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Dyes and Pigments 45 (2000) 65–74

DYES and PIGMENTS

The dyeing of nylon 6,6 with sulphur dyes

Stephen M. Burkinshaw [a,*], Samit N. Chevli [a], David J. Marfell [b]

[a] *School of Textile Industries, The University, Leeds LS2 9JT, UK*
[b] *Du Pont Nylon (UK), Brockworth, Gloucester GL3 4HP, UK*

Received 12 November 1999; accepted 13 December 1999

Abstract

When nylon 6,6 was dyed with five sulphur dyes using two reduction systems, dyeings on nylon 6,6 were of comparable depth of shade to dyeings produced on cotton. The dyeings on nylon 6,6 displayed very good fastness to repeated washing and high resistance to oxygen bleach fading. The fastness of the dyeings to these agencies was enhanced by means of an aftertreatment with a commercial cationic fixing agent. Both the dry and wet rub fastness of the dyeings was very good but the dyeings displayed poor fastness to light. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Nylon 6,6; Sulphur dyes; Repeated wash fastness; UKTO test

1. Introduction

Nylon 6,6 can be dyed using many types of dye, namely:

- anionic, acid (including pre-metallised acid), mordant, direct and reactive classes;
- cationic, basic dyes used predominantly on modified (cationic dyeable) nylon 6,6;
- nonionic, disperse and vat classes.

The merits and demerits of using these dye types on nylon 6,6 have been well documented elsewhere [1–3]. It is widely held that only one of the dye types, videlicet the pre-metallised acid dyes, can furnish deep shades on nylon 6,6 of good/very good fastness to light and to wet and washing treatments. However, the high level of wet fastness displayed often is secured only by recourse to an aftertreatment with a synthetic tanning agent (syntan); in addition, the use of pre-metallised acid dyes has attracted environmental interest in recent years.

It was against this background that a decision was made to look at the feasibility of dyeing nylon 6,6 with sulphur dyes in deep shades using an exhaust (immersion) dyeing method.

Sulphur dyes are one of the most popular dye classes for cellulosic fibres and their blends, being widely used to produce inexpensive, medium to heavy depths. It is considered that sulphur dyes constitute the largest class of dye used in terms of quantity consumed globally and that Sulphur Black 1, in all its forms (C.I. Sulphur Black 1, C.I. Solubilised Sulphur Black 1 and C.I. Leuco Sulphur Black 1), is the most important black dye in the world [4]. Typically, sulphur dyes possess moderate to good fastness to light and wet treatments on cellulosic substrates but are less resistant

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* Corresponding author. Tel.: +44-113-233-3722; fax: +44-113-233-3704.
E-mail address: s.m.burkinshaw@leeds.ac.uk (S.M. Burkinshaw).

PII: S0143-7208(00)00003-6

to washing with detergent/perborate formulations that are now common in domestic washing powders [4,5]. The so-called *sulphur vat dyes* or *sulphurized vat dyes*, which are either sulfur or vat dyes that often are applied to cellulosic fibres using a different reduction system to that of sulphur dyes, display higher wet fastness and greater resistance to bleaching than traditional sulphur dyes on cellulosic fibres [4,5].

In the context of nylon 6,6, sulphur dyes are used on blend materials, notably nylon/cellulosic blends [6–8] and recent patent literature suggests continuing commercial interest in the application of sulphur and sulphur vat dyes to nylon blend substrates [9–13]. In contrast, there appears to have been little, if any, reference in the open literature to the use of the dyes on 100% nylon 6,6 since the 1939 study of the dyeability of the fibre which concluded that sulphur dyes had very little substantivity for nylon fibre and would not hold much commercial importance for the dyer [14].

This paper describes the dyeing of nylon 6,6 with sulphur dyes in deep shades using an exhaust (immersion) dyeing method and an investigation of the fastness properties of the dyeings. In addition, the effects on dyeability of a traditional, commercial, sulphide-based reduction system and a non sulphide-based reduction system are discussed.

2. Experimental

2.1. Materials

Scoured, knitted, nylon 6,6 fabric (78f68, 1.15 dtex per filament) was kindly supplied by Du Pont UK; scoured, woven, fluorescent brightener-free cotton fabric was obtained from Whaleys.

Five sulphur dyes were chosen, arbitrarily; these are listed in Table 1. Leucad 71, a commercially available, aqueous solution of sodium sulfide and sodium sulfhydrate, was kindly supplied by J Robinson Ltd. A commercial sample of the cationic fixing agent Solfix E was obtained from Ciba-Geigy and a commercial sample of the non-ionic surfactant Lanapex R was provided by Uniqema. All other chemicals used were laboratory grade reagents obtained from Aldrich.

2.2. Procedures

Four dyeing methods were used (Table 2) which are designated methods 1, 2, 3 and 4. In each case, a 10:1 liquor ratio was used and dyeing was carried out in 300 cm^3 capacity sealed, stainless steel dyepots, housed in a Roaches Pyrotec S infrared dyeing machine.

2.2.1. Method 1

This was the standard method recommended by J Robinson Ltd for the application of the Sulphosol range of C.I. Solubilised Sulphur dyes to cotton. In this method, pre-wetted samples of cotton were dyed using Leucad 71 as reducing agent (Fig. 1); at the end of dyeing, the samples were oxidised using the procedure described below.

2.2.2. Method 2

Nylon 6,6 was dyed following the method shown in Fig. 1 using Leucad 71 as reduction system (Fig. 1); at the end of dyeing, the samples were oxidised using the procedure described below.

2.2.3. Method 3

Nylon 6,6 was dyed following the method shown in Fig. 2 using glucose/NaOH as reduction

Table 1
Sulphur dyes used

Commerical name	C.I. generic name	Manufacturer
Sulphosol Yellow SR	Solubilised Sulphur Yellow 23	J Robinson
Sulphosol Green SBCF 125%	Solubilised Sulphur Green 2	J Robinson
Sulphosol Bordeaux SB	Solubilised Sulphur Red 6	J Robinson
Hydrosol Blue R	Solubilised Sulphur Blue 7	J Robinson
Immedial Indocarbon Black CL	Sulphur Black 11	DyStar

Table 2
Dyeing methods

Method	Fibre type	Process	Reducing system
1	Cotton	Dyeing only	Leucad 71
2	Nylon 6,6	Dyeing only	Leucad 71
3	Nylon 6,6	Dyeing only	Glucose/NaOH
4	Nylon 6,6	Combined scouring and dyeing	Glucose/NaOH

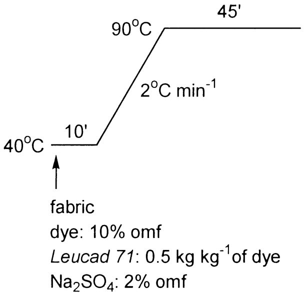

Fig. 1. Methods 1 and 2.

system; at the end of dyeing, the samples were oxidised using the procedure described below.

2.2.4. Method 4

This combined scouring and dyeing method (Fig. 3) utilised a non-ionic surfactant (Lanapex R) and glucose/NaOH as reduction system. At the end of dyeing, the samples were oxidised using the procedure described below.

2.2.5. Oxidation

At the end of dyeing, the samples were rinsed for 5 min in cold water and then for 5 min in hot (60°C) water and then oxidised, using a liquor ratio of 50:1, at 60°C in a bath containing 2 gl^{-1} 35% H_2O_2 at pH 4.5, for 15 min. At the end of oxidation, the samples were rinsed in running cold water for 5 min and allowed to dry in the open air.

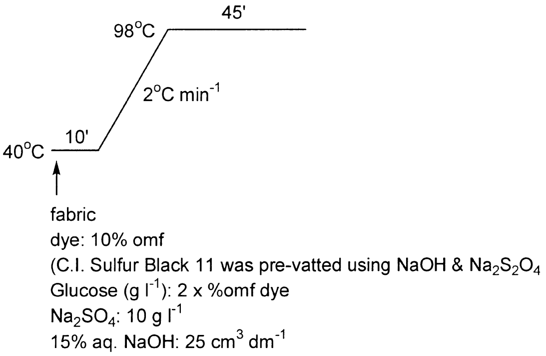

Fig. 2. Method 3.

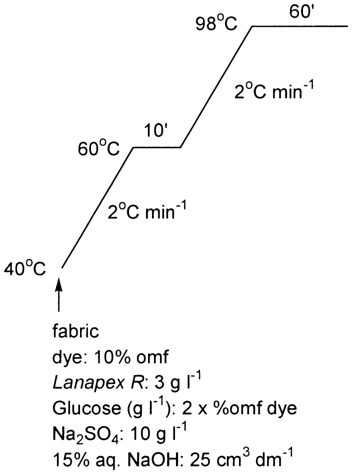

Fig. 3. Method 4.

2.2.6. Aftertreatment with cationic fixing agent

The oxidised, sulphur dyed samples of cotton and nylon 6,6 were aftertreated with Solfix E in an attempt to improve the wash fastness of the dyeings. Aftertreatment was carried out using a liquor ratio of 20:1 in 300 cm^3 capacity, sealed stainless steel dyepots housed in a Roaches Pyrotec S infrared dyeing machine following the method shown in Fig. 4. At the end of aftertreatment, the dyed samples were rinsed in running cold water for 5 min and allowed to dry in the open air.

2.2.7. Wash-fastness

The dyed fabric was subjected to five consecutive ISO CO6/C2 [15] wash tests; at the end of each wash test, the washed sample was rinsed thoroughly in tap water but was not dried. A fresh sample of SDC multifibre strip was used to assess the extent of staining for each of the five wash tests. The extent of the staining of the adjacent multifibre strip samples was expressed in the appropriate staining grey scale whereas the change

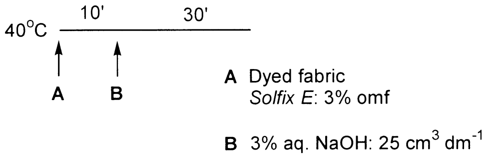

Fig. 4. Aftertreatment using commerical cationic fixing agent.

in shade of the sample after washing was expressed in Δ*E* CMC (2,1) units.

2.2.8. *UKTO test*

Dyeings were subjected to the UKTO [16] test at 60°C and the change in shade reported in Δ*E* CMC (2,1) units.

2.2.9. *Rub fastness*

Sulphur dyed samples were subjected to the ISO X12 test method (15).

2.2.10. *Light fastness*

The fastness of the dyeings to light was determined using the ISO B02 method (15).

2.2.11. *Colour measurement*

All measurements were carried out using an X-rite spectrophotometer interfaced to a PC using D_{65} illumination, 10° standard observer with specular component excluded and UV component included. Each fabric was folded once to give two thickness and an average of four readings was taken each time.

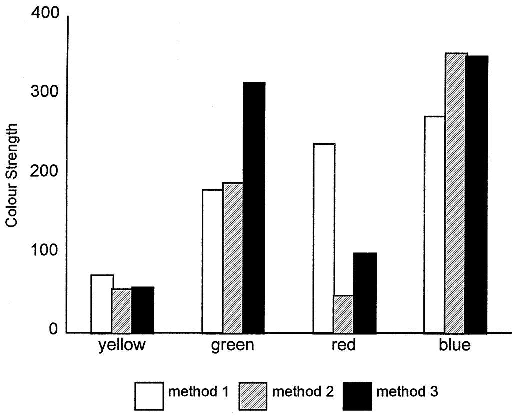

Fig. 5. Colour yield achieved using dyeing methods 1–3.

3. Results and discussion

Fig. 5 shows the colour yield (f_k values) achieved using dyeing methods 1–3. It is evident that in the case of cotton fabric which had been dyed using method 1 (the dye maker's recommended dyeing method that used the commercial, sodium sulfide/sodium sulfhydrate reduction system, Leucad 71), the colour strength achieved for the four dyes used varied from around 75 to 275 f_k units. Fig. 5 also reveals that when the same, traditional, sulfide-based dyeing method for cotton was used to apply the dyes to nylon 6,6 fabric (method 2), the colour strength of the nylon 6,6 dyeings was comparable to that achieved on cotton, with the exception of the red dye used. The use of the sulphide-free, glucose/NaOH reduction system (method 3) instead of Leucad 71 proved to be advantageous in terms of the f_k values of the yellow, green and red dyes.

Hence, the results shown in Fig. 5 clearly demonstrate that the four sulphur dyes displayed high substantivity towards nylon 6,6. This substantivity may be attributable to polar forces of attraction such as dispersion forces, ion–dipole forces, dipole–dipole interactions and hydrogen bonding; while it is possible that ion–ion forces could operate between the reduced form of the dye, namely the anionic, thiolate derivative and protonated sites in the fibre, such forces can be assumed to be negligible under the alkaline application conditions used. This particular aspect of the research work is receiving further attention.

Table 3 shows the colorimetric data obtained for cotton which had been dyed using method 1 and for nylon 6,6 fabric which had been dyed using method 2. Results are presented for the dyeings both before and after five, consecutive, ISO CO6/C2 wash tests. Evidently, there was a difference in shade obtained for the same dye on the two different types of substrate. The Δ*E* values quoted in Table 3 refer to the colour difference between a dyeing on a given substrate before and after five consecutive ISO CO6/C2 wash tests; as such, the Δ*E* values provide a measure of the extent of dye loss that occurred from the dyeing during repeated wash testing. A comparison of the Δ*E* values

Table 3
Colorimetric data obtained for dyeing methods 1 (cotton) and 2 (nylon 6,6)

Dye	Fibre	Aftertreatment	Washes	*L**	*a**	*b**	ΔE
Yellow 23	Cotton	Nil	0	61.2	12.7	55.0	6.5
		Solfix E	5	71.2	5.7	54.2	
			0	60.3	13.2	53.0	3.8
			5	65.3	9.7	56.5	
	Nylon 6,6	Nil	0	68.5	10.0	59.4	3.6
			5	73.4	5.7	60.7	
		Solfix E	0	68.1	9.2	57.6	2.3
			5	71.2	6.6	58.9	
Green 2	Cotton	Nil	0	27.4	−15.7	−6.5	5.8
			5	34.2	−18.0	−10.9	
			0	27.1	−15.9	−7.4	2.5
			5	28.4	−16.5	−10.4	
	Nylon 6,6	Nil	0	30.5	−25.2	−6.5	2.1
			5	31.4	−25.7	−8.7	
		Solfix E	0	30.5	−24.8	−6.7	1.7
			5	30.8	−25.1	−8.5	
Red 6	Cotton	Nil	0	22.1	14.4	2.5	12.7
			5	37.9	20.0	3.5	
		Solfix E	0	22.6	15.8	3.7	7.3
			5	31.1	19.3	6.7	
	Nylon 6,6	Nil	0	44.0	15.5	3.4	3.5
			5	49.4	16.1	5.6	
		Solfix E	0	45.2	16.1	5.3	1.5
			5	47.6	15.7	6.0	
Blue 7	Cotton	Nil	0	18.6	2.9	−12.4	7.9
			5	22.2	7.6	−20.2	
		Solfix E	0	18.3	4.7	−14.8	2.8
			5	19.1	7.0	−17.5	
	Nylon 6,6	Nil	0	16.5	2.1	−17.3	2.9
			5	15.9	4.5	−19.7	
		Solfix E	0	16.3	2.2	−17.5	2.4
			5	16.2	4.2	−19.6	

obtained for each of the dyes on the two different substrates reveals that the extent of dye loss was markedly lower for the nylon 6,6 dyeings. In turn, this result implies that the fastness, to repeated wash testing, of the nylon 6,6 dyeings was superior to that of the corresponding dyeing on cotton.

Fig. 6 shows graphically the f_k values obtained for the cotton dyeings quoted in Table 3 and Fig. 7 shows the f_k values secured for the nylon 6,6 dyeings. The reduction in colour strength that occurred as a result of five repeated ISO CO6/C2 wash tests is apparent, especially in the case of the cotton dyeings.

Figs. 6 and 7 also show that the aftertreatment of both the cotton and the nylon 6,6 dyeings with the commercial cationic fixing agent, Solfix E, enhanced the fastness of the dyeings to repeated wash testing. Previous work [17–19] has shown that the fastness to detergent/perborate washing of the oxidised dyeings of C.I. Solubilised Sulphur, C.I. Leuco Sulphur and C.I. Sulphur dyes on cotton was markedly improved by the use of cationic fixing agents that were applied using simple exhaust or continuous aftertreatment procedures. It was postulated [17–19] that this improved wash fastness could be attributed to:

- the formation of a large molecular size dye–cationic agent of reduced aqueous solubility within the fibre and/or;
- the formation of a 'layer' of the polymeric cationic fixing agent at the periphery of the dyed fibre.

It was considered that such a mechanism would lower the rate at which the dye diffused out of the dyed substrate during washing and thus improve wash fastness. However, while no direct evidence was obtained to support this mechanism, indirect evidence, in the form of findings reported in other publications, was advanced [17–19]. Whilst it seems reasonable to propose that the above mechanism could be applied to the present work to explain the enhancement of wash fastness imparted by aftertreatment with the Solfix E, further work is clearly required to establish the precise mechanism by which such enhanced wash fastness is imparted.

When Figs. 6 and 7 are compared, it is obvious that the nylon 6,6 dyeings underwent considerably less reduction in colour strength during repeated wash testing than the corresponding cotton dyeings. The grey scale ratings of the stained adjacent cotton and nylon 6,6 materials after wash testing (Table 4) clearly show that the extent of staining of the adjacent nylon 6,6 and cotton fabrics was considerably lower in the case of the nylon 6,6 dyeings.

In Table 4, when the grey scale ratings for the aftertreated dyeings are compared to those secured for the non-aftertreated dyeings, it is clear

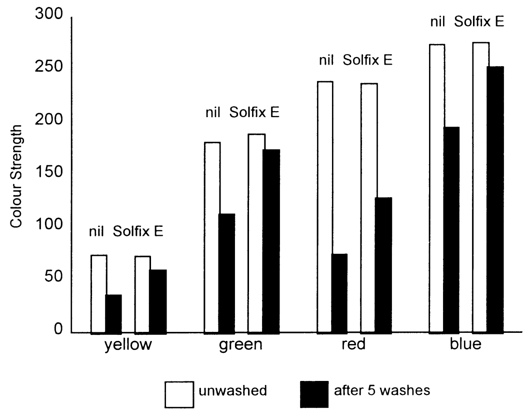

Fig. 6. f_k values for cotton dyed using method 1.

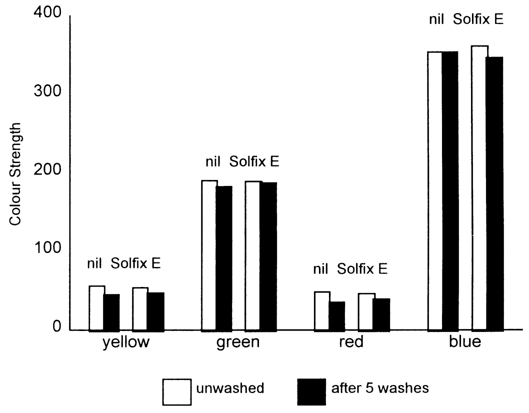

Fig. 7. f_k values for nylon 6,6 dyed using method 2.

Table 4
Staining results obtained using dyeing method 1 (cotton) and method 2 (nylon 6,6)[a]

Wash	Dyed cotton		Dyed nylon 6,6	
	Cotton	Nylon 6,6	Cotton	Nylon 6,6
Yellow 23				
1	3 (3/4)	3/4 (3/4)	3/4 (4)	4 (4/5)
2	3 (3/4)	3/4 (4)	3/4 (4)	4 (4/5)
3	4 (3/4)	4 (4)	4 (4/5)	4 (5)
4	4 (4)	4 (4/5)	4 (4/5)	4/5 (5)
5	4 (4/5)	4/5 (4/5)	4/5 (4/5)	4/5 (5)
Green 2				
1	3 (3)	3 (3/4)	4 (4)	4 (4/5)
2	3 (3/4)	3 (3/4)	4 (4)	4/5 (4/5)
3	3 (3/4)	3/4 (3/4)	4 (4/5)	5 (5)
4	3 (3/4)	3/4 (4)	4 (4/5)	5 (5)
5	3/4 (4)	3/4 (4)	4/5 (5)	5 (5)
Red 6				
1	2/3 (3/4)	5 (5)	5 (5)	5 (5)
2	2/3 (3/4)	5 (5)	4/5 (4/5)	5 (5)
3	3 (3/4)	5 (5)	4/5 (5)	5 (5)
4	3 (4)	5 (5)	5 (5)	5 (5)
5	3/4 (4)	5 (5)	5 (5)	5 (5)
Blue 7				
1	2 (2/3)	5 (5)	4/5 (4/5)	5 (5)
2	2 (2/3)	5 (5)	4/5 (4/5)	5 (5)
3	2 (3)	5 (5)	5 (5)	5 (5)
4	3 (3)	5 (5)	5 (5)	5 (5)
5	3 (4)	5 (5)	5 (5)	5 (5)

[a] Figures in brackets refer to Solfix E aftertreated samples.

that the cationic fixing agent reduced the extent of staining of the adjacent materials during repeated wash testing.

Table 5 shows the colorimetric data obtained for nylon 6,6 which had been dyed using method 3 in which a glucose/NaOH reduction system was used instead of the commercial Leucad 71 reduction system previously employed in method 2; the corresponding f_k values for the dyeings are displayed in Fig. 8. The f_k values in Fig. 8 and the ΔE values in Table 5 reveal that the dyeings displayed good fastness to repeated wash testing; this finding was confirmed by the very good/excellent grey scale staining assignments presented in Table 6.

The f_k values in Fig. 8 and the ΔE values in Table 5 also show that aftertreatment with Solfix E enhanced the wash fastness of all four dyes used. When the ΔE results presented in Table 5 are compared with those displayed in Table 3 for the nylon 6,6 dyeings, it can be concluded that generally deeper dyeings were obtained using method 3 and also, that these particular dyeings displayed higher fastness to repeated wash testing. The reasons for the increased depth of shade and superior wash fastness of the dyeings on nylon 6,6 obtained using the glucose/NaOH application method (method 3) are currently being investigated; the

Table 5
Colorimetic data obtained for nylon 6,6 using dyeing method 3

Dye	Aftertreatment	Washes	L^*	a^*	b^*	ΔE
Yellow 23	Nil	0	67.1	10.3	59.4	3.4
		5	72.6	7.3	63.2	
	Solfix E	0	65.8	10.2	58.6	1.4
		5	68.2	8.9	60.2	
Green 2	Nil	0	22.5	−19.4	−5.9	1.0
		5	22.7	−20.2	−7.2	
	Solfix E	0	23.2	−19.6	−5.8	0.9
		5	23.0	−19.0	−6.9	
Red 6	Nil	0	33.1	18.4	3.9	2.4
		5	36.5	20.0	5.1	
	Solfix E	0	34.8	18.7	5.3	1.0
		5	36.1	19.8	5.7	
Blue 7	Nil	0	16.5	2.2	−16.0	2.6
		5	16.4	4.1	−18.7	
	Solfix E	0	15.9	2.1	−16.4	0.6
		5	15.8	2.3	−17.2	

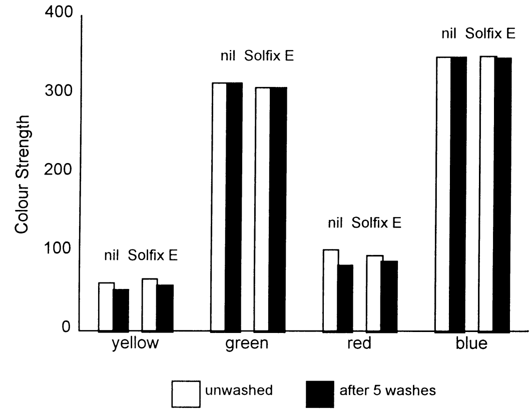

Fig. 8. Colour strength data obtained for dyeing method 3 on nylon 6,6.

Table 6
Staining results obtained for nylon 6,6 using dyeing method 3[a]

Wash	Staining of	
	Cotton	Nylon 6,6
Yellow 23		
1	3/4 (4)	4 (4/5)
2	3/4 (4)	4 (4/5)
3	4 (4/5)	4 (5)
4	4 (4/5)	4/5 (5)
5	4/5 (5)	4/5 (5)
Green 2		
1	4 (4)	4/5 (4/5)
2	4 (4)	4/5 (4/5)
3	4 (4/5)	5 (5)
4	4 (4/5)	5 (5)
5	4/5 (5)	5 (5)
Red 6		
1	4 (4)	5 (5)
2	4/5 (4/5)	5 (5)
3	4/5 (4/5)	5 (5)
4	4/5 (4/5)	5 (5)
5	4/5 (4/5)	5 (5)
Blue 7		
1	4/5 (4/5)	5 (5)
2	4/5 (4/5)	5 (5)
3	4/5 (5)	5 (5)
4	4/5 (5)	5 (5)
5	5 (5)	5 (5)

[a] Figures in brackets refer to Solfix E aftertreatted samples.

higher dyeing temperature used in method 3 may be a contributory factor.

The staining ratings displayed in Table 6 clearly show the high fastness of the nylon 6,6 dyeings to repeated wash testing and also, that aftertreatment with the cationic fixing agent enhanced this fastness.

As mentioned earlier, while sulphur dyes on cellulosic fibres possess moderate to good fastness to light and wet treatments, they are much less resistant to washing with detergent/perborate formulations that are now common in domestic washing powders. The recently introduced UKTO test method [16,20] is a diagnostic single wash test protocol that was designed to identify coloured cotton fabrics susceptible to oxygen bleach fading through repeated washing with domestic detergents. Consequently, sulphur dyeings on cellulosic fibres can be expected to show poor fastness to the UKTO test method, as was demonstrated [16,20] for several sulphur dyes. According to the UKTO methodology, when the colour difference [ΔE CMC (2,1)] between a dyed cotton sample before and after testing is <4 units, the sample is considered to be robust to oxygen bleach fading while a $\Delta E > 4$ units indicates bleach sensitivity.

Table 7 shows the colorimetric data obtained for cotton which had been dyed using the commercial

Table 7
Colorimetric data obtained for the UKTO wash test

Dye	Fibre	Aftertreatment	Washes	L^*	a^*	b^*	ΔE
Yellow 23	Cotton	Nil	0	61.1	12.5	55.0	7.2
		Solfix E	1	72.8	5.8	58.9	
			0	60.8	12.8	52.9	4.0
			1	67.2	9.6	56.4	
	Nylon 6,6	Nil	0	66.2	10.2	58.5	4.5
			1	73.4	7.0	64.5	2.6
		Solfix E	0	61.6	10.5	54.1	
			1	66.4	8.9	56.9	
Green 2	Cotton	Nil	0	27.9	−16.0	−7.2	6.6
			1	30.2	−14.9	−15.1	
			0	27.9	−16.3	−7.6	4.6
			1	29.1	−13.4	−12.1	
	Nylon 6,6	Nil	0	22.3	−19.4	−5.9	2.7
			1	22.6	−17.4	−8.7	
		Solfix E	0	23.1	−20.3	−6.1	2.5
			1	23.1	−17.9	−8.6	
Red 6	Cotton	Nil	0	22.0	14.2	2.9	15.5
			1	41.6	19.3	3.6	
		Solfix E	0	21.8	15.5	4.1	9.3
			1	32.6	19.9	7.4	
	Nylon 6,6	Nil	0	34.5	18.8	5.0	1.4
			1	37.0	18.8	4.9	
		Solfix E	0	33.6	18.4	4.0	1.4
			1	36.1	18.6	4.1	
Blue 7	Cotton	Nil	0	18.7	2.9	−12.6	8.6
			1	23.4	7.2	−21.5	
		Solfix E	0	18.3	4.7	−14.7	3.2
			1	20.2	6.3	−18.2	
	Nylon 6,6	Nil	0	16.4	2.2	−16.2	2.3
			1	16.3	3.7	−18.9	
		Solfix E	0	15.4	2.7	−15.8	1.3
			1	15.6	3.6	−17.2	

Table 8
Rub fastness of sulphur dyes on nylon 6,6

Dye	Wet	Dry
Yellow 23	5	5
Green 2	5	5
Red 6	5	5
Blue 7	5	5

reduction system (method 1; Leucad 71) as well as nylon 6.6 fabric which had been dyed using the glucose/NaOH reduction system (method 3). Evidently, the ΔE values obtained for the non-aftertreated cotton dyeings were very high showing the susceptibility of the dyeing to oxygen bleach fading; however, aftertreatment with the commercial cationic fixing agent reduced the ΔE values and so lowered the susceptibility of the dyeings to oxygen fading. The ΔE values secured for the non-aftertreated nylon 6.6 dyeings were very much lower than those of the corresponding cotton dyeings; aftertreatment with Solfix E also improved the bleach resistance of the nylon 6.6 dyeings.

Table 9
Light fastness of sulphur dyes on nylon 6,6

Dye	Wet
Yellow 23	1–2
Green 2	2
Red 7	2
Blue 7	3/4
Black 11	> 4

Thus, from the data presented in Table 7, it is clear that the four sulphur dyes showed very poor resistance to the UKTO test method on cotton but very good bleach resistance on nylon 6.6. This difference in the behaviour of the dyes on the two substrates may be attributed to the more hydrophobic nature of the nylon 6.6 fibre leading to lower oxidative degradation of the sulphur linkages in the dyes.

Table 8 shows the rub fastness of nylon 6,6 which had been dyed with the sulphur dyes using method 3 (glucose/NaOH), from which it is clear that both the dry and wet rub fastness of the sulphur dyeings was excellent. The light fastness of the dyes on nylon 6,6 when applied using method 3 (Table 9) left much to be desired, the ratings obtained being much lower than can be expected for the dyes on cellulosic fibres.

As the sulphur dyeing of nylon 6,6, shown in Figs 1–3 had been carried out under alkaline conditions and, because the scouring of nylon 6,6 is also typically carried out under alkaline conditions, it was decided to combine these two operations.

Table 11
Colorimetric data obtained for a deep black shade on nylon 6,6

Test	Wash	L^*	a^*	b^*	f_K	ΔE
CO6/C2	0	12.7	1.0	−1.5	554.7	0.9
	5	12.2	1.2	−2.0	563.7	
UKTO	0	12.4	1.0	−1.5	560.2	1.0
	1	11.9	1.2	−2.0	587.4	

Table 10
Colorimetric data obtained using conventional dye after scour and combined scour and dye methods

Process	L^*	a^*	b^*	C	$h°$	f_k
Yellow 23						
Dyed after scouring	67.1	10.3	59.4	60.3	80.2	60.8
Combined scour and dye	65.8	10.2	58.6	69.5	80.1	65.6
Green 2						
Dyed after scouring	22.5	−19.4	−5.9	20.3	196.9	314.7
Combined scour and dye	22.7	−19.6	−5.8	20.4	196.5	30.92
Blue 7						
Dyed after scouring	16.5	2.2	−16.0	16.2	277.8	348.8
Combined scour and dye	16.9	2.0	−16.4	16.5	277.1	337.7

Table 10 shows the colorimetric data obtained for nylon 6,6 samples which had been dyed using the combined scouring and dyeing process (method 4) that used the glucose/NaOH reduction system as well as the corresponding data secured when nylon 6,6 had been dyed after scouring using method 3 (glucose/NaOH). Investigation of the results displayed in Table 10 shows that there was little difference, between the two dyeing methods used, in terms of both the colour and the colour strength of the dyeings.

Perhaps the most important shade that could be obtained using sulphur dyes on nylon 6,6 would be a deep black. Currently, a fast, deep black shade on nylon 6,6 is obtained using pre-metallised acid dyes in conjunction with a commercial aftertreatment.

Table 11 shows the colorimetric data secured for a deep shade obtained when C.I. Sulphur Black 11 was applied to nylon 6,6 using method 3 (glucose/NaOH), both before and after five repeated ISO CO6/C2 wash tests and the UKTO test method. The very high fastness of the dyeing is obvious.

4. Conclusions

Nylon 6,6 can be dyed with selected sulphur dyes using a sulphide-based reduction system that is intended for the application of the dyes to cellulosic fibres. However, the use of a glucose/NaOH reduction system enabled dyeings of higher colour yield and wash fastness to be achieved. The fastness of sulphur dyeings on nylon 6,6 to repeated wash testing in the presence of bleach was superior to that of comparable dyeings on cotton. The sulphur dyeings on nylon 6,6 also showed very good resistance to oxygen bleach fading insofar as many of the sulphur dyes used on nylon 6,6 satisfied the criterion of the UKTO test method. The observed resistance to both repeated wash testing and the UKTO test method was found to be enhanced by aftertreating the sulphur dyed fabric with a commercial, cationic fixing agent. The sulphur dyeings on nylon 6,6 showed excellent wet and rub fastness but the light fastness of the dyeings was poor.

The study implies that sulphur dyes may provide an alternative to metallised acid dyes in obtaining economical, deep shades on nylon 6,6, especially for outlets where high light fastness is not an issue. Efforts are now being focussed to improve the light fastness of the dyeings and to extend the dye colour gamut.

References

[1] Burkinshaw SM. In: Hallas G, Waring D, editors. The chemistry and application of dyes. New York: Plenum, 1990.

[2] Burkinshaw SM. Chemical principles of synthetic fibre dyeing. London: Blackie Acad. & Prof, 1997.

[3] Blackburn RS, Burkinshaw SM, Collins GW, Gandhi K, Gotsopoulos A, Wills AE. Confluences: fashioning intercultural perspectives. Lyon: Université de Mode, 1997.

[4] Senior C. In: Shorre J, editor. Cellulosics dyeing. Bradford: SDC, 1995.

[5] Clarke D, Senior C. In: Preston C, editor. The dyeing of cellulosic fibres. Bradford: SDC, 1986.

[6] Cheetham RC. Dyeing fibre blends. London: Van Nostrand, 1966.

[7] Shore J. In: Shore J, editor. Colorants and auxiliaries, vol. 2. Bradford: Society of Dyers and Colourists, 1990.

[8] Shore J. Blends dyeing. Bradford: Society of Dyers and Colourists, 1998.

[9] Diamond Shamrock, US patent 4531946 A, 1985.

[10] Toray, JP patent 61019889 A, 1986.

[11] Ciba-Geigy DE Patent 19613671 A, 1996.

[12] Toyobo, JP Patent 10025670 A, 1998.

[13] Kurakay Co, EP Patent 833005 A, 1998.

[14] Stott PH. Amer Dyest Rep 1939;28:582.

[15] Anon. Standard methods for the determination of the colour fastness of textiles and leather. 5th ed. Society of Dyers and Colourists, 1990.

[16] Phillips DAS, Duncan M, Jenkins E, Bevan G, Lloyd J, Hoffmeister J. J Soc Dyers Col 1996;112:289.

[17] Burkinshaw SM, Collins GW, Gordon R. Proceedings of the AATCC International Conference, Atlanta, 1995.

[18] Burkinshaw SM, Collins GW. Dyes and Pigments 1995;29:323.

[19] Burkinshaw SM, Collins GW, Gordon R. Proceedings of the AATCC International Conference, Nashville, 1996.

[20] Phillips DAS, Duncan M, Graydon A, Bevan G, Lloyd J, Harbon C, Hoffmeister J. J Soc Dyers Col 1996;113:289.