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Sulphur dyes on nylon 6,6—part 2: the effects of reductant, oxidant and wash-off

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Abstract

Nylon 6.6 was dyed with five commercial suphur dyes using seven different reducing systems and three oxidation systems and the dyeings were subected to repeated wash testing and to light fastness assessment. It was found that the different reductants effected not only the colour strength of the dyeings but also influenced the colour of the dyeings. Two of the reducing systems studied had a deleterious effect on colour strength achieved for some of the dyes. From a wash fastness viewpoint, while the same two reducing systems had a deliterious effect on both the extent of shade change and staining of adjacent multifibres, overall, the dyeings displayed very good fastness to the five repeated wash tests. There was very little difference between the three oxidising systems examined in terms of the colour strength of the dyeings, with the $f(k)$ values obtained for the five dyes being virtually identical for each of the three oxidation systems used. However, the colour of the dyeings differed for the three oxidation systems studied. The wash fastness of the dyeings was little effected by the type of oxidant used. The wash-off of dyeings markedly reduced the extent of staining of adjacent multifibre strip but did not improve the colour change that occurred upon repeated washing. With the exception of the black dye, the dyes displayed poor fastness to light and this was, in general, little influenced by reductant, oxidant and wash-off.

Keywords: Nylon 6,6; Sulphur dyes; Repeated wash fastness; Wash-off

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1. Introduction

Although nylon 6,6 can be dyed using many types of dye (acid, mordant, direct, reactive, disperse, vat and basic) and a vast amount of literature has been published on the use of these dye classes on nylon 6,6 over the past 60 or so years, very little interest has attended the application of sulphur dyes to nylon 6,6. Indeed, it is only quite recently that, as a result of a research study [1], commercial interest in the sulphur dyeing of nylon was stimulated and led to the introduction of ranges of sulphur dyes intended for use on nylon.

This paper concerns the effects of application parameters (pH, temperature, liquor ratio, etc.) on the colour strength and fastness properties of commercial sulphur dyes on nylon 6,6. The first

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part of the paper [2] showed that maximum colour strength was achieved at an application pH 7 and that the colour of dyeings was influenced by pH. Although the pH of dyeing had no influence on the wash fastness of the resultant dyeings, maximum light fastness was also achieved at an application pH of 7. While the five dyes varied in terms of the effect of dyeing temperature on colour strength, temperature had little effect on the colour of the dyeings within the range 70–98 °C; dyeing temperature had little effect on wash fastness. With the exception of the black dye used, the dyeings displayed poor fastness to light.

This part of the paper concerns the effects of reductant, oxidant and wash-off on the colour strength, fastness to light and to repeated washing of five sulphur dyes on nylon 6,6. Subsequent parts of the paper will deal with the mechanism of dyeing nylon 6,6 with sulphur dyes.

2. Experimental

2.1. Fabric

The scoured, knitted, nylon 6,6 *Coloursafe* fabric (78f68) previously described [2] was used.

2.2. Dyeing

The five, arbitarily chosen, commercial sulphur dyes that were used in the previous part of this paper [2] were employed, namely *Diresul Green RDT-N* (C.I Sulphur Green 2), *Diresul Yellow RDT-E* (C.I. Sulphur Yellow 22), *Diresul Brown RDT-GN* (C.I. Sulphur Brown 1:1), *Diresul Navy 2R* (C.I. Sulphur Navy 11) and *Diresul Black RDT-LS200%* (C.I. Sulphur Black 1); the commercial samples of the dyes were supplied by Clariant UK. Dyeings (10% omf) were obtained using the equipment and procedures described earlier [2]; the dyeing method is shown in Fig. 1. Seven reducing systems, involving six commercial reductants, were examined (Table 1). At the end of dyeing, the dyed samples were removed, rinsed thoroughly in tap water and were oxidised.

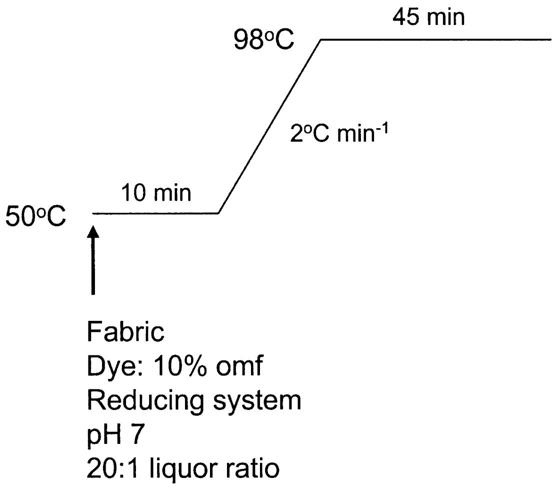

Fig. 1. Dyeing method.

Table 1
Reducing systems used

	Reducing system	Amount used	Supplier
1	*Formusol GR*	1 g per g of dye	Clariant
2	*Leucad 71*/*Stabilisal S*	1 cm^3 per g of dye/0.5 cm^3	DyStar
3	Glucose/$Na_2S_2O_4$	1 g per g of dye/0.5 g	Aldrich
4	*Reducing agent D*/NaOH	1 g per g of dye/0.5 g	Clariant
5	*Reducing agent PA p*	1 g per g of dye	
6	*Cyclanon ECO*/$Na_2S_2O_4$	0.8 g per g of dye/1.2 g	BASF
7	*Rongalit*/$Na_2S_2O_4$	0.8 g per g of dye/1.2 g	

2.3. Oxidation

Three oxidation systems were used (Table 2). In the cases of the two liquid systems, oxidation was carried out at pH 4.5 employing a liquor ratio of 50:1, at 70 °C, for 15 min in 300 cm^3 capacity sealed stainless steel dyepots, housed in a *Roaches Pyrotec S* dyeing machine; the pH was adjusted using McIlvaine buffer [2]. Air oxidation was carried out at 21 °C, 65%RH for 24 h. At the end of

Table 2
Oxidation systems used

	System	Amount	Supplier
1	H_2O_2	2 g l^{-1}	Aldrich
2	*Diresul oxidation liquid BRI*	5 g l^{-1}	Clariant
3	Air	–	–

oxidation, the samples were rinsed in running cold water for 5 min and allowed to dry in the open air.

2.4. Wash-off

At the end of dyeing the samples were subjected to four wash-off treatments which entailed immersion of the dyeings in a stirred aqueous solution comprising 5 g l^{-1} *Formosul GR* (Clariant), 15 cm^3 l^{-1} *Sandoclean PC* (Clariant), 2 g l^{-1} *Diresul EW* (Clariant) or 3 g l^{-1} *Cyclanon ECO* (BASF), at 98 °C for 20 min, at pH 8 (adjusted using McIlvaine buffer [2]) using a 50:1 liquor ratio; the commercial reagents were kindly supplied by the respective manufacturer. At the end of wash-off, the samples were rinsed in running cold water for 5 min and allowed to dry in the open air. A contol dyeing, which had been rinsed in running tap water for 5 min prior to drying in the open air, was used as a control against which the washed-off dyeings were compared, in colorimetric and wash fastness terms. In order to express the amount of dye removed by the different wash-off methods, the colour difference (expressed in ΔE^* units) between a given washed-off sample and the corresponding control dyeing was calculated from the appropriate CIE $L^*a^*b^*$ coordinates.

2.5. Fastness

The dyed fabrics were subjected to five, consecutive ISO CO6/C2 wash tests as described earlier [2] and the fastness of the dyeings to light was determined as previously described [2].

2.6. Colour measurement

All measurements were carried out using the equipment and procedure described earlier [2].

3. Results and discussion

In the first part of this paper [2], it was found that little, if any advantage in colour strength, wash fastness or light fastness, was gained using a dyeing temperature other than 98 °C. Furthermore, it was observed [2] that maximum colour strength was achieved at pH 7 and, also, that while the pH of dyeing had no influence on the wash fastness of the resultant dyeings, maximum light fastness was achieved at an application pH of 7. As a consequence of these earlier findings, it was decided that for the work described in this section of the paper, the five dyes would be applied (Fig. 1) at 98 °C, using a 20:1 liquor ratio and at pH 7.

3.1. Effect of reducing system

Several commercial reducing systems are available for the application of sulphur dyes to cellulosic fibres and it is well known that different reducing systems can have different effects on different sulphur dyes [3]. Indeed, some reducing systems are recommended as being unsuitable for use with certain dyes [3] and the use of the incorrect reductant or incorrect amount of a given reductant can result in either under-reduction or over-reduction of a particular dye. In the case of the dyeing of nylon 6,6 with sulphur dyes, no such general recommendations are available since no detailed study has been published of the effects of reducing systems on dyeing. With these facts in mind, a total of seven reducing systems (Table 1) were used in this work. Of these, only two have been recommended for use in the commercial application of sulphur dyes to polyamide fibres, namely *Formosul GR* and *Reducing agent PA p* [4]. The remaining reducing systems were selected on the basis of their use either in a previous study of the sulphur dyeing of nylon 6,6 (*Leucad 71*/*Stabisal S* and, glucose/NaOH) [5] or due to their effectiveness as reductants in the application of vat dyes to polyamide fibres (*Cyclanon ECO*/$Na_2S_2O_4$ and *Rongalit*/$Na_2S_2O_4$) [6] or use in the sulphur dyeing of cotton (*Reducing agent D*/NaOH). In this part of the work, the dyeings (10% omf) were oxidised using oxidation system 2 in Table 2 *(Diresul oxidation liquid (BRI)*.

Fig. 2 shows, for each of the five dyes, the variation in colour strength $f(k)$ obtained for the seven reducing systems used; it is evident that the dyes varied in terms of the effect of the different reducing systems. Although there appeared to be little pattern to the effects of the reducing systems on the individual dyes, it is evident that both the

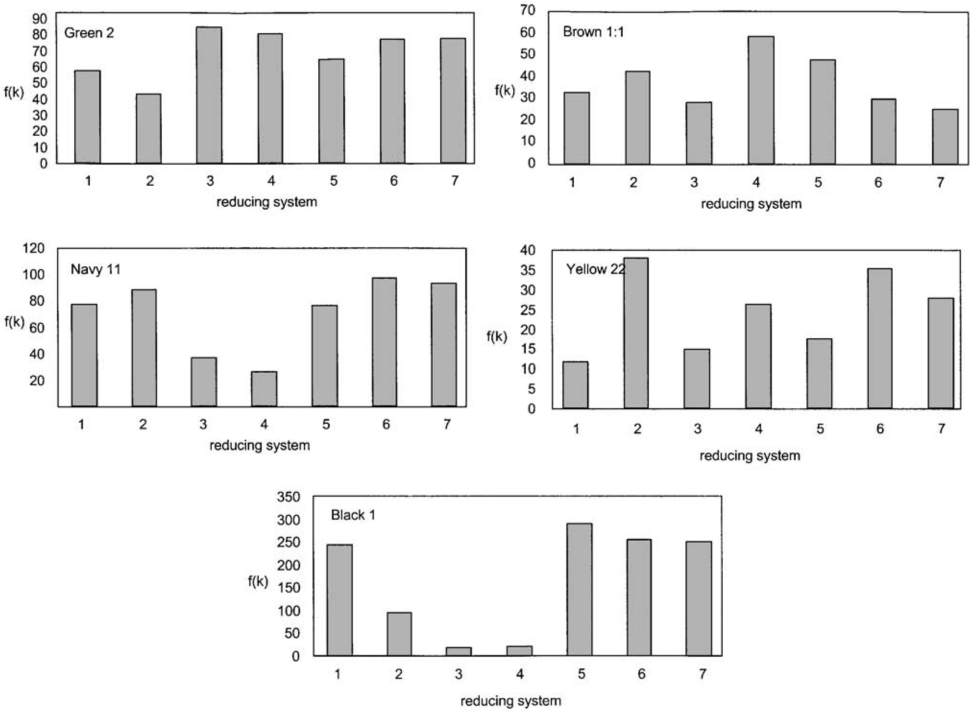

Fig. 2. Effect of reducing system on colour strength (pH 7; 98 °C; 20:1 liquor ratio; oxidation system 2).

glucose/Na_2SO_4 and *Reducing agent D*/NaOH combinations had a deleterious effect on the colour strength achieved for the navy and, especially, the black dyes. The reasons for this remain unclear because it was not possible to obtain information from all of the manufacturers about the composition of their products.

The corresponding colorimetric data (Table 3) shows that the different reductants affected not only the colour strength of the dyeings but also influenced the colour of the dyeings; in the latter context, the brown, green and, especially, the black dyes seemed to be most effected. As previously mentioned [2], little is known about the chemical structure of sulphur dyes and the mechanism of their interaction with cellulosic fibres, despite their widespread use on these fibres over several decades; even less is known of the mechanism of dyeing nylon 6,6 with sulphur dyes. If it is assumed that the overall reduction and oxidation mechanisms which are thought to apply the dyeing of cellulosic fibres with sulphur dyes also apply to the dyeing of nylon 6,6 with sulphur dyes, the observed dependency of the colour of the dyeings on the reductant used can be explained in terms of the state of reduction of the dyes and their subsequent oxidative condensation. Reduction of the water-insoluble, macromolecular sulphur dyes under alkaline conditions, affects the constituent di- and polysulfide bonds in the dye and results in cleavage of the large M_r dye, with the formation of the low M_r, alkali-soluble, thiol form of the dye. Subsequent oxidation, at the end of dyeing, of this *leuco* form of the dye, results in the oxidative condensation of the insoluble, macromolecular sulphur dye *in situ* within the fibre. Thus, it follows that the final colour achieved in sulphur dyeing will depend upon the nature of the reduced species present in the dyebath (i.e. the state of reduction of the dye) and their subsequent oxidative condensation (i.e. the nature of the oxidation process). In the context of the observed influence of the different reductants on both the colour strength and the colour of the dyeings (Fig. 2 and Table 3), it seems reasonable to suggest that the different reductants would affect dye

Table 3
Effect of reducing system on shade change achieved for 10% omf dyeings (pH 7; 98 °C; 20:1 liquor ratio; oxidation system 2)

Dye		Reducing system	Number of washes	*L**	*a**	*b**	*C*	*h*°	λ_{max}
Green 2	1	*Formosul GR*	0	32.1	−16.0	−11.3	21.1	212.8	660
			5	32.2	−15.9	−11.2	21.0	213.2	660
	2	*Leucad 71/Stabilisal S*	0	31.8	−16.9	−11.0	21.8	208.9	660
			5	32.9	−16.8	−11.0	21.6	209.1	660
	3	Glucose/Na_2SO_4	0	36.2	−16.7	−9.7	22.1	210.5	640
			5	36.6	−16.6	−9.7	22.1	211.2	640
	4	*Reducing agent D*/NaOH	0	38.8	−18.8	−11.2	22.9	210.0	660
			5	38.8	−18.2	−11.2	22.8	210.9	660
	5	*Reducing agent PA p*	0	31.3	−15.5	−11.5	22.0	208.3	660
			5	31.6	−15.4	−11.5	21.9	209.1	660
	6	*Cyclanon ECO*/$Na_2S_2O_4$	0	35.1	−15.4	−10.6	22.2	207.2	660
			5	35.1	−15.3	−10.6	22.1	208.2	660
	7	*Rongalit*/$Na_2S_2O_4$	0	31.4	−16.2	−10.7	21.3	209.5	660
			5	31.5	−16.2	−10.7	21.2	209.8	660
Brown 1:1	1	*Formosul GR*	0	52.2	1.8	11.5	11.7	81.3	420
			5	52.3	1.9	11.5	11.6	81.3	420
	2	*Leucad 71/Stabilisal S*	0	48.9	2.1	13.8	13.9	81.3	400
			5	49.1	2.3	13.9	13.8	81.2	400
	3	Glucose/Na_2SO_4	0	54.2	1.3	10.7	10.8	82.9	420
			5	53.8	1.5	10.8	10.7	83.1	420
	4	*Reducing agent D*/NaOH	0	42.9	0.7	9.4	9.5	85.9	400
			5	43.5	0.8	9.5	9.4	85.9	400
	5	*Reducing agent PA p*	0	46.2	0.4	10.0	10.1	87.5	400
			5	46.9	0.5	10.2	10.3	87.4	400
	6	*CyclanonECO*/$Na_2S_2O_4$	0	56.1	0.5	18.0	18.0	88.5	400
			5	56.3	0.6	18.2	17.6	88.4	400
	7	*Rongalit*/$Na_2S_2O_4$	0	56.5	2.1	12.6	12.8	80.7	420
			5	56.8	2.2	12.8	12.5	80.5	420
Navy 11	1	*Formosul GR*	0	35.3	0.0	−12.2	12.2	270.2	600
			5	35.8	0.0	−11.9	12.1	270.6	600
	2	*Leucad 71/Stabilisal S*	0	33.6	−1.1	−15.6	15.6	266.2	600
			5	33.6	−1.1	−15.6	15.6	266.9	600
	3	Glucose/Na_2SO_4	0	46.6	−2.2	−16.1	16.3	262.2	600
			5	48.2	−2.7	−15.8	16.1	270.1	600
	4	*Reducing agent D*/NaOH	0	51.7	−2.7	−15.8	16.1	260.3	600
			5	51.9	−2.9	−15.7	16.0	262.7	600
	5	*Reducing agent PA p*	0	35.5	0.1	−12.1	12.1	270.5	600
			5	35.8	0.0	−11.8	12.1	270.7	600
	6	*CyclanonECO*/$Na_2S_2O_4$	0	32.0	0.5	−13.7	13.7	272.0	600
			5	32.7	0.5	−13.4	13.6	272.6	600
	7	*Rongalit*/$Na_2S_2O_4$	0	32.6	0.0	−13.2	13.2	270.2	600
			5	32.9	0.1	−13.0	13.0	270.8	600
Yellow 22	1	*Formosul GR*	0	79.0	0.4	36.4	36.4	89.4	400
			5	82.7	0.4	36.4	36.0	87.3	400
	2	*Leucad 71/Stabilisal S*	0	65.4	3.8	42.4	42.6	84.9	400
			5	66.3	3.8	42.4	41.1	84.0	400
	3	Glucose/Na_2SO_4	0	72.5	1.0	30.1	30.1	88.1	400
			5	73.2	1.0	30.1	29.2	88.0	400
	4	*Reducing agent D*/NaOH	0	73.4	2.0	45.6	45.6	87.5	400
			5	73.5	2.1	45.5	45.6	87.3	400

(*continued on next page*)

Table 3 (*continued*)

Dye		Reducing system	Number of washes	L^*	a^*	b^*	C	h°	λ_{max}
	5	*Reducing agent PA p*	0	77.8	−0.4	41.8	41.8	90.6	400
			5	77.9	−0.4	41.7	41.6	90.0	400
	6	*Cyclanon ECO*/$Na_2S_2O_4$	0	69.5	3.6	45.7	45.8	85.5	400
			5	70.1	3.6	45.6	45.8	85.4	400
	7	*Rongalit*/$Na_2S_2O_4$	0	72.9	2.4	46.0	46.1	87.0	400
			5	83.2	2.5	46.0	45.6	87.0	400
Black 1	1	*Formosul GR*	0	21.1	−0.4	−1.8	1.9	257.7	580
			5	22.2	−0.3	−1.8	1.8	252.6	580
	2	*Leucad 71/Stabilisal S*	0	33.0	1.1	−2.1	2.4	297.1	580
			5	33.7	1.1	−2.0	2.3	298.4	580
	3	Glucose/Na_2SO_4	0	57.8	−0.1	−1.9	1.9	265.6	620
			5	58.7	−0.1	−1.8	1.7	271.3	620
	4	*Reducing agent D*/NaOH	0	55.4	0.7	−1.9	2.0	291.2	580
			5	56.3	0.9	−1.8	1.9	297.6	580
	5	*Reducing agent PA p*	0	19.1	0.2	−1.9	1.9	276.6	580
			5	20.1	0.3	−1.8	1.7	278.9	580
	6	*CyclanonECO*/$Na_2S_2O_4$	0	20.5	0.3	−2.5	2.5	277.3	580
			5	21.4	0.5	−2.1	2.5	281.2	580
	7	*Rongalit*/$Na_2S_2O_4$	0	20.7	0.3	−2.5	2.5	275.8	580
			5	20.8	0.3	−2.4	2.4	282.1	580

reduction in terms of the solubility, M_r and relative amounts of the alkali-soluble thiols generated. Subsequent oxidation can also be considered to contribute to the colour of the final dyeings in terms of the solubility, M_r and relative amounts of dye macromolecules that were generated. It seems reasonable to suggest that the variations observed in both the colour (Table 3) and colour strength (Fig. 2) of the dyeings would be more influenced by the nature of the reducing system rather than the oxidation stage, as only one oxidation process was used in this particular part of the work.

In terms of the fastness of the 10% omf dyeings to repeated washing at 60 °C, the colorimteric data obtained for dyeings both before and after washing five times (Table 3) reveals that in the cases of the green, brown, navy and yellow dyes, the hue and chroma of the dyeings after five washes was very similar to that of the samples before washing. However, for the black dye, in the cases of some of the reducing systems used, repeated washing imparted a change to the hue and chroma of the dyeings, suggesting that a stable, final colour had not been achieved at the end of the dyeing/oxidation processes.

The results in Table 4 show that the dyeings displayed very good fastness overall to repeated washing in terms of shade change and that, with the exception of both the glucose/Na_2SO_4 and *Reducing agent D*/NaOH combinations, the reducing systems had little effect on the change in shade of the dyeings. Generally, the fastness ratings were lower for the first two washes than for the remaining three washes in the five cycle wash system; in the case of the latter two or three washes, fastness was, for all dyes investigated, excellent. From the viewpoint of the staining of adjacent cotton and nylon 6,6 multifibre that occurred during repeated wash testing, Table 5 reveals that the cotton component was more heavily stained than its nylon 6,6 counterpart, for each of the dyes used. This can be attributed to the fact that the sulphur dyes used were designed for application to cellulosic fibres and, therefore, their subtantivity can be expected to be greater towards the cotton rather than the nylon 6,6 multifibre. Table 5 shows that the extent of staining decreased with increasing number of washes and that for the last two or three wash tests, the general level of staining was very good/excellent.

Table 4
Effect of reducing system on shade change (98 °C; pH 7; 20:1 liquor ratio; oxidation system 2)

Reducing system	Green 2					Brown 1:1					Navy 11					Yellow 22					Black 1				
	No. of washes					No. of washes					No. of washes					No. of washes					No. of washes				
	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
1	5	5	5	5	5	4	4	4	5	5	4	4	5	5	5	4	4	5	5	5	4/5	5	5	5	5
2	4	5	5	5	5	3/4	4	4	5	5	3/4	4	4	5	5	4	4	5	5	5	4	5	5	5	5
3	4/5	5	5	5	5	4	5	5	5	5	3	3/4	4	4	4	3/4	4	4	5	5	4	4/5	5	5	5
4	5	5	5	5	5	3/4	4	4	5	5	4	4	5	5	5	3/4	4	4	4	5	4/5	5	5	5	5
5	5	5	5	5	5	4	4	5	5	5	4	4	5	5	5	4/5	4	4	4	4	4	4/5	5	5	5
6	5	5	5	5	5	4	4	4	4	4/5	4	4/5	5	5	5	4	4	5	5	5	4/5	5	5	5	5
7	5	5	5	5	5/4	4	5	5	5	4	4	4	5	5	4	4	5	5	5	4/5	5	5	5	5	

Presumably, the lower ratings observed in the cases of both shade change (Table 4) and staining (Table 5) obtained for the first one or two wash cycles can be attributed to insufficient removal of ‘surface’ or ‘surplus’ dye at the end of the oxidation process, because, the initially low ratings achieved for the first one or two washes increased for subsequent washes, eventually reaching a rating of very good/excellent for the last two or three wash cycles. The subject of the ‘wash-off’ of the dyeings is discussed later in this paper.

If, once again, it is assumed that similar reduction and oxidation mechanisms apply to the dyeing of nylon 6,6 with sulphur dyes as to the dyeing of cellulosic fibres, then the generally excellent fastness achieved for the dyeings to repeated washing can be attributed to the water insolubility of the oxidised dyes. However, the fact that dye was removed during washing (Table 4) and, also, that vagrant dye was re-deposited upon adjacent multifibre strip (Table 5) warrants discussion. Several authors [7–9] have proposed that although little is known of the structure of sulphur dyes, some dyes may contain sulfonic acid groups and it has been suggested that the suitability of many sulphur dyes for ‘topping’ with cationic dyes may be due to the presence of sulfonic or other acid groups within the dye introduced by oxidation [10]. Furthermore, it is well known that certain oxidants (including H_2O_2 that was used in this part of the work) can over-oxidise [3,11] thiolate groups in sulphur dyes, which imparts a certain degree of water-solubilty [7] and reduced wet fastness [3]. Thus, while the findings in Tables 4 and 5 demonstrate that during washing, dye was removed from the dyeings and some of this became re-deposited upon adjacent multifibre strip, they do not provide evidence to support the view that the sulphur dyes contained sulfonic or other anionc groups; nevertheless, such a view would explain these findings. This particular aspect concerns an area of study, namely the mechanism of the dyeing of nylon 6,6 with sulphur dyes, which is the subject of a subsequent part of this paper.

Table 6 reveals that with the exception of the black dye, the dyeings displayed poor fastness to light and, again with the exception of the black dye, the reductants had no effect on the light fastness of the dyeings. In the case of the dyeings of C.I. Sulphur Black 1, it is evident that both the glucose/Na_2SO_4 and *Reducing agent D*/NaOH combinations had a deleterious effect on light fastness.

In view of the findings (Table 3 and Fig. 2) that the glucose/Na_2SO_4 and *Reducing agent D*/NaOH reducing systems had a deleterious effect upon the colour strength and hue of the dyeings obtained using C.I. Sulphur Black 1 and that the use of these two systems also resulted in lower wash fastness (Tables 4 and 5) and light fastness (Table 6) for this particular dye, it seems reasonable to suggest that these two reducing systems appear to be unsuitable for use with C.I. Sulphur Black 1 and may have over-reduced the dye.

3.2. *Effect of oxidation system*

Several commercial oxidation systems are used in the application of sulphur dyes to cellulosic

Table 5
Effect of reducing system on staining (98 °C; pH 7; 20:1 liquor ratio; oxidation system 1)

Dye	Reducing system	Number of washes									
		1		2		3		4		5	
		Cotton	Nylon 6,6	Cotton	Nylon 6,6	Cotton	Nylon 6,6	Cotton	Nylon 6,6	Cotton	Nylon 6,6
Green 2	1	4/5	5	4/5	5	5	5	5	5	5	5
	2	4	5	4/5	5	5	5	5	5	5	5
	3	4	4/5	4/5	5	5	5	5	5	5	5
	4	4	4	4	4/5	5	5	5	5	5	5
	5	4	5	4/5	5	5	5	5	5	5	5
	6	4	5	4	5	4	5	4/5	5	4/5	5
	7	4	5	4	5	4	5	4/5	5	4/5	5
Brown 1:1	1	3/4	4	4	4/5	4/5	5	5	5	5	5
	2	3	4	4	4	4	5	4	5	4	5
	3	4	4	4	4	4	5	4	5	4	5
	4	3/4	4	3/4	4	5	4	5	5	5	5
	5	3/4	5	4	5	4	5	4	5	4	5
	6	3	4	3/4	5	4	5	4	5	4	5
	7	3	3	4	5	5	5	5	5	5	5
Navy 11	1	3/4	4	3/4	4	3/4	4/5	4	5	4	5
	2	3/4	5	4/5	5	5	5	5	5	5	5
	3	3	4/5	4/5	5	5	5	5	5	5	5
	4	3	4	3/4	4/5	3/4	5	4	5	4	5
	5	3/4	5	4/5	5	5	5	5	5	5	5
	6	3	5	3/4	5	4	5	4/5	5	4/5	5
	7	3	5	3/4	5	4	5	4/5	5	4/5	5
Yellow 22	1	3/4	4	3/4	4	4	5	4	5	4	5
	2	4	4	4	4	4	5	4	5	4	5
	3	4	4	4	4	4	5	4	5	4	5
	4	3/4	4	3/4	4	5	4	5	5	5	5
	5	3/4	5	4	5	4	5	4	5	4	5
	6	3	4	3/4	5	4	5	4	5	4	5
	7	3	4	3	5	4	5	4	5	4	5
Black 1	1	4	5	4/5	5	5	5	5	5	5	5
	2	4	5	4/5	5	5	5	5	5	5	5
	3	3	4/5	4/5	5	4/5	5	4/5	5	5	5
	4	3	4	3	4/5	3/4	5	4	5	4	5
	5	3/4	5	4/5	5	5	5	5	5	5	5
	6	3	5	3/4	5	4	5		5	5	5
	7	3	5	3/4	5	4	5	4/5	5	5	5

fibres and it is well known that different oxidants can have different effects on different sulphur dyes [3]. Indeed, recommendations are often made as to the suitability of some oxidation systems for use with certain dyes. Furthermore, as was discussed earlier, several authors suggest that the oxidation of sulphur dyes can result in the introduction of sulfonic acid or other anionic groups within the dyes. Also, it is proposed that certain oxidants (including H_2O_2 that was used in this work), can over-oxidise thiolate groups in sulphur dyes, imparting a degree of water-solubilty and reduced wet fastness. However, such suggestions and observations concern the dyeing of cellulosic fibres with sulphur dyes; no study has been published of the effects of oxidation systems on the dyeing of nylon 6,6 with sulphur dyes. Thus, an investigation was made of the effects of three oxidation systems (Table 2). Of these, only *Diresul BRI* has been recommended, commercially, for use in the application of sulphur

Table 6
Effect of reducing system on light fastness of 10% omf dyeings (98 °C; pH 7; 20:1 liquor ratio; oxidation system 2)

Reducing system	Green 2	Brown 1:1	Navy 11	Yellow 22	Black 1
1 *Formosul GR*	2	2	2	2	6
2 *Leucad 71*/*Stabilisal S*	2/3	2/3	2	2/3	6
3 Glucose/Na_2SO_4	2	2	2	2/3	2
4 *Reducing agent D*/NaOH	2	2	2	2	3
5 *Reducing agent PA p*	2	2	2	2	6
6 *Cyclanon ECO*/$Na_2S_2O_4$	2	2	2/3	2	6
7 *Rongalit*/$Na_2S_2O_4$	2	2	2	2	6

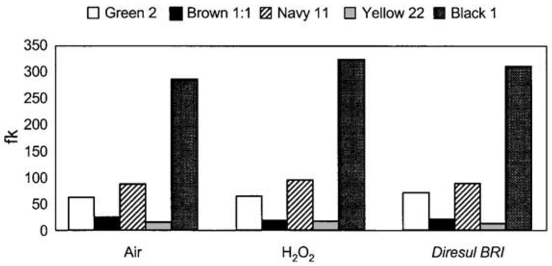

Fig. 3. Effect of oxidation system on colour strength (pH 7; 98 °C; 20:1 liquor ratio; reducing system 1).

dyes to polyamide fibres [4] while H_2O_2 was selected on the basis of its use in a previous study of the sulphur dyeing of nylon 6,6 [5].

In this part of the study, the five dyes were applied (Fig. 1) at 98 °C, pH 7 using a liquor ratio of 20:1 and employing *Formosul GR* as reducing agent; the ensuing dyeings were oxidised using each of the three oxidants shown in Table 2. Fig. 3 clearly shows that in terms of colour strength, there was very little difference between the three oxidising systems examined; indeed, the *f*(*k*) values obtained for the five dyes were virtually identical for each of the three oxidation systems used. Table 7 shows that, for each dye used, the three oxidants effected the colour of the dyeings obtained. This finding was not unexpected as it is well known that in the dyeing of cellulosic fibres with sulphur dyes, different shades are obtained using different oxidants. In turn, this can be attributed to the fact that, as discussed earlier, the final colour of the dyeing will depend upon the nature of the particular dye macromolecules (e.g. M_r, M_r distribution) generated during oxidative condensation.

Table 7
Effect of oxidation system on colorimetric data for 10% omf dyeings (pH 7; 98 °C; 20:1 liquor ratio; reducing system 1)

Dye	Oxidation system	Number of washes	L^*	a^*	b^*	h°	λ_{max}	
Green 2	*Diresul BRI*	0	41.4	−18.7	−10.4	21.4	209.1	640
		5	41.8	−18.5	−10.4	21.3	208.9	640
	H_2O_2	0	45.1	−24.2	−15.4	28.7	212.4	620
		5	44.8	−24.4	−15.5	28.8	212.5	620
	Air	0	41.8	−14.6	−11.2	18.4	217.5	640
		5	42.2	−14.4	−11.1	18.3	217.4	640
Brown 1:1	*Diresul BRI*	0	58.6	1.6	10.7	10.8	81.7	400
		5	58.8	1.7	10.8	10.8	81.8	400
	H_2O_2	0	60.4	−1.3	9.0	9.1	97.9	400
		5	61.2	−1.3	9.2	9.2	98.2	400
	Air	0	56.5	−0.6	10.7	10.8	93.2	400
		5	57.1	−0.6	10.8	10.9	93.1	400
Navy 11	*Diresul BRI*	0	33.3	1.0	−13.9	14.0	273.9	600
		5	33.8	1.0	−13.8	14.0	273.2	600
	H_2O_2	0	32.1	3.7	−21.1	21.4	279.9	580
		5	31.8	3.6	−20.8	21.3	279.3	580
	Air	0	33.8	−0.9	−15.6	15.7	266.8	600
		5	34.3	−0.8	−15.5	15.6	266.5	600
Yellow 22	*Diresul BRI*	0	78.9	0.4	36.4	36.9	89.7	400
		5	79.1	0.5	36.2	36.8	89.6	400
	H_2O_2	0	77.8	−0.4	41.8	40.8	88.1	400
		5	77.9	−0.3	41.7	40.9	88.2	400
	Air	0	72.5	1.0	30.1	30.1	88.1	400
		5	72.8	1.3	29.9	30.2	88.2	400
Black 1	*Diresul BRI*	0	18.4	−0.5	−2.2	2.3	257.7	600/620
		5	18.8	−0.4	−2.1	2.4	257.6	600
	H_2O_2	0	17.8	−0.5	−3.7	3.7	262.6	620
		5	18.2	−0.4	−3.5	3.5	261.3	620
	Air	0	19.8	2.5	1.1	2.7	203.6	400
		5	20.1	2.5	1.3	2.6	202.1	400

In terms of the effects of the three oxidation systems on the fastness of the 10% omf dyeings to repeated washing, the colorimteric data obtained for dyeings both before and after washing five times (Table 8) reveals that the dyeings displayed very good fastness overall to repeated washing in terms of shade change and that, with the exception of the navy, yellow and black dyes, the oxidation systems had little effect on the change in shade of the dyeings. In the cases of the aforementioned three dyes, air oxidation resulted in slightly lower

Table 8
Effect of oxidation system on shade change for 10% omf dyeings (pH 7; 98 °C; 20:1 liquor ratio; reducing system 1)

Dye	Oxidation system	Number of washes				
		1	2	3	4	5
Green2	*Diresul BRI*	4/5	5	5	5	5
	H_2O_2	5	5	5	5	5
	Air	4/5	5	5	5	5
Brown 1:1	*Diresul BRI*	3/4	4	4	5	5
	H_2O_2	4	4	4	5	5
	Air	3	5	5	5	5
Navy 11	*Diresul BRI*	4	4	5	5	5
	H_2O_2	4	4	5	5	5
	Air	3	4	4	4	4
Yellow 12	*Diresul BRI*	4	4	5	5	5
	H_2O_2	4	4	5	5	5
	Air	3/4	4	4	5	5
Black 1	*Diresul BRI*	4/5	5	5	5	5
	H_2O_2	4/5	5	5	5	5
	Air	4	4/5	5	5	5

fastness to washing than oxidation using the two liquid oxidation systems. Generally, the fastness ratings were lower for the first two washes than for the remaining three washes in the five cycle wash system. This finding concurrs with that made previously in the case of the effect of the various reducing systems on shade change and can be attributed, as before, to insufficient removal of surface dye at the end of the oxidation process, which infers, again, that the dyeings had not been adequately washed-off after oxidation; this matter is discussed later.

From the viewpoint of the staining of adjacent cotton and nylon 6,6 multifibre that occurred during repeated wash testing, Table 9 shows that was observed earlier for the seven reducing systems, the extent of staining decreased with increasing number of washes; also, for the last two or three wash tests, the general level of staining was very good/excellent. Presumably, the lower ratings observed in the extent of staining (Table 9) obtained for the first one or two wash cycles can, once again, be attributed to insufficient removal of surface dye at the end of oxidation.

Table 10 shows that with the exception of the black dye, the dyeings displayed poor fastness to light and, also, that with the exception of the black dye, the three oxidation systems had no effect on the light fastness of the dyeings.

3.3. *Wash-off*

As discussed earlier in terms of the effects of reducing agent and oxidation system on dyeing, it was observed that lower ratings were obtained in the cases of both shade change and staining obtained for the first one or two of the five washing cycles. This was assumed to be attributable to insufficient removal of surface dye at the end of the oxidation process, because, the initially low ratings achieved for the first one or two washes increased for subsequent washes, eventually reaching a rating of very good/excellent for the last two or three wash cycles. To investigate this assumption, dyeings were subjected to four different ‘wash-off’ treatments, each of which involved treating dyed samples in stirred, aqueous solutions of four different compounds (*Formosul GR*, *Sandoclean PC*, *Diresul EW* and *Cyclanon ECO*) at 98 °C for 20 min using a 50:1 liquor ratio. A dyeing which had been rinsed only in running tap water for five minutes prior to drying was used as a control against which the washed-off dyeings were compared, in colorimetric and wash fastness terms. Of the compounds used, only one is recommended, commercially, for the wash-off of sulphur dyes on polyamide fibres, namely *Diresul EW* [4]; *Formosul GR* was selected on the basis of its use in the stripping of sulphur dyes from dyed nylon [4] and the remaining two compounds were chosen because of their effectiveness in the wash-off of vat dyes on polyamide fibres [6]. In this part of the study, the five dyes were applied (Fig. 1) at 98 °C, pH 7 using a liquor ratio of 20:1, employing *Formosul GR* as reducing agent and oxidation system 2 (*Diresul BRI*; Table 2).

Table 11 shows the colorimetric data obtained for the four wash-off methods together with that of the control dyeing (one which had been rinsed in tap water before drying). For each of the five dyes used, it is evident that each wash-off method removed more dye than had been removed from the control dyeing by rinsing in water only. This is clearly illustrated by Fig. 4 which shows the colour difference (expressed in ΔE^* units) between a

Table 9
Effect of oxidation system on staining (98 °C; pH 7; 20:1 liquor ratio; reducing system 1)

Dye	Oxidation system	Number of washes									
		1		2		3		4		5	
		Cotton	Nylon 6,6	Cotton	Nylon 6,6	Cotton	Nylon 6,6	Cotton	Nylon 6,6	Cotton	Nylon 6,6
Green 2	*Diresul BRI*	4/5	5	4/5	5	5	5	5	5	5	5
	H_2O_2	4	5	4/5	5	5	5	5	5	5	5
	Air	4	4/5	4/5	5	5	5	5	5	5	5
Brown 1:1	*Diresul BRI*	3/4	4	4	4/5	4/5	5	5	5	5	5
	H_2O_2	3/4	4	4	4	4	5	4	5	4	5
	Air	4	4	4	4	4	5	4	5	4	5
Navy 11	*Diresul BRI*	3/4	4	3/4	4	3/4	4/5	4	5	4	5
	H_2O_2	3/4	5	4/5	5	5	5	5	5	5	5
	Air	3	4/5	4/5	5	5	5	5	5	5	5
Yellow 22	*Diresul BRI*	3/4	4	3/4	4	4	5	4	5	4	5
	H_2O_2	4	4	4	4	4	5	4	5	4	5
	Air	4	4	4	4	4	5	4	5	4	5
Black 1	*Diresul BRI*	4	5	4/5	5	5	5	5	5	5	5
	H_2O_2	4	5	4/5	5	5	5	5	5	5	5
	Air	3/4	4/5	4/5	5	4/5	5	4/5	5	5	5

Table 10
Effect of oxidation system on light fastness of 10% omf dyeings (98 °C; pH 7; 20:1 liquor ratio; reducing system 1)

Dye	Oxidation system	Rating
Green 2	*Diresul BRI*	2
	H_2O_2	2
	Air	2
Brown 1:1	*Diresul BRI*	2
	H_2O_2	2
	Air	2
Navy 11	*Diresul BRI*	2
	H_2O_2	2
	Air	2
Yellow 22	*Diresul BRI*	2
	H_2O_2	2
	Air	2
Black 1	*Diresul BRI*	6
	H_2O_2	6
	Air	4

given washed-off sample and the corresponding control dyeing. It is clear that the four compounds used for wash-off varied in the extent of removal of dye and also, that the effectiveness of a given compound varied for different dyes.

The results in Fig. 4 show that with the exception of the yellow dye, *Formosul GR* and *Cyclanon ECO* removed more dye during wash-off than

Table 11
Effect of wash-off on colorimetric data for 10% omf dyeings (pH 7; 98 °C; 20:1 liquor ratio; reducing system 1; oxidation system 2)

Dye	Wash-off	L^*	a^*	b^*	C^*	$h°$	λ_{max}
Green 2	Nil	32.1	−16.0	−11.3	63.8	21.1	660
	Formosul GR	45.4	−19.1	−7.2	52.8	20.4	660
	Diresul EW	44.3	−18.7	−9.2	56.9	20.8	640
	Cyclanon ECO	43.9	−20.8	−9.7	62.1	22.9	640
	Sandoclean PC	47.3	−19.9	−4.6	51.7	20.5	640
Brown 1:1	Nil	52.2	1.8	11.5	38.0	11.7	420
	Formosul GR	59.8	0.1	15.1	21.6	15.1	400
	Diresul EW	52.8	0.2	10.7	31.4	10.7	400
	Cyclanon ECO	60.1	1.6	12.3	19.9	12.4	400
	Sandoclean PC	62.2	0.9	15.2	20.2	15.2	400
Navy 11	Nil	35.3	0.0	−12.2	83.5	12.2	600
	Formosul GR	42.2	−3.4	−10.5	50.3	5.1	600
	Diresul EW	36.8	0.0	−13.6	69.5	13.6	600
	Cyclanon ECO	36.0	0.0	−15.3	73.1	15.3	600
	Sandoclean PC	39.0	−0.5	−12.5	60.1	12.5	600
Yellow 22	Nil	79.0	0.4	36.4	26.7	36.4	400
	Formosul GR	80.5	−5.8	33.4	9.7	33.9	400
	Diresul EW	81.0	−4.2	34.6	9.8	34.9	400
	Cyclanon ECO	81.2	−4.2	33.5	9.1	33.7	400
	Sandoclean PC	81.0	−4.2	34.6	9.8	34.9	400
Black 1	Nil	21.1	−0.4	−1.8	315.8	1.9	580
	Formosul GR	21.9	−2.8	−0.6	239.4	2.8	400
	Diresul EW	20.0	−1.3	−2.2	269.8	2.6	620
	Cyclanon ECO	19.5	−0.7	−2.4	278.9	2.5	600
	Sandoclean PC	22.0	−2.4	0.0	237.5	0.4	400

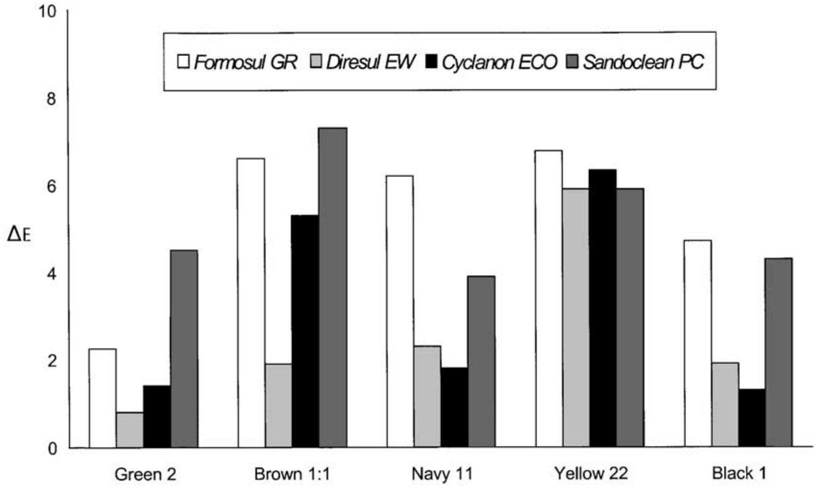

Fig. 4. Colour difference obtained for different wash-off methods (pH 7; 98 °C; 20:1 liquor ratio; reducing system 1; oxidation system 1).

Sandoclean PC and *Diresul EW*. Although precise details of the four commercial compounds were not available, it is believed that *Formosul GR* and *Cyclanon ECO* are reducing agents while *Sandoclean PC* and *Diresul EW* are surfactants [12]. If this is the case, then the observed differences in the extent to which the two pairs of compounds removed dye can be attributed to a difference in the mode of action of the two different types of compound. Whereas a reducing agent might be expected to solubilise a large M_r sulphur dye and generate smaller size, water soluble thiol derivatives, a detergent may not be expected to alter the macromolecular state of a sulphur dye and thus, would be expected to remove a lower amount of dye from dyeings. The data in Table 11 also reveals that the different wash-off methods effected the colour of the dyeings, this being especially marked in the case of the black dye. Although the precise reasons for this are not clear, it can be postulated that this can be attributed to the different ways in which the wash-off compounds removed surplus dye.

Table 12
Effect of wash-off on shade change for 10% omf dyeings (pH 7; 98 °C; 20:1 liquor ratio; reducing system 1; oxidation system 2)

Dye	Wash-off	Number of washes				
		1	2	3	4	5
Green 2	*Formosul GR*	5	5	5	5	5
	Diresul EW	4/5	5	5	5	5
	Cyclanon ECO	4/5	5	5	5	5
	Sandoclean PC	5	5	5	5	5
Brown 1:1	*Formosul GR*	4	4	4	5	5
	Diresul EW	4	4	5	5	5
	Cyclanon ECO	3/4	4	4	5	5
	Sandoclean PC	4	4	5	5	5
Navy 11	*Formosul GR*	5	5	5	5	5
	Diresul EW	4	4	5	5	5
	Cyclanon ECO	4	4	5	5	5
	Sandoclean PC	4	5	5	5	5
Yellow 22	*Formosul GR*	4	4	5	5	5
	Diresul EW	3/4	5	5	5	5
	Cyclanon ECO	3/4	4	5	5	5
	Sandoclean PC	4/5	5	5	5	5
Black 1	*Formosul GR*	4/5	5	5	5	5
	Diresul EW	4/5	4/5	5	5	5
	Cyclanon ECO	4	5	5	5	5
	Sandoclean PC	4	4/5	5	5	5

In terms of the effect of wash-off on fastness to repeated washing, Table 12 shows that the fastness ratings were lower for the first wash and the second washes than for the remaining three washes in the five cycle wash system. In cases of the latter three washes, fastness was, for all dyes investigated, excellent. These findings are very similar to those previously obtained (Tables 4 and 8) for dyeings which had been only rinsed in water after dyeing. Furthermore, comparision of the shade change results displayed in Tables 4 and 8 with

Table 13
Effect of wash-off on staining obtained for 10% omf dyeings (pH 7; 98 °C; 20:1 liquor ratio; reducing system 1; oxidation system 2)

Dye	Wash-off	Number of washes									
		1		2		3		4		5	
		Cotton	Nylon 6,6	Cotton	Nylon 6,6	Cotton	Nylon 6,6	Cotton	Nylon 6,6	Cotton	Nylon 6,6
Green 2	*Formosul GR*	4/5	5	4/5	5	5	5	5	5	5	5
	Diresul EW	5	5	5	5	5	5	5	5	5	5
	Cyclanon ECO	4	5	4	5	5	5	5	5	5	5
	Sandoclean PC	4	5	4/5	5	5	5	5	5	5	5
Brown 1:1	*Formosul GR*	5	5	4	4/5	4	4/5	5	5	5	5
	Diresul EW	5	5	5	5	5	5	5	5	5	5
	Cyclanon ECO	4	5	4	5	5	5	5	5	5	5
	Sandoclean PC	5	5	5	5	5	5	5	5	5	5
Navy 11	*Formosol GR*	3/4	5	5	5	5	5	5	5	5	5
	Diresul EW	5	5	5	5	5	5	5	5	5	5
	Cyclanon ECO	4	5	4	5	4	5	4	5	5	5
	Sandoclean PC	5	5	5	5	5	5	5	5	5	5
Yellow 22	*Formosul GR*	5	5	5	5	5	5	5	5	5	5
	Diresul EW	5	5	5	5	5	5	5	5	5	5
	Cyclanon ECO	4	5	4	4	4/5	5	5	5	5	5
	Sandoclean PC	5	5	5	5	5	5	5	5	5	5
Black 1	*Formosul GR*	5	5	5	5	5	5	5	5	5	5
	Diresul EW	5	5	5	5	5	5	5	5	5	5
	Cyclanon ECO	4	5	4	5	5	5	5	5	5	5
	Sandoclean PC	5	5	5	5	5	5	5	5	5	5

those in Table 12 reveals that the additional wash-off stage, using the four different comounds, did not improve the level of shade change obtained for the first two washes.

The staining results presented in Table 13 clearly show that a very low level of staining was obtained as a result of repeated washing at 60 °C. Indeed, the nylon 6,6 component was unstained for each of the dyes used and the level of staining of the cotton component was very low. A comparison of the results in Table 13 with those obtained earlier (Tables 5 and 9) clearly shows that wash-off, with each of the four compounds used, markedly improved the staining of the adjacent multifibre strip materials. This may be due to the lower colour strength of the washed-off dyeings.

Table 14 shows that with the exception of the black dye, the dyeings displayed poor fastness to light and, with the exception of the black dye, the four wash-off methods had no effect on the light fastness of the dyeings.

Table 14
Effect of wash-off on light fastness for 10% omf dyeings (pH 7; 98 °C; 20:1 liquor ratio; reducing system 1; oxidation system 2)

Dye	Wash-off	Rating
Green 2	*Formosul GR*	2
	Diresul EW	2
	Cyclanon ECO	2
	Sandoclean PC	2
Brown 1:1	*Formosul GR*	2
	Diresul EW	2
	Cyclanon ECO	2
	Sandoclean PC	2
Navy 11	*Formosul GR*	2
	Diresul EW	2
	Cyclanon ECO	2
	Sandoclean PC	2
Yellow 22	*Formosul GR*	2
	Diresul EW	2
	Cyclanon EGO	2
	Sandoclean PC	2
Black 1	*Formosul GR*	6
	Diresul EW	6
	Cyclanon ECO	6
	Sandoclean PC	6

4. Conclusions

For the five dyes used, It was found that the different reductants affected not only the colour strength of the dyeings but also the colour of the dyeings. Two of the reducing systems studied had a deleterious effect on colour strength and the level of wash fastness achieved for some of the dyes. However, overall, the dyeings displayed very good fastness to the five repeated wash tests. There was very little difference between the three oxidising systems examined in terms of the colour strength of the dyeings, but the colour of the dyeings differed for the three oxidation systems studied; the wash fastness of the dyeings was little effected by the type of oxidant used. Washing-off of the dyeings markedly reduced the extent of staining of adjacent multifibre strip but did not improve the colour change that occurred upon repeated washing. With the exception of the black dye, the dyes displayed poor fastness to light and this was, in general, little influenced either by reductant, oxidant or wash-off.

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