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The Aftertreatment of Sulphur Dyes on Cotton

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ABSTRACT

The effect on wash fastness of aftertreating the dyeings of six C.I. Solubilised Sulphur dyes on cotton with a proprietary, reactive, cationic fixing agent was examined. The fixing agent improved wash fastness when applied to the oxidised dyeings and also when applied to the leuco derivative of the dye in place of the oxidation stage in the dyeing process. The possible mechanisms in operation are discussed. © 1997 Elsevier Science Ltd

Keywords: Sulphur dyes, cotton, aftertreatment, wash fastness.

INTRODUCTION

The aftertreatment of dyeings on cellulosic fibres to confer improved wash fastness is mostly confined to direct dyes and, in this context, a plethora of appropriate cationic fixing agents is commercially available. The vast majority of such compounds are, typically, polycations of high molecular mass that enhance wash fastness by the means of a large molecular size, low aqueous solubility complex that is formed between the anionic direct dye and the cationic fixing agent.

Recent work has shown that the wash fastness of the oxidised dyeings of C.I. Solubilised Sulphur, C.I. Leuco Sulphur and C.I. Sulphur dyes on cotton was improved by an aftertreatment with cationic fixing agents, that were intended for use with direct dyes, applied using a simple exhaust application method[1]. Further work revealed that the wash fastness of C.I. Leuco Sulphur dyes on cotton was improved by the application of two commercial cationic fixing agents when applied as an aftertreatment using both Pad-Dry and Pad-Flash Cure methods.[2] The improved wash fastness of the sulphur dyeings on cotton was considered to occur by a mechanism that was identical to that operating in the case of direct dyeings, namely the formation of a large molecular size, sulphur dye–cationic agent complex of low aqueous solubility.[1,2]

A reactive cationic fixing agent, *Solfix E* (Ciba-Geigy), was recently introduced for the aftertreatment of direct dyes on cellulosic fibres[3,4] and, in a study of the pre-treatment of cotton to enhance its dyeability with reduced C.I. Solubilised Sulphur dyes,[5] it was found that of three commercial cationic fixing agents, pre-treatment with *Solfix E* not only imparted the greatest enhancement of colour strength but also resulted in dyeings of highest wash fastness. It was suggested that these findings were possibly due to the fixing agent having reacted with nucleophilic thiol groups in the reduced sulphur dye resulting in the formation of a large molecular size, sulphur dye–*Solfix E* compound that possessed low diffusional power within the fibre.

The work reported in this paper comprises an examination of the effect, on the wash fastness of several C.I. Solubilised Sulphur dyes on cotton, of aftertreating the oxidised and/or the reduced forms of the dyes with the proprietary reactive, cationic fixing agent, *Solfix E*.

EXPERIMENTAL

Materials

Fabric

Scoured and bleached woven cotton (150 g/m^2) was used.

Dyes

The dyes listed in Table 1 were used, each generously supplied J. Robinson Ltd; the dyes were used without purification.

TABLE 1
Dyes Used and Additions Made to Dyebath

Sulphosol	C.I. Solubilised Sulphur	cm^3 of 5% aqueous *Leucad 71* solution		
		2% omf	6% omf	10% omf
Black SG	Black 1	3	9	15
Yellow SR	Yellow 23	7	12	20
Green SBCF	Green 2	3	9	15
Dark Blue SL	Blue 5	2.1	4.5	7.5
Sky Blue	Blue 15	3	9	15
Bordeaux SB	Red 6	2	6	10

Reducing agent

A commercial sample of *Leucad 71* was supplied by J. Robinson Ltd.

Cationic fixing agent

A commercial sample of *Solfix E* was generously provided by Ciba-Geigy.

All other reagents were of general purpose grade.

Procedures

Dyeing

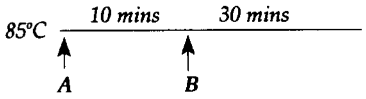
All dyeings (2%, 6% and 10% omf), using fabric samples (10 g) which had been wetted in cold distilled water, were carried out in sealed, PTFE dyeing tubes of 100 cm^3 capacity housed in a John Jeffries Rota Dyer laboratory-scale dyeing machine, using a 7:1 liquor ratio. The addition of 2 cm^3 of a 30% aqueous solution of sodium chloride was made to each dyebath. The dyeing method is shown in Fig. 1 and the additions made to the dyebaths are displayed in Table 1.

Oxidation

At the end of dyeing, samples were removed, rinsed thoroughly in cold water and then in hot water and treated in a stirred, aqueous (distilled water) solution (50:1 LR) containing 1 g l^{-1} hydrogen peroxide (30% w/v) and 1 g l^{-1} glacial acetic acid at 60°C for 15 min. At the end of this time, the oxidised samples were removed, rinsed in cold water and allowed to dry in the open air.

Aftertreatment with cationic fixing agent

This was carried out at two different stages in the dyeing process, namely instead of oxidation (i.e. at the end of the application of the reduced [thiolate] form of the dye) and after oxidation. At each of the two stages, the dyed sample was rinsed in cold tap water and aftertreatment performed using the dyeing tubes and machine that were employed in the dyeing process using a



A Dye
Fabric
5% Leucad 71 (Table 1)

B 2 cm^3 of 300 gl^{-1} NaCl

Fig. 1. Dyeing method.

25:1 liquor ratio. The two aftertreatment methods are shown in Fig. 2 and Fig. 3; various concentrations of the cationic fixing agent were used. At the end of aftertreatment, the sample was removed, rinsed in cold water and allowed to dry in the open air.

Colour measurement

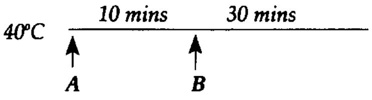
The reflectance values of the dry, dyed samples, were measured using a Colorgen reflectance spectrophotometer interfaced to a personal computer, under illuminant D_{65} using a 10° standard observer with specular component excluded and UV component included. The K/S values and CIE L*, a*, b*, C*, and h° co-ordinates were calculated at the appropriate λ_{max} of each dye. Each fabric sample was folded twice so as to realise a total of four thicknesses of fabric.

The amount of dye that was removed from dyeings during washing was expressed in terms of ΔK/S, the difference in colour strength between dyeings which had been washed and dyeings which had not been washed, which was calculated using eqution (1).

$$\Delta K/S = K/S_{before\ washing} - K/S_{after\ washing} \tag{1}$$

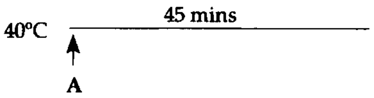
Determination of wash fastness

The fastness of the dry, dyed samples to the ISO CO6/C2 and ISO 4 wash fastness tests was determined using the standard methods[6].



A Solfix E
B 2 cm^3 of 36°Bé (7.5M) NaOH

Fig. 2. Aftertreatment method for oxidised dyeings.



A *Solfix E*

Fig. 3. Aftertreatment method for leuco dyeings.

RESULTS AND DISCUSSION

As mentioned, previous work had shown that the wash fastness of the oxidised dyeings of C.I. Solubilised Sulphur, C.I. Leuco Sulphur and C.I. Sulphur dyes on cotton was markedly improved by an aftertreatment with various cationic fixing agents that were intended for use with direct dyes.[1,2] In this context, *Solfix E*, the proprietary compound used in this work, is a cationic fixing agent intended for use with direct dyes. Thus, an initial study was made of the ability of the fixing agent to enhance the wash fastness of oxidised C.I. Solubilised Sulphur dyeings on cotton.

Dyeings (2%, 6%, and 10% omf) of C.I. Solubilised Sulphur Blue 5 were oxidised and then aftertreated with various concentrations of *Solfix E* using the aftertreatment method shown in Fig. 2; the aftertreated samples were then subjected to the ISO CO6/C2 wash test. From Table 2 it is apparent that aftertreatment markedly improved the wash fastness of each of the three depths of shade used in terms of the three parameters assessed in the wash test (change in shade and staining of adjacent cotton and viscose fabrics). Table 2 also shows the colour strength of the untreated and aftertreated dyeings before wash fastness testing from which it is evident that aftertreatment was accompanied by an increase in colour strength. From the corresponding colorimetric parameters of the dyeings displayed in Table 3, the increased colour strength that accompanied aftertreatment was reflected in the lower L* values of the aftertreated dyeings. The results in Table 3 also reveal that aftertreatment generally caused a slight reddening of shade of the dyeings which persisted after washing. As aftertreatment had markedly improved wash fastness, it was anticipated that aftertreatment with the cationic fixing agent should also have reduced the amount of dye that was removed from the dyeings during washing so that the difference in colour strength between dyeings which had been washed and dyeings which had not been washed ($\Delta K/S$) should have been reduced. The $\Delta K/S$ values in Table 2 show that aftertreatment significantly reduced the extent of 'washdown' of the dyeings that occurred during washing; furthermore, it is apparent that for each of the three depths of shade used, the greatest reduction in $\Delta K/S$ was achieved using the higher of the three concentrations of *Solfix E* used, namely 2%, 4% and 6% omf.

Table 4 reveals that the aftertreatment of 2%, 6%, and 10% omf oxidised dyeings of C.I. Solubilised Sulphur Yellow 23 with 2%, 4% and 6% omf *Solfix E* significantly increased the wash fastness of the dyeings. However, the K/S values in Table 4 demonstrate that aftertreatment reduced the colour strength of the dyeings prior to washing, a finding that was endorsed by the L* values displayed in Table 5; furthermore, the $\Delta K/S$ values in Table 4 show that aftertreatment did not reduce the extent of washdown that

TABLE 2
Wash Fastness (ISO CO6/C2) Results for C.I. Solubilised Sulphur Blue 5

Dye (omf)	After-treatment (omf)	Oxidised					Leuco				
		Shade change	Staining of adjacent Viscose	Staining of adjacent Cotton	K/S before washing	ΔK/S	Shade change	Staining of adjacent Viscose	Staining of adjacent Cotton	K/S before washing	ΔK/S
2%	Nil	2/3	3/4	3	3.81	1.40	2/3	3/4	3	3.76	0.98
6%	Nil	3	3/4	3	8.72	1.02	3	3/4	3	8.65	1.60
10%	Nil	3	3/4	3	13.64	0.80	3	3/4	3/4	12.49	0.61
2%	1%	5	5	4/5	3.65	0.04	5	5	5	3.61	0.09
6%	2%	5	5	4/5	10.04	0.52	5	5	5	10.16	0.12
10%	3%	5	5	4/5	14.64	0.30	5	5	5	14.74	0.11
2%	2%	5	5	4/5	4.92	0.11	5	5	5	4.04	0.03
6%	4%	5	5	4/5	10.21	0.10	5	5	5	10.21	0.10
10%	6%	5	5	4/5	15.04	0.13	5	5	5	14.21	0.13

TABLE 3

Colorimetric Data for C.I. Solubilised Sulphur Blue 5

Dyeing	Dye (omf)	Aftertreatment (omf)	L*	a*	b*	C*	h°	L*	a*	b*	C*	h°
Oxidised					*before washing*					*after washing*		
	2%	Nil	42.44	2.05	−19.43	19.54	276.02	43.54	2.65	−19.33	19.51	277.81
	6%	Nil	30.62	2.57	−18.80	18.97	277.78	31.82	2.68	−18.61	18.79	278.20
	10%	Nil	24.47	2.90	−16.87	17.12	279.75	25.74	3.1	−16.07	16.37	280.92
	2%	2%	39.33	2.60	−22.40	22.55	276.62	40.11	2.41	−22.34	22.47	276.16
	6%	4%	29.01	3.33	−20.88	21.14	279.06	29.94	3.1	−20.61	20.84	278.55
	10%	6%	23.92	3.96	−19.59	19.99	281.43	24.30	2.01	−19.41	19.51	275.91
	2%	1%	43.66	2.14	−22.04	22.14	275.55	43.40	3.22	−23.05	23.22	277.97
	6%	2%	29.01	3.81	−21.14	21.48	280.22	29.99	3.51	−21.09	21.38	279.45
	10%	3%	24.07	4.25	−19.71	20.16	282.17	24.48	5.02	−20.99	21.58	283.45
Leuco					*before washing*					*after washing*		
	2%	Nil	41.40	2.56	−18.45	18.63	277.90	44.21	2.86	−22.81	22.99	277.15
	6%	Nil	29.56	2.75	−18.45	18.65	278.48	30.56	3.30	−22.45	22.69	278.36
	10%	Nil	25.47	2.89	−16.76	17.01	279.78	26.57	3.10	−18.76	19.01	279.38
	2%	2%	42.14	2.38	−22.11	22.24	276.14	45.03	3.34	−23.54	23.78	278.08
	6%	4%	29.02	3.64	−21.52	21.83	279.60	29.31	4.67	−24.14	24.59	280.95
	10%	6%	24.67	3.73	−19.98	20.33	280.57	25.55	5.15	−22.06	22.65	283.14
	2%	1%	43.54	2.36	−21.51	21.64	276.26	46.12	3.40	−22.88	23.13	278.45
	6%	2%	28.96	3.56	−21.62	21.91	279.35	29.18	4.93	−22.68	23.21	282.26
	10%	3%	24.18	3.57	−19.50	19.82	280.37	23.34	5.38	−21.28	21.95	284.19

TABLE 4

Wash Fastness (ISO CO6/C2) Results for C.I. Solubilised Sulphur Yellow 23

Dye (omf)	After-treatment (omf)	Oxidised					Leuco				
		Shade change	Staining of adjacent Viscose	Cotton	K/S before washing	ΔK/S	Shade change	Staining of adjacent Viscose	Cotton	K/S be fore washing	ΔK/S
2%	Nil	3/4	4	4	5.84	0.20	3/4	4	4	6.11	0.89
6%	Nil	3/4	4	4	10.21	0.42	3/4	4	4	10.44	1.07
10%	Nil	3/4	4	4	10.84	0.90	3/4	4	4	10.96	0.71
2%	2%	5	5	4/5	3.89	0.91	4/5	5	4/5	8.95	0.12
6%	4%	5	5	4/5	8.96	0.46	5	5	4/5	8.88	0.20
10%	6%	5	5	4/5	10.89	0.72	5	5	4/5	10.98	0.22

TABLE 5
Colorimetric Data for C.I. Solubilised Sulphur Yellow 23

Dyeing	Dye (omf)	After-treatment (omf)	L*	a*	b*	C*	h°	L*	a*	b*	C*	h°
Oxidised						*before washing*					*after washing*	
	2%	Nil	69.51	10.33	49.21	50.28	78.14	70.36	10.78	50.04	51.51	77.84
	6%	Nil	62.41	14.10	54.31	56.40	75.52	63.18	14.48	55.02	56.89	75.82
	10%	Nil	57.92	16.35	53.10	55.56	72.89	58.48	17.05	53.81	56.45	72.42
	2%	2%	71.61	6.86	46.71	47.21	81.25	72.82	7.44	47.12	47.70	81.03
	6%	4%	64.86	11.77	53.80	55.07	77.66	65.16	12.30	54.13	55.51	77.20
	10%	6%	60.87	12.54	54.04	55.48	76.94	61.46	13.05	54.63	56.17	76.56
Leuco						*before washing*					*after washing*	
	2%	Nil	71.23	8.10	48.21	48.89	80.46	71.86	8.43	48.63	49.36	80.17
	6%	Nil	60.11	13.77	50.76	52.59	74.82	60.91	14.15	51.03	52.96	74.50
	10%	Nil	58.77	14.21	14.33	20.18	45.24	59.32	14.71	14.71	20.80	45.00
	2%	2%	64.21	12.03	52.89	54.24	77.19	64.83	12.33	53.27	54.68	76.97
	6%	4%	65.01	10.18	52.11	53.10	78.95	65.42	10.94	52.49	53.62	78.23
	10%	6%	60.44	11.81	52.71	54.02	77.37	61.31	12.29	53.12	54.52	76.97

occurred during washing. These latter findings differ to those obtained for C.I. Solubilised Sulphur Blue 5. The colorimetric parameters in Table 5 show that aftertreatment caused a slight greening of shade of the dyeings; this relatively small alteration of shade remained after washing.

It seems pertinent to discuss the possible mechanism by which *Solfix E* increased the wash fastness of the oxidised dyeings of C.I. Sulphur Blue 5. The particular aftertreatment method used (Fig. 2) was based on that recommended by the maker of the cationic fixing agent for use on direct dyeings on cotton[6] in that after an initial holding period of 10 min, NaOH was added to the treatment bath. As proposed in a previous paper,[5] under the alkaline application conditions used to apply *Solfix E* to dyed cotton, it is possible that the cationic polyamine self–reacts to form a larger molecular size, cationic polymer within the dyed fibre. From the results so far presented, it is proposed that the enhanced wash fastness conferred upon the oxidised dyeings of C.I. Solubilised Sulphur Blue 5 by *Solfix E* aftertreatment can be attributed to the formation of a large molecular size, sulphur dye–cationic agent complex of low aqueous solubility in the fibre and/or a 'layer' of polycation molecules at the periphery of the dyed substrate which reduced the diffusion of dye out of the dyed, treated fibre during washing. This proposal imitates that made earlier to explain the finding that the oxidised dyeings of C.I. Solubilised Sulphur, C.I. Leuco Sulphur and C.I. Sulphur dyes on cotton was markedly improved by an aftertreatment with other cationic fixing agents.[1,2]

However, *Solfix E* differs to the cationic agents previously employed in the aftertreatment of sulphur dyeings[1,2] in that it is reactive and, as a result, an additional argument can be extended to explain the possible mechanism of its action. Theoretically, at the end of the oxidation stage in the dyeing process, the resulting sulphur dye should be insoluble and contain no free, nucleophilic thiolate groups. However, it may be possible that thiolate groups were present in the oxidised dye; also, other nucleophilic groups such as amino might also be present in the dye. If this were the case then these strong nucleophiles in the dye could attack the reactive groups in the cationic fixing agent and so form a large molecular size, sulphur dye–*Solfix E* compound which, owing to its large size, could be expected to possess very low diffusional power within the substrate and thus display high wash fastness. It was decided to investigate this possibility of covalent sulphur dye–*Solfix E* reaction by treating the leuco forms of C.I. Solubilised Sulphur Blue 5 and C.I. Solubilised Sulphur Yellow 23 with the reactive cationic fixing agent.

As mentioned earlier, the particular aftertreatment method which had been used to apply the fixing agent to the oxidised dyeings (Fig. 2) involved an initial holding period of 10 min, after which NaOH was added to the treatment bath, so that, presumably, the cationic polyamine self–reacts to form a larger molecular size, cationic polymer within the dyed fibre. In this part of the work, it was decided to apply the fixing agent to the rinsed dyeing in its leuco (i.e. un–oxidised) form. Since the thiol groups in the leuco derivative of the dye are very strong nucleophiles, it was decided to dispense with the addition of NaOH in the treatment bath (Fig. 3), as it was considered that reaction between the fixing agent and the nucleophilic thiolate groups in the dye should be capable of occurring readily at 40°C under neutral pH conditions.

Table 2 shows the wash fastness results obtained for 2%, 6% and 10% omf dyeings of C.I. Solubilised Sulphur Blue 5 which had been treated, in the reduced (leuco) form, with various concentrations of *Solfix E* using the application method shown in Fig. 3. In Table 2, the untreated dyeings against which the treated dyeings have been compared had been oxidised using hydrogen peroxide. Clearly, treatment with the fixing agent resulted in a major improvement in the fastness of the dye to the ISO CO6/C2 wash test. The K/S values of the dyeings before washing reveal that treatment of the thiolate derivative of the dye with *Solfix E* resulted in dyeings that were generally deeper in depth than their oxidised counterparts. Furthermore, the K/S values quoted in Table 2 demonstrate that the wash fastness test removed much less dye from the treated leuco dyeings than from the corresponding oxidised dyeings. The colorimetric parameters presented in Table 3 show that treatment of the leuco derivative of the dye caused a slight change in the shade of the dyeings both before and after washing.

Table 4 shows the wash fastness results obtained for 2%, 6% and 10% omf dyeings of C.I. Solubilised Sulphur Yellow 23 which had been treated in the thiolate form with the cationic fixing agent as well as those secured for untreated, oxidised dyeings. It is quite apparent that the aftertreated leuco dyeings were of much higher wash fastness than the corresponding untreated, oxidised dyeings. The K/S values of the dyeings before washing reveal that treatment of the thiolate derivative of the dye with *Solfix E* resulted in dyeings that were slightly paler in depth than their oxidised counterparts although the ΔK/S values show that the wash fastness test removed much less dye from the treated leuco dyeings than from the corresponding oxidised dyeings. The colorimetric parameters in Table 5 show that treatment of the leuco derivative of the dye caused a slight greening of shade both before and after washing.

From the results presented in Tables 2 and 4, it is possible to make a comparison of the findings obtained for the aftertreated oxidised dyeing with those secured for the aftertreated leuco dyeings. Although the colour strength of the treated leuco dyeings was either very similar to or slightly higher than that of the aftertreated oxidised dyeings, the wash fastness of the treated leuco dyeings was 0.5 to 1 point higher than the corresponding aftertreated oxidised dyeing. Furthermore, the ΔK/S values in Tables 2–4 show that, in general, the amount of dye removed from the two sets of dyeings during washing was similar. Hence, the application of *Solfix E* to the leuco form of the dye yielded dyeings that were very similar, in terms of

TABLE 6
Wash Fastness (ISO 4) Results for 6% omf Leuco Dyeings

Aftertreatment (omf)	Leuco				
	Shade change	Staining of adjacent		K/S before washing	ΔK/S
		Viscose	Cotton		
C.I. Solubilised Sulphur Black 1					
Nil	4	5	2/3	14.50	1.33
1%	5	5	4/5	14.08	0.05
2%	5	5	4/5	14.50	0.67
4%	5	5	4/5	14.45	1.11
6%	5	5	4/5	14.21	0.44
8%	5	5	4/5	14.12	0.10
C.I. Solubilised Sulphur Blue 15					
Nil	2/3	3	3/4	15.50	3.17
1%	3	3	3/4	14.17	0.38
2%	3	3/4	3/4	14.54	0.45
4%	4	4	3/4	14.45	0.91
6%	4	4/5	3/4	14.50	0.54
8%	4	4/5	3/4	14.09	0.18

TABLE 7
Wash Fastness (ISO 4) Results for 6% omf Leuco Dyeings

Aftertreatment (omf)	Leuco				
	Shade change	Staining of adjacent		K/S before washing	ΔK/S
		Viscose	Cotton		
C.I. Solubilised Sulphur Green 2					
Nil	3/4	4	3/4	12.21	1.18
1%	4	4/5	4	12.75	1.56
2%	4	4/5	4	13.05	1.50
4%	4/5	5	4	13.39	0.73
6%	4/5	5	4	12.72	0.38
8%	4/5	5	4	13.64	0.77
C.I. Solubilised Sulphur Red 6					
Nil	2	3	1/2	13.77	0.87
1%	3	3/4	3/4	15.57	3.24
2%	3	3/4	3/4	14.79	3.08
4%	3/4	3/4	3/4	14.99	1.77
6%	3/4	4	3/4	14.69	2.78
8%	3/4	4	3/4	14.54	2.31

TABLE 8

Colorimetric Data for 6% omf Leuco Dyeings

C.I. Solubilised Sulphur	After-treatment (omf)	L*	a*	b*	C*	h°	L*	a*	b*	C*	h°
Black 1			*before washing*						*after washing*		
	Nil	21.21	−0.46	−4.09	4.18	263.58	21.90	−0.84	−4.79	4.86	260.05
	1%	22.68	−0.87	−3.31	3.42	255.27	22.48	−0.43	−3.98	4.00	263.83
	2%	22.50	−0.78	−3.85	3.93	258.55	23.65	−0.52	−4.00	4.03	262.59
	4%	22.28	−0.70	−3.79	3.85	259.54	23.24	−0.40	−4.23	4.25	264.20
	6%	22.56	−0.87	−3.68	3.78	256.70	22.92	−0.60	−4.10	4.14	261.67
	8%	22.41	−0.54	−3.63	3.67	261.54	22.57	−0.61	−4.17	4.21	261.68
Blue 15			*before washing*						*after washing*		
	Nil	29.95	−8.55	−19.11	20.94	245.90	30.61	−9.04	−19.88	21.84	245.55
	1%	29.77	−8.18	−17.60	19.41	245.07	30.01	−8.64	−19.13	20.99	245.69
	2%	29.25	−7.93	−17.75	19.44	245.93	30.18	−8.79	−19.03	20.96	245.21
	4%	29.34	−8.10	−17.56	19.34	245.24	29.92	−8.57	−19.27	21.09	246.02
	6%	29.11	−7.79	−17.61	19.26	246.14	30.48	−8.90	−19.38	21.33	245.33
	8%	29.34	−8.22	−18.11	19.89	245.59	30.10	−8.65	−19.04	20.91	245.57

TABLE 9
Colorimetric Data for 6% omf Leuco Dyeings

C.I. Solubilised Sulphur	After-treatment (omf)	L*	a*	b*	C*	h°	L*	a*	b*	C*	h°
Green 2			*before washing*						*after washing*		
	Nil	33.14	−17.87	−7.53	19.21	203.08	33.74	−17.98	−7.89	19.63	203.69
	1%	34.23	−18.86	−8.39	20.64	203.95	31.87	−17.56	−9.48	19.96	208.36
	2%	33.46	−18.45	−8.23	20.20	204.04	32.30	−19.31	−9.52	21.37	206.46
	4%	32.97	−18.32	−8.16	20.06	204.01	32.57	−17.61	−9.38	19.95	208.04
	6%	33.78	−18.52	−7.98	20.17	203.13	33.38	−17.83	−9.37	20.14	207.72
	8%	33.57	−19.01	−8.58	20.86	204.29	33.72	−17.66	−9.22	20.21	207.89
Red 6			*before washing*						*after washing*		
	Nil	29.55	16.64	3.78	17.06	12.80	29.91	16.93	4.11	17.42	13.65
	1%	24.45	15.18	4.12	15.73	15.18	28.34	17.56	4.42	18.11	14.13
	2%	25.56	16.18	4.11	16.69	14.25	29.04	17.56	4.77	18.20	15.20
	4%	24.96	16.05	4.23	16.60	14.76	27.51	17.08	4.14	17.57	13.63
	6%	25.24	16.03	4.12	16.55	14.41	28.48	17.00	4.23	17.52	13.97
	8%	25.53	16.50	4.11	17.00	13.99	28.41	17.43	4.11	17.91	13.27

depth of shade and colour, but marginally superior in terms of wash fastness, to those obtained by the application of the fixing agent to the oxidised dyeings.

It was decided to further examine the effect, on wash fastness, of applying *Solfix E* to the leuco forms of other C.I. Solubilised Sulphur dyes; in this case, the ISO 4 wash test method was employed. Tables 6 and 7 show the effect of different concentrations of *Solfix E* (1% to 8% omf) on the wash fastness of 6% omf dyeings of four different C.I. Solubilised Sulphur dyes; the untreated dyeings, against which the aftertreated dyeings have been compared, had been oxidised using hydrogen peroxide. In all cases, treatment of the thiolate derivative of the dye with the cationic fixing agent enhanced the fastness of the dyeings. Generally, wash fastness improved with increasing amount of *Solfix E* used up to 4% omf, after which, wash fastness was unaffected by further increase in concentration of fixing agent used. Typically, the colour strength of the treated leuco dyeings was similar to or slightly higher than that of the corresponding untreated, oxidised dyeing; generally, the ΔK/S values showed that the amount of dye removed during washing was lower from the aftertreated thiolate dyeings than from the corresponding untreated oxidised dyeings. The colorimetric data (Tables 8 and 9) show that for each of the four dyes used, treatment with the fixing agent caused a slight change in shade of the dyeings when compared to that of the corresponding untreated, oxidised dyeing.

CONCLUSIONS

The proprietary, reactive, cationic fixing agent improved the wash fastness of oxidised dyeings of C.I. Solubilised Sulphur dyes when applied using an exhaust method based on that recommended for the aftertreatment of direct dyes on cotton. Similar and also higher levels of wash fastness improvement were secured when the fixing agent was applied to the leuco (unoxidised) form of the dyes. The findings suggest that treatment of the leuco form of the dye with *Solfix E* could replace the traditional oxidation stage in the dyeing process and thereby offer enhanced wash fastness without recourse to an additional, time-consuming and thus expensive, aftertreatment.

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