98 and 115°C, that of CI Acid Red 337 was virtually independent of temperature and that of CI Acid Yellow 42 increased with increasing application temperature. Furthermore, the extent of exhaustion of CI Acid Blue 41 was generally lower, at each concentration of dye and at each temperature employed, than that of its two counterparts. The lower extent of dyebath exhaustion recorded for CI Acid Blue 41 was emphasised by the finding (Figs 5–7) that the colour strength of the

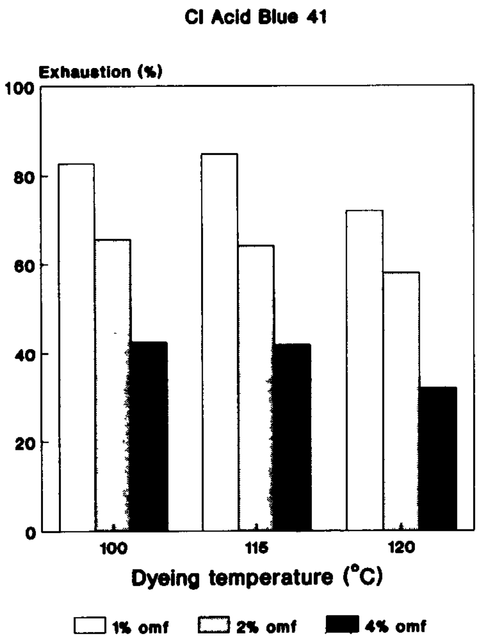

Fig. 2. Effect of temperature on dyebath exhaustion.

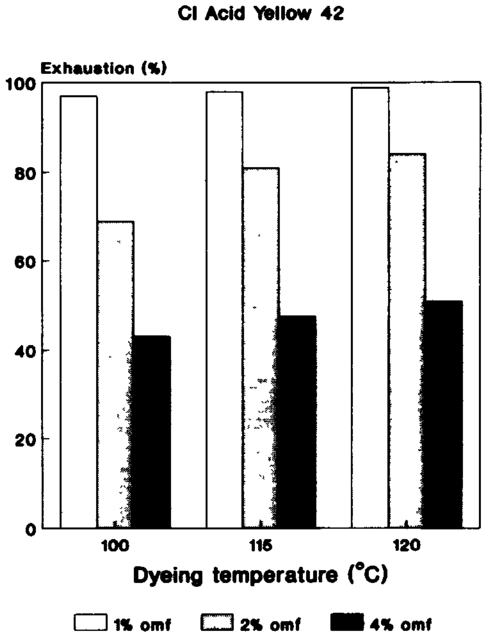

Fig. 3. Effect of temperature on dyebath exhaustion.

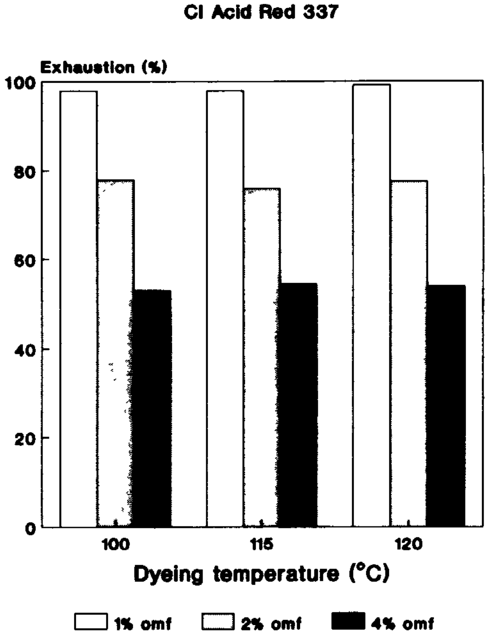

Fig. 4. Effect of temperature on dyebath exhaustion.

dyeings secured using CI Acid Blue 41 were lower, at each concentration of dye and at each temperature employed, than those achieved using the two other Tertroxyl dyes. CI Acid Blue 41 further exhibited different behaviour to its two counterparts in terms of the effects of both dye concentration and temperature on colour yield; the build-up of CI Acid Blue 41 increased with increasing concentration of dye applied and also with increasing application temperature, whilst that of the two other dyes was greatest when dyeing had been carried out at 115°C.

Figures 8 to 10 show that, as found for the Tertroxyl dyes (Figs 2–4), for each of the three Nylanthrene dyes used, dyebath exhaustion decreased with increasing concentration of dye applied. Also, the three dyes varied in their temperature dependence in that the degree of dyebath exhaustion achieved for CI Acid Blue 129 and CI Acid Yellow 159 was highest at 98°C and lowest for 115°C, whereas for CI Acid Red 299, dyebath exhaustion was lower at 98°C than at the other two temperatures used. Furthermore, the extent of exhaustion of CI Acid Blue 129 was markedly lower, especially in the cases of the 2 and 4% omf dyeings, at each temperature employed, than that of its two counterparts. However, the lower extent of dyebath exhaustion recorded for CI Acid Blue 129 was not reflected in the colour strength of the dyeings (Figs 11–13), insofar as those secured for CI Acid Blue 129 were similar to those obtained for the other two dyes. CI Acid Blue 129 did exhibit different behaviour to its two counterparts in terms of the effects of both dye concentration and temperature on colour yield; the build-up of CI Acid Blue 129 increased with increasing concentration of dye applied and also with increasing application temperature (Fig. 11), whilst that of the two other dyes was markedly less temperature- and dye concentration-dependent (Figs 12 and 13).

The results obtained for exhaustion of the 2:1 metal–complex Neutrilan dyes revealed (Figs 14–16) that, with the exception of CI Acid Blue 348, dyebath exhaustion decreased with increasing dye concentration at each of the three temperatures used. Generally, for each of the three dyes employed, dyebath exhaustion was lowest at 115°C for each concentration of dye applied; furthermore, dyeing at 120°C resulted in the highest dyebath exhaustion. Figures 17 to 19 show that the colour strength of the dyeings increased with increasing amount of dye applied and with increasing temperature of application; also, the build-up characteristics of each dye were similar.

Tables 3 to 5 show the colorimetric parameters for each of the nine dyes under consideration, from which it is evident that each dye exhibited on-tone build-up. The findings displayed in Figs 2 to 19 and Tables 3 to 5 demonstrate that, in terms of dyebath exhaustion and build-up,

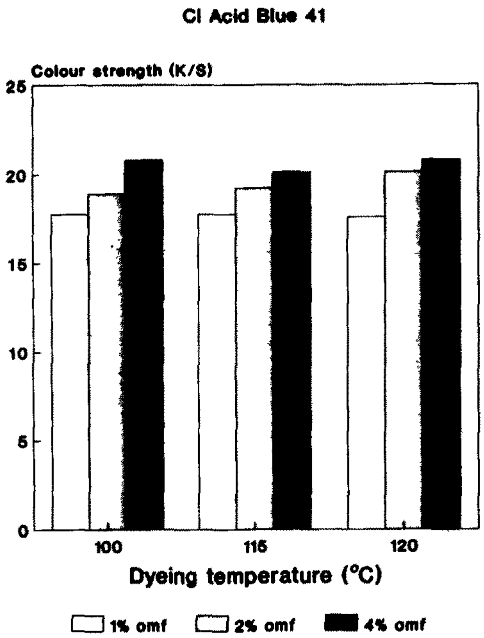

Fig. 5. Effect of temperature on colour strength.

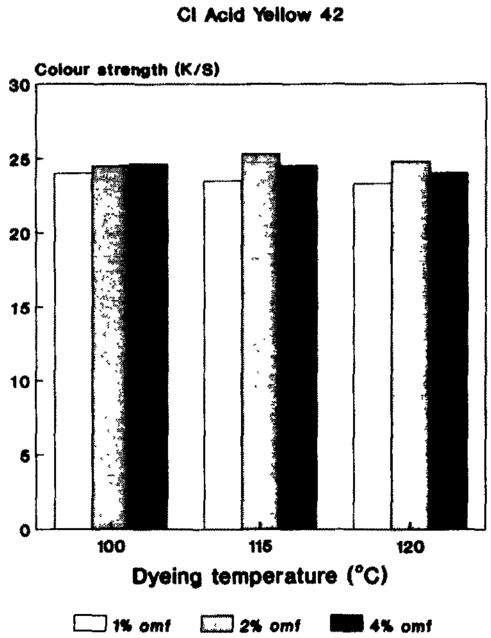

Fig. 6. Effect of temperature on colour strength.

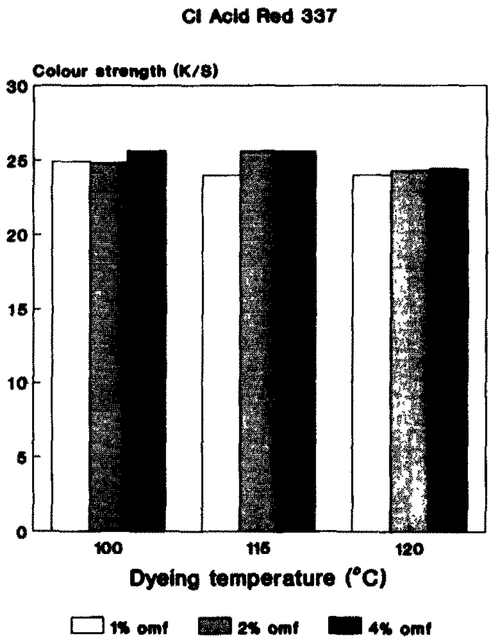

Fig. 7. Effect of temperature on colour strength.

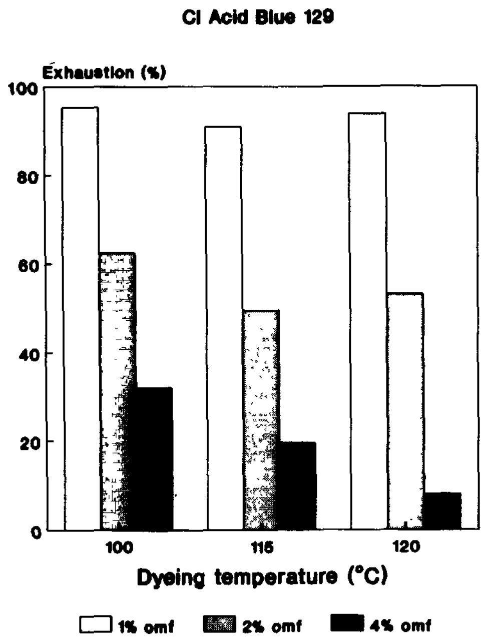

Fig. 8. Effect of temperature on dyebath exhaustion.

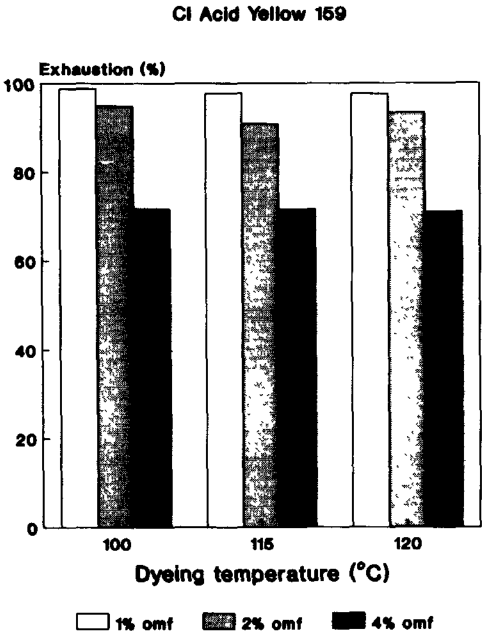

Fig. 9. Effect of temperature on dyebath exhaustion.

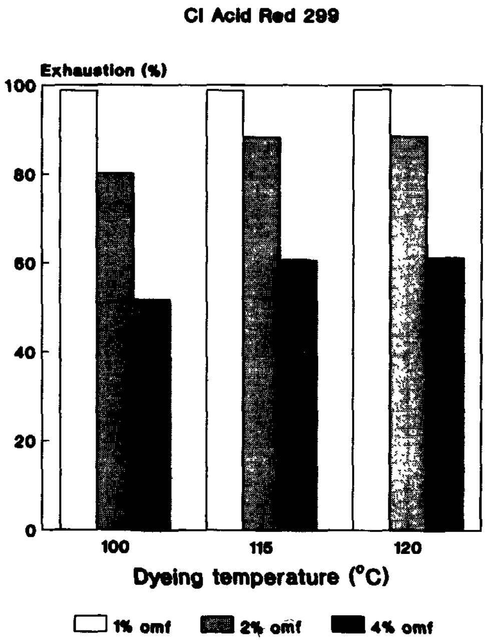

Fig. 10. Effect of temperature on dyebath exhaustion.

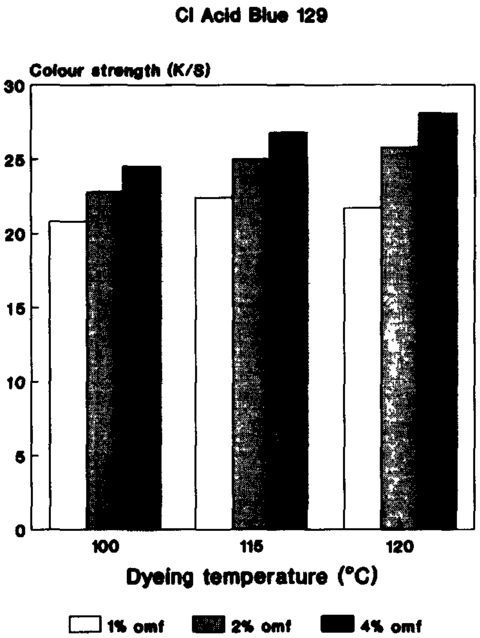

Fig. 11. Effect of temperature on colour strength.

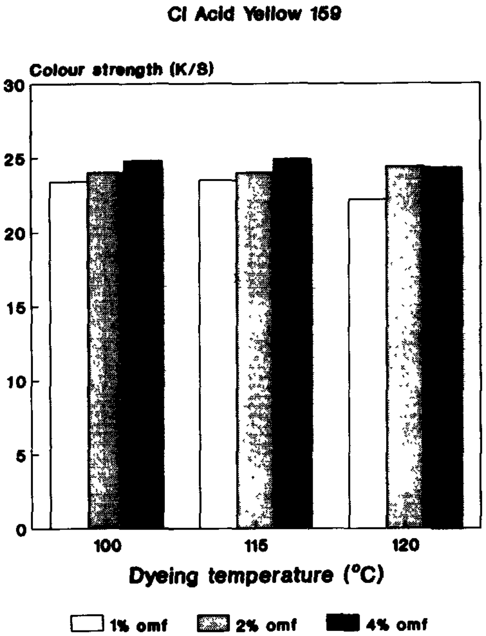

Fig. 12. Effect of temperature on colour strength.

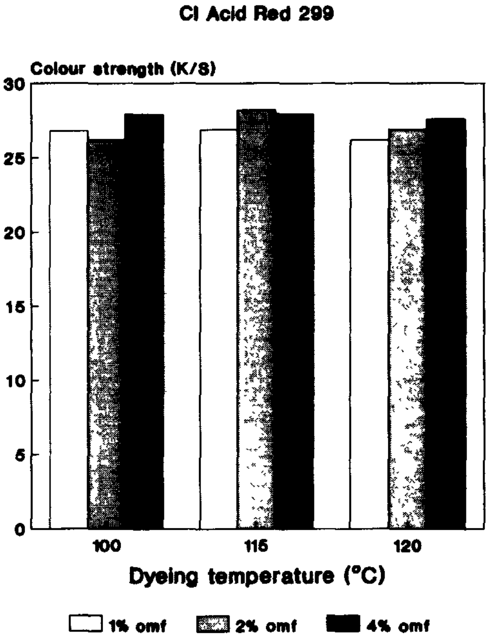

Fig. 13. Effect of temperature on colour strength.

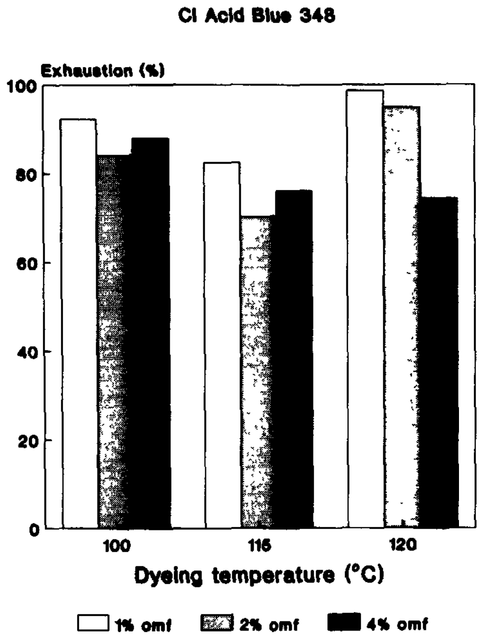

Fig. 14. Effect of temperature on dyebath exhaustion.

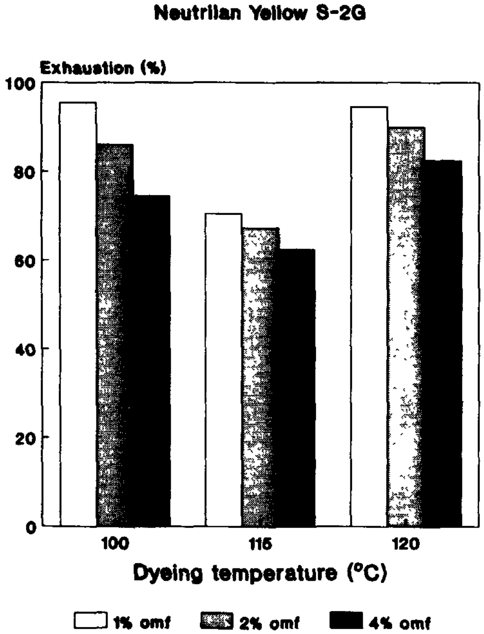

Fig. 15. Effect of temperature on dyebath exhaustion.

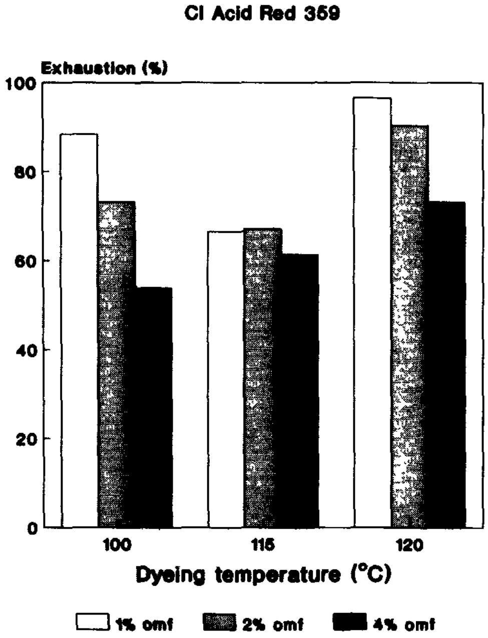

Fig. 16. Effect of temperature on dyebath exhaustion.

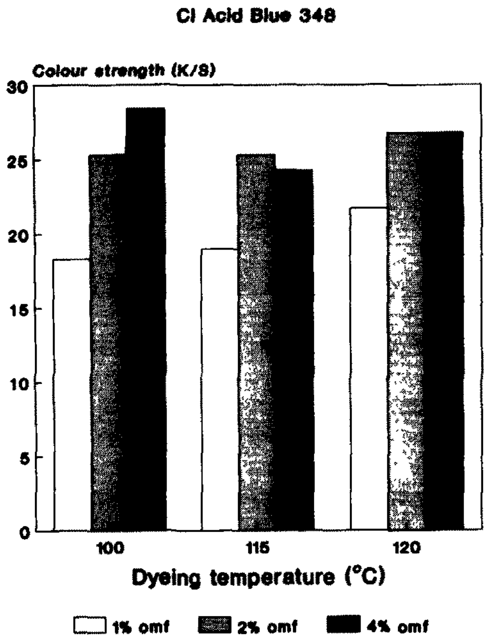

Fig. 17. Effect of temperature on colour strength.

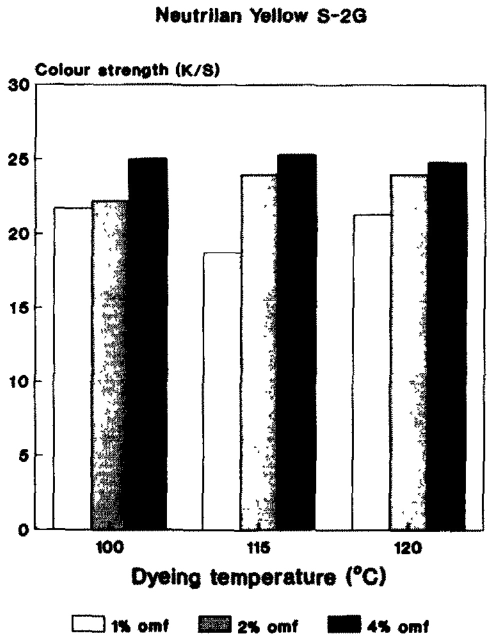

Fig. 18. Effect of temperature on colour strength.

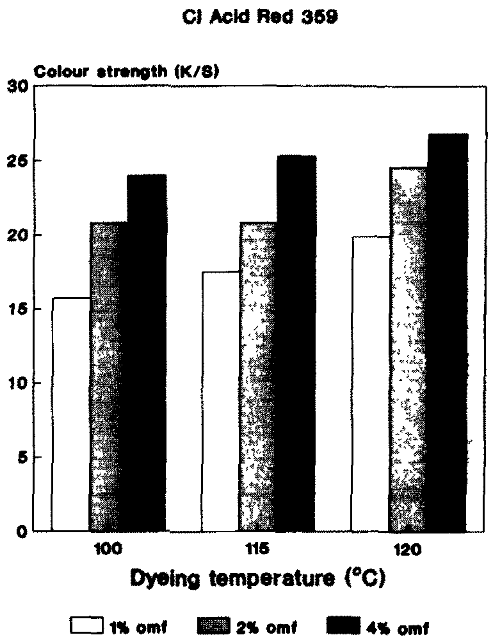

Fig. 19. Effect of temperature on colour strength.

TABLE 3
Colorimetric Data for Tertroxyl Dyeings

Dye	*Dyeing temp. (°C)*	*Dye applied (omf)*	L*	a*	b*	C*	h^{0}
CI Acid Blue 41	98	1	30·5	−0·1	−34·2	34·2	269·8
		2	27·8	1·3	−33·3	33·3	272·2
		4	26·9	1·7	−32·6	33·7	273·1
	115	1	30·1	0·2	−34·5	34·5	270·4
		2	28·6	1·2	−34·1	34·1	272·1
		4	27·4	1·4	−32·5	32·6	272·4
	120	1	30·2	−0·1	−34·2	34·2	269·8
		2	27·6	1·1	−33·0	33·0	271·9
		4	26·6	1·9	−32·2	32·2	273·4
CI Acid Yellow 42	98	1	66·6	18·3	82·7	84·7	77·4
		2	62·8	18·1	77·9	79·9	76·9
		4	62·6	20·7	78·1	80·9	75·2
	115	1	66·9	21·1	83·7	86·4	75·9
		2	64·2	23·0	81·7	84·9	74·3
		4	64·6	26·3	83·1	87·2	72·5
	120	1	66·9	20·9	83·2	85·8	75·9
		2	62·2	19·8	78·1	80·5	75·8
		4	62·7	23·6	78·9	82·4	73·3
CI Acid Red 337	98	1	36·2	53·3	23·3	25·1	58·9
		2	34·5	51·3	25·5	57·3	26·5
		4	32·5	48·9	25·4	55·1	27·5
	115	1	35·8	51·6	23·7	56·8	24·6
		2	33·7	49·9	24·9	55·7	26·5
		4	31·9	47·6	24·9	53·7	27·6
	120	1	36·2	52·4	23·7	43·5	24·3
		2	34·8	50·8	24·4	56·3	25·7
		4	33·1	48·4	24·5	54·2	26·6

TABLE 4
Colorimetric Data for Nylanthrene Dyeings

Dye	*Dyeing temp. (°C)*	*Dye applied (omf)*	L*	a*	b*	C*	h^0
CI Acid Blue 129	98	1	29·0	13·3	−46·0	47·9	286·1
		2	26·6	15·8	−45·6	48·2	289·1
		4	23·9	17·7	−44·1	47·5	291·8
	115	1	27·8	14·8	−46·3	46·6	287·7
		2	24·7	16·9	−44·6	47·7	290·7
		4	22·2	17·2	−41·6	41·8	292·4
	120	1	27·9	15·3	−46·5	48·9	288·2
		2	24·2	17·3	−44·5	47·7	291·2
		4	21·9	17·9	−42·2	45·8	292·8
CI Acid Yellow 159	98	1	61·0	29·5	62·7	69·4	64·8
		2	57·6	36·4	61·1	71·1	59·3
		4	53·5	41·4	56·9	70·4	54·0
	115	1	59·1	33·4	61·7	70·2	61·6
		2	52·6	33·5	54·4	63·8	58·4
		4	50·5	40·2	52·3	66·0	52·5
	120	1	59·9	31·1	61·7	69·2	63·1
		2	54·9	37·9	58·3	69·6	56·9
		4	51·5	41·9	53·9	68·2	52·3
CI Acid Red 299	98	1	16·5	15·5	−8·2	17·6	332·1
		2	15·9	11·9	−7·3	13·9	328·5
		4	14·9	10·0	−7·1	12·3	324·5
	115	1	16·3	15·2	−7·8	17·1	332·8
		2	15·1	11·3	−7·1	13·4	327·8
		4	14·9	9·6	−6·8	11·8	324·6
	120	1	16·8	16·1	−7·9	17·9	333·8
		2	15·6	11·4	−7·3	13·5	327·3
		4	15·0	9·6	−6·9	11·8	324·3

TABLE 5
Colorimetric Data for Neutrilan Dyeings

Dye	*Dyeing temp. (°C)*	*Dye applied (omf)*	L*	a*	b*	C*	h^0
CI Acid Blue 348	98	1	22·9	−2·1	−11·6	11·6	252·3
		2	17·3	−0·3	−7·9	7·92	267·8
		4	14·7	0·3	−2·6	−83·5	276·6
	115	1	22·2	−1·8	−11·4	11·5	261·0
		2	17·4	−0·4	−7·7	7·7	267·0
		4	15·9	0·4	−3·4	3·4	276·7
	120	1	20·6	−1·6	−10·9	11·1	261·5
		2	16·2	−0·09	−6·8	6·8	269·2
		4	15·2	0·4	−3·7	3·7	276·2
Neutrilan Yellow S2G	98	1	57·3	19·9	66·5	69·4	73·3
		2	55·1	22·1	64·8	68·4	71·2
		4	50·0	24·9	58·9	64·0	67·1
	115	1	59·0	16·5	65·9	67·9	75·9
		2	54·7	22·6	65·9	68·7	70·8
		4	49·2	24·7	57·7	62·8	66·9
	120	1	56·5	20·2	65·4	68·5	72·8
		2	52·2	24·1	61·5	66·0	68·6
		4	47·2	24·7	54·2	59·6	65·5
CI Acid Red 359	98	1	36·7	43·1	18·3	46·8	23·0
		2	32·8	41·6	19·2	45·8	24·8
		4	29·3	38·4	18·8	42·8	26·1
	115	1	34·2	39·4	16·0	38·8	22·1
		2	32·9	42·4	20·3	47·0	25·5
		4	28·4	38·3	19·4	42·9	26·9
	120	1	33·9	42·4	18·9	46·5	24·1
		2	29·6	39·5	19·2	43·9	25·9
		4	25·9	35·4	17·7	39·5	26·5

the behaviour of the experimental nylon 4.6 fibre was typical of that to be expected of its conventional polyamide counterparts, nylons 6.6 and 6.

The wash fastness results obtained for the untreated 1/1 standard depth dyeings of each dye (Table 6) can be considered as being typical for such acid dyes on nylons 6 and 6.6; the meritorious effect of the syntan aftertreatment on the wash fastness of the dyeings is clearly evident from the results shown in Table 6. The light fastness of the dyeings (Table 6) were, with the exceptions of CI Acid Blue 41 and CI Acid Red 337, higher than is commonly encountered for such acid dyes on both untreated and syntanned dyed nylons 6 and 6.6.

TABLE 6

Fastness of 1/1 Standard Depth Dyeings

Dye	*ISOC06*			*BO2*
	E	*C*	*N*	
CI Acid Blue 41	4–5	3–4	4	6
	4–5[a]	4–5[a]	4–5[a]	5–6[a]
CI Acid Yellow 42	5	4	4–5	8
	4–5[a]	4–5[a]	4–5[a]	8[a]
CI Acid Red 337	4	3	2	6
	5[a]	4[a]	3–4[a]	5–6[a]
CI Acid Blue 129	5	4	2–3	8
	4–5[a]	4–5[a]	3–4[a]	8[a]
CI Acid Yellow 159	5	2–3	2	8
	4–5[a]	3–4[a]	3–4[a]	8[a]
CI Acid Red 229	4–5	2–3	2	8
	4–5[a]	3[a]	3[a]	7[a]
CI Acid Blue 348	4–5	4–5	4	8
	5[a]	5[a]	4–5[a]	8[a]
Neutrilan Yellow S-2G	4–5	4–5	4–5	8
	5[a]	5[a]	4–5[a]	8[a]
CI Acid Red 359	4–5	4–5	4	8
	5[a]	4–5[a]	4–5[a]	8[a]

E: Change in shade; C: staining of adjacent cotton.
N: Staining of adjacent nylon 4.6.
[a] After syntan treatment.

CONCLUSIONS

The behaviour of the experimental nylon 4.6 fibre, in terms of dyebath exhaustion, build-up and wash fastness, towards the nine commercial acid dyes employed can be considered as being very similar to that of its conventional nylons 6 and 6.6 counterparts; however, the light fastness of the standard depth dyeings of seven of the dyes under consideration was higher than is typically encountered for such dyes on conventional nylon fibres.

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