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Aftertreatments to Improve the Wash Fastness of Sulphur Dyeings on Cotton

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ABSTRACT

The effectiveness of five cationic agents, when applied to the oxidised dyeings of four CI Solubilised Sulphur dyes, four CI Leuco Sulphur dyes and four CI Sulphur dyes, in improving the fastness of the dyeings to the ISOC06/C2 wash test was assessed. Each of the five cationic agents markedly improved the wash fastness properties of the twelve dyes used. Whilst aftertreatment caused a slight flattening of shade it had little effect on the colour strength (K/S) of the dyeings. As the enhanced wash fastness clearly indicates that the polycationic agents were adsorbed on to the dyed substrate, it is postulated that this adsorption may have arisen by virtue of electrostatic forces operating between the cationic agents and anionic carboxyl groups in the fibre and/or anionic groups in the dye molecules; alternatively, intermolecular forces other than ion–ion may have contributed towards uptake of the polycations. The mechanism by which the improvement in wash fastness was effected may be the formation of a large molecular size, dye–cationic agent complex of reduced aqueous solubility or the presence of a peripheral 'layer' of polycation molecules having reduced the diffusion of dye out of the dyed, treated fibre during washing. Further work is required to clearly establish the mechanism by which the observed enhanced fastness is achieved.

INTRODUCTION

Sulphur dyes are one of the most popular of all dye classes used on cellulosic fibres and their blends.[1-3] On cellulosic fibres, the dyes

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characteristically furnish inexpensive medium to heavy depth shades of moderate to good light fastness, good wet fastness but poor fastness to bleaching.[2-4]

With each of the three commercially used types of sulphur dye, namely CI Sulphur, CI Leuco Sulphur and CI Solubilised Sulphur, the cellulosic material is dyed using the reduced or leuco form of the dye (thiolate); at the end of dyeing, the thiol derivative is commonly oxidised *in situ* in order to reform the parent, insoluble sulphur dye in the fibre. Although oxidation is commonly carried out using conventional oxidants such as sodium dichromate/acetic acid, H_2O_2 or sodium chlorite,[2,4-8] other compounds, such as isocyanates,[5] diazonium salts,[5,8] metal salts[5,8] and alkylating agents[2,5-10] will perform this function as they are capable of removing an electron from the thiolate dye and, therefore, of oxidising the reduced form of the dye. Whilst the reaction of the latter compounds with the thiolate form of the sulphur dye on the fibre is, by definition, oxidation, Aspland[5] considers that the reaction should preferably be referred to as fixation and that the compounds be referred to as fixing agents.

The fastness of sulphur dyes on cellulosic fibres to severe washing conditions, especially those that use peroxide-containing detergent, can be improved by treatment with alkylating agents.[2,6-10] In general, this treatment is carried out using the thiolate derivative of the dye and thus replaces a conventional oxidation treatment,[6,8-10] except for dyes that have a marked yellow thiolate colour which require oxidation prior to alkylation.[2] Typically,[2,5-9] such compounds are cationic, fibre-substantive, reactive compounds such as polyhalogenohydrins,[7] which, under alkaline conditions, react with the nucleophilic thiolate or amino groups in the dye resulting in simultaneous alkylation and cross-linking.[7] The use of such alkylating agents to improve the wash fastness of sulphur dyeings on cellulosic fibres, especially towards peroxide-containing detergent, has received much attention;[2,5-8,10-13] in this context, emphasis has mainly been directed towards replacing conventional oxidants such as dichromate/acetic acid with alkylating agents.

In contrast, comparatively less interest appears to have attended the use of compounds, which, when applied to the oxidised dyeing, furnish improved wet fastness of sulphur dyes on cellulosic fibres; in this context, compounds that have been recommended include quaternary ammonium alkyl compounds,[7,8] dicyandiamide-formaldehyde condensates[14-17] and crease-resist finishing agents.[2,18,19]

The purpose of the work reported in this paper was to assess the effect of aftertreating oxidised sulphur dyes on cotton with several cationic agents on the fastness of the dyeings to peroxide-based washing.

TABLE 1
CI Solubilised Sulphur Dyes Used

Sulphosol	*CI Solubilised*	*Vol. of 5% aqueous Leucad 71 solution (cm^3)*		
		2%	*6%*	*10% omf dyeing*
Black SG	Sulphur Black 1	3	9	15
Yellow SR	Sulphur Yellow 23	7	12	20
Green SBCF	Sulphur Green 2	3	9	15
Dark Blue SL	Sulphur Blue 5	2·1	4·5	7·5

EXPERIMENTAL

Fabric

Scoured and bleached, fluorescent brightener-free woven cotton (150 g m^{-2}) was used.

Dyes

Commercial samples of four CI Solubilised Sulphur dyes, four CI Leuco Sulphur dyes as well as four CI Sulphur dyes, all generously supplied by J. Robinson Ltd, were used (Tables 1–3).

Reducing agent

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

Cationic agents

Five cationic agents, namely two commercially available products, Matexil FC-ER and Matexil FC-PN, as well as three development products, Com-

TABLE 2
CI Leuco Sulphur Dyes Used

Sulphol Liquid	*CI Leuco*
Liquid Black QG	Sulphur Black 1
Liquid Yellow QR	Sulphur Yellow 23
Liquid Green QGCF	Sulphur Green 2
Liquid Dark Blue QL	Sulphur Blue 5

TABLE 3
CI Sulphur Dyes Used

Sulphol	*CI Sulphur*	*Dye: Leucad 71*
Black BS	Black 1	1:1·2
Yellow YN	Yellow 23	1:3·0
Green GCF	Green 2	1:1·0
Dark Blue L	Blue 5	1:1·5

pounds A, B and C, were used. All five compounds were kindly supplied by ICI Surfactants.

All other reagents were of general purpose grade.

Preparation of dyebaths

(i) CI Solubilised Sulphur dyes

Stock solutions of 20 g dm^{-3} of 100% strength dye were prepared. The dye was pasted with distilled water and heated at the boil for 1 min. After cooling, the ensuing solution was made up to 1 dm^3 by the addition of distilled water. The required amount of stock dye solution (10 cm^3 for a 2% omf shade, 30 cm^3 for a 6% omf shade and 50 cm^3 for a 10% omf shade) was added to the dyebath together with the appropriate amount (Table 1) of a 5% aqueous solution of Leucad 71.

(ii) CI Leuco Sulphur dyes

Stock dye solutions of 20 g dm^{-3} were prepared using distilled water. Each dyebath required only the appropriate amount (10 cm^3 for a 2% omf shade, 30 cm^3 for a 6% omf shade and 50 cm^3 for a 10% omf shade) of stock dye solution together with 3 cm^3 of a 5% aqueous solution of Leucad 71.

(iii) CI Sulphur dyes

The dye powder was pasted with distilled water and an appropriate amount of Leucad 71 added to give the dye:Leucad 71 ratio shown in Table 3. The ensuing dispersion was then heated to the boil to facilitate dissolution of the dye and, after cooling, the volume was made up to 1 dm^3 using distilled water. The appropriate amount (10 cm^3 for a 2% omf shade, 30 cm^3 for a 6% omf shade and 50 cm^3 for a 10% omf shade) of the stock dye solution was then added to the dyebath.

Dyeing

All dyeings (2%, 6% and 10% omf) were carried out in sealed, 100 cm^3 capacity PTFE dyeing tubes housed in a John Jeffries Rota Dyer laboratory-

10 min 30 min
85°C ————————
↑ ↑
A **B**

A Fabric (10 g)
Dye (2, 6 or 10% omf)
5% aqueous solution of Leucad 71 as described in Table 1.
B 2 cm^3 of 300 g dm^{-3} aqueous NaCl solution.

Fig. 1. Dyeing method.

scale dyeing machine. A 7:1 liquor ratio, using 10 g cotton pieces, was used and an addition of 2 cm^3 of a 30% aqueous solution of sodium chloride was made to each dyebath; the dyeing method used is shown in Fig. 1.

Oxidation

At the end of dyeing, the dyed sample was removed, rinsed thoroughly in cold water and then in hot water and treated in a stirred, aqueous (distilled water) solution (50:1 liquor ratio) containing 1 g dm^{-3} hydrogen peroxide (30% w/v) and 1 g dm^{-3} glacial acetic acid at 60°C for 15 min. At the end of this time, the oxidised sample was removed, rinsed thoroughly in cold water and allowed to dry in the open air.

Aftertreatment

Each of the five cationic agents was applied at 2% omf to the 2% omf dyeing, at 4% omf to the 6% omf dyeing and at 6% omf to the 10% omf dyeing, using a 25:1 liquor ratio; the methods used to apply the cationic agents are shown in Fig. 2.

Compound A

15 min 30 min
40°C ————————
↑ ↑
A **B**

A 2%, 4% or 6% omf cationic compound
pH 6–7.
B pH 10·5–11 using 25 cm^3 dm^{-3} of 3% aqueous NaOH solution.

Matexil FC-ER, Matexil FC-PN, Compounds B and C

30 min
40°C ————
↑
A

A 2%, 4% or 6% omf cationic agent,
pH 6–7.

Fig. 2. Application methods for cationic compounds.

Colour measurement

The reflectance values and the corresponding CIE L^*, a^*, b^*, C^* and h° coordinates and K/S values (at the appropriate λ_{max} for each dyeing) of the dyed samples were measured using a Macbeth 2020 spectrophotometer interfaced to a Digital PC under illuminant D_{65}, with UV component included and specular component excluded. Each fabric sample was folded so as to realise a total of eight thicknesses of fabric; a total of four measurements were made of each sample, from which the average value was calculated. The difference ($\Delta K/S$) between the colour strength of the dyeings before and after aftertreatment was calculated by subtracting the K/S of the aftertreated sample from that of the sample before aftertreatment.

Fastness determination

The fastness of the dyeings to washing was determined using the ISO C06/C2 test method.[20]

RESULTS AND DISCUSSION

Figures 3–6 show the wash fastness results obtained for each of the four CI Solubilised Sulphur dyes, from which it is evident that aftertreatment with each of the five compounds improved the fastness of the three depths

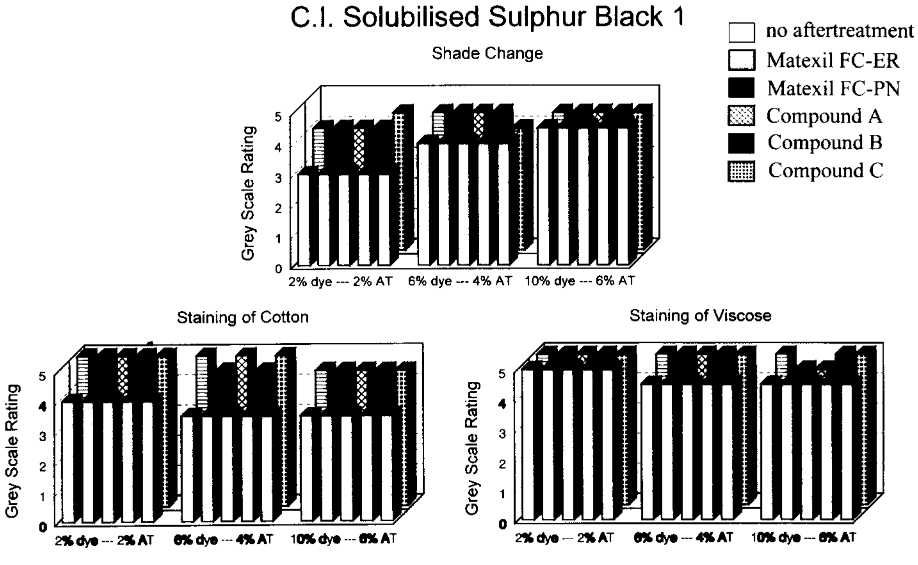

Fig. 3. Wash fastness results for CI Solubilised Sulphur Black 1.

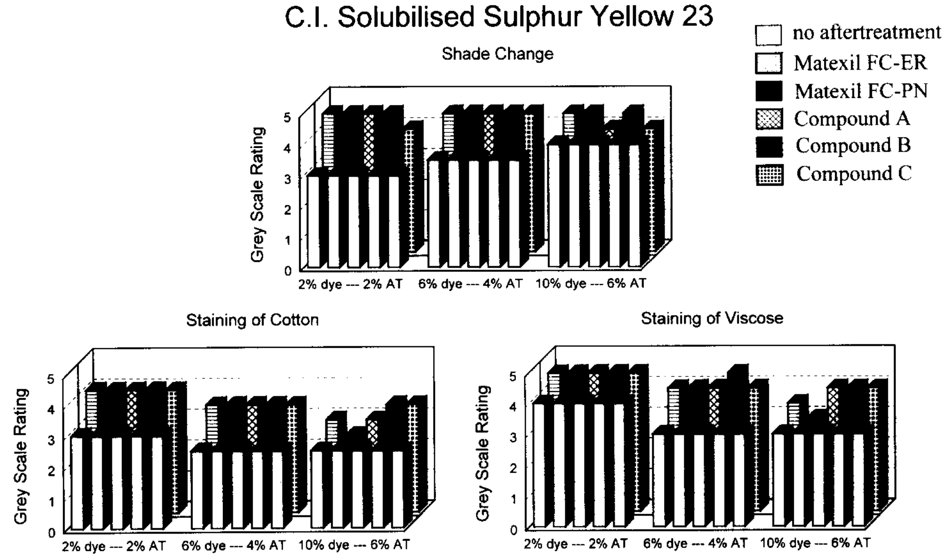

Fig. 4. Wash fastness results for CI Solubilised Yellow 23.

of shade examined. Similar findings were obtained in the cases of both the CI Leuco Sulphur dyes and the CI Sulphur dyes used (Figs 7–10 and 11–14, respectively). Thus, aftertreatment with the five compounds increased the wash fastness of each of the three types of sulphur dyes used.

Figures 3–14 also show that the extent of the improvement in wash

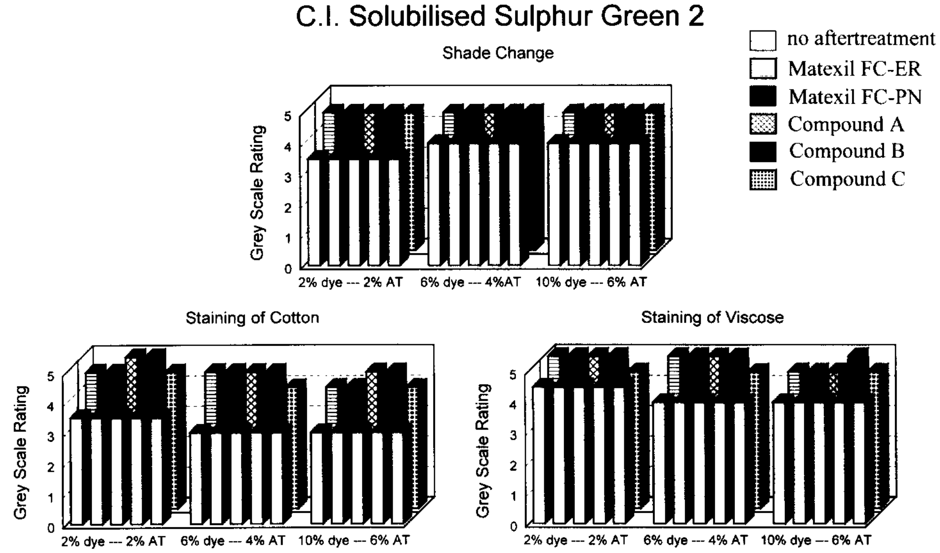

Fig. 5. Wash fastness results for CI Solubilised Sulphur Green 2.

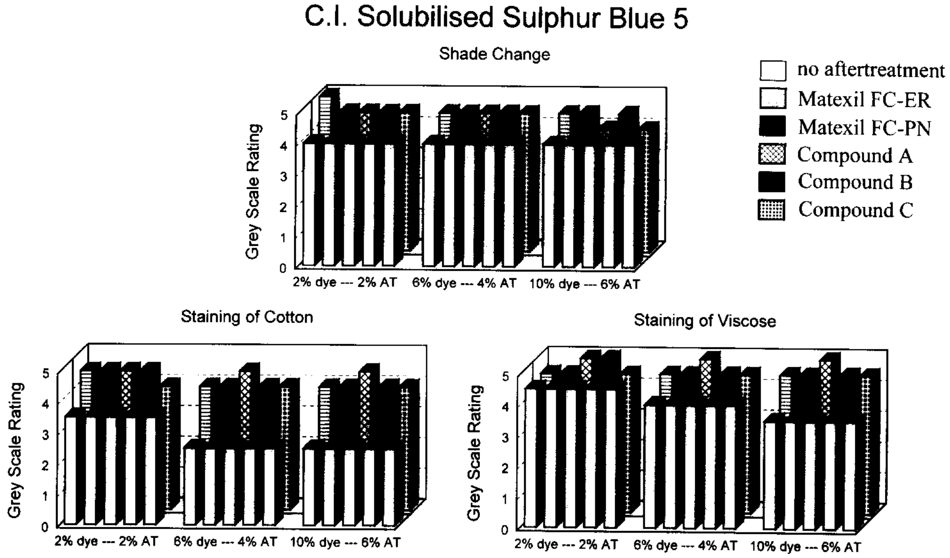

Fig. 6. Wash fastness results for CI Solubilised Sulphur Blue 5.

fastness imparted to the twelve dyes varied for the five cationic agents. The results presented reveal that, overall, the two commercial cationic agents (Matexil FC-PN and Matexil FC-ER) were slightly less effective than the three development products in improving wash fastness; of the three development products, compound C was less effective than its two counterparts. A discussion of these latter findings cannot be made without

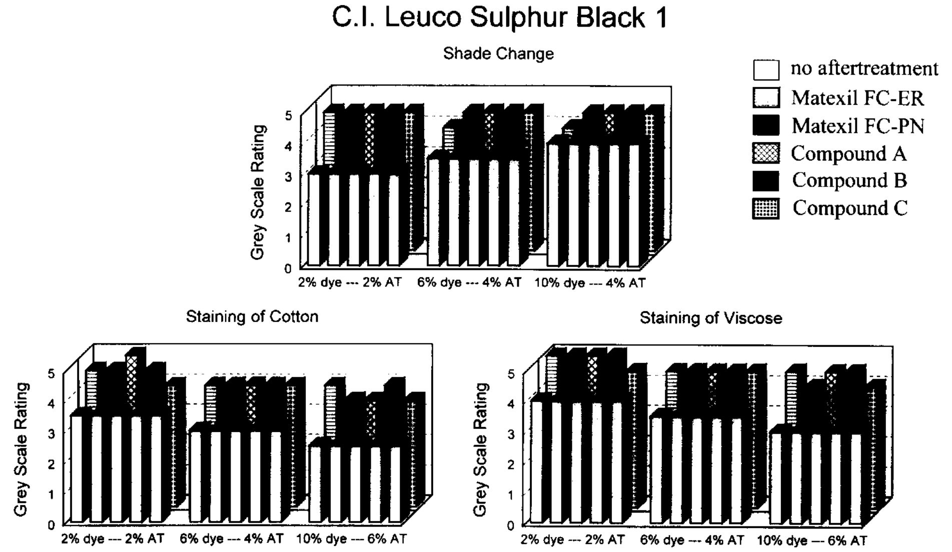

Fig. 7. Wash fastness results for CI Leuco Sulphur Black 1.

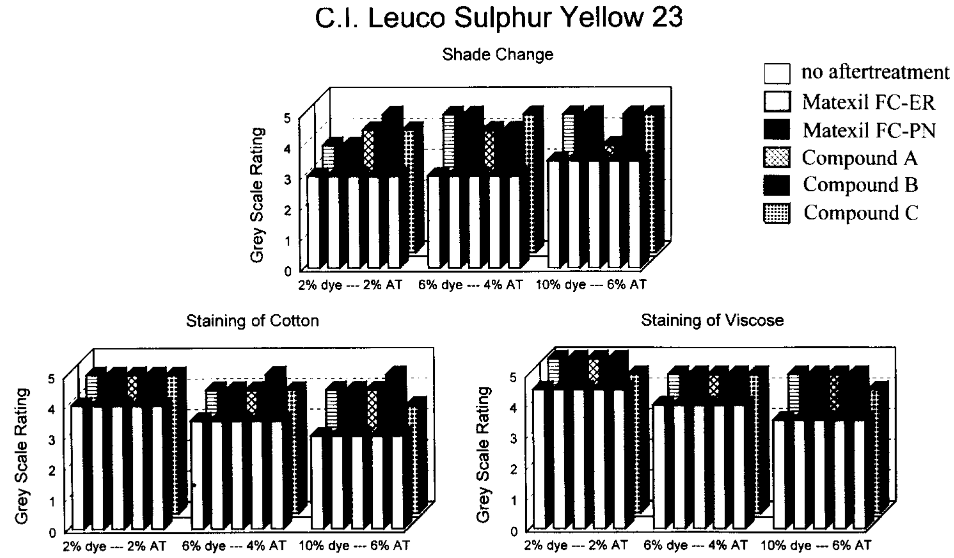

Fig. 8. Wash fastness results for CI Leuco Sulphur Yellow 23.

revealing information concerning the composition of the five products; for commercial reasons, such a discussion is, unfortunately, not possible.

The results displayed in Tables 4–15 show the colorimetric data obtained for the dyeings both prior to and following aftertreatment with each of the five agents. The difference in colour strength ($\Delta K/S$) between the dyeings before and after aftertreatment shows the extent of dye loss that occurred

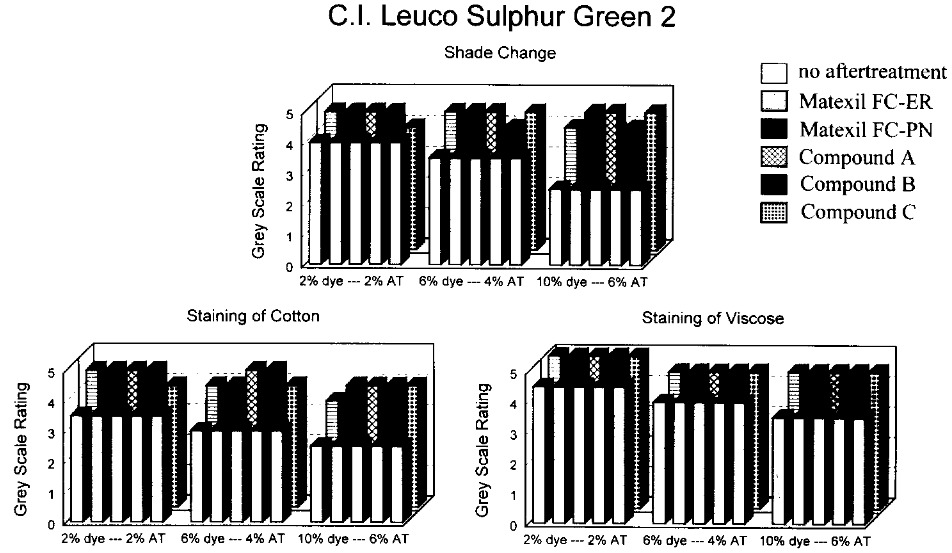

Fig. 9. Wash fastness results for CI Leuco Sulphur Green 2.

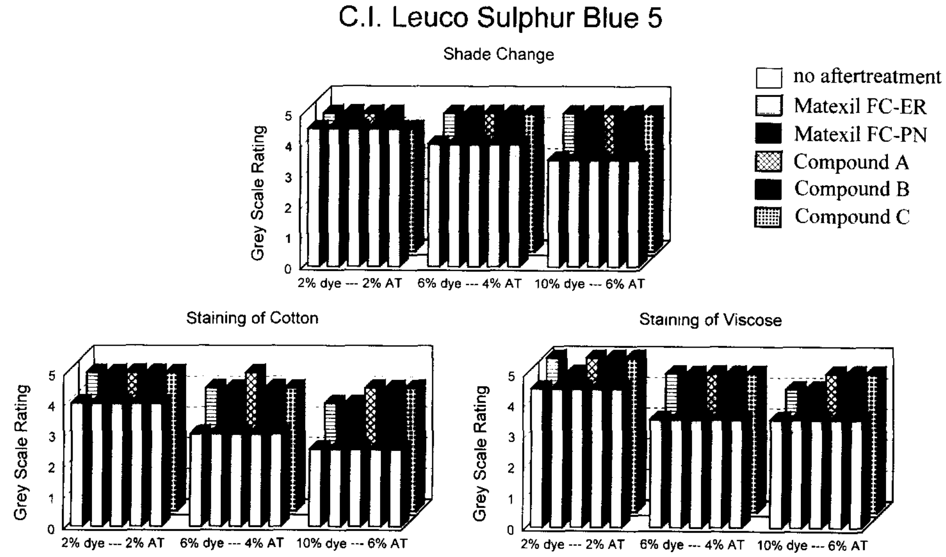

Fig. 10. Wash fastness results for CI Leuco Sulphur Blue 5.

as a result of aftertreatment. A discussion of this loss is important for two reasons. Firstly, any reduction in colour strength that arose from aftertreatment has obvious commercial implications for the dyer and, secondly, in general, as wash fastness increases with decreasing depth of shade, then the observed improved wash fastness secured by aftertreatment (Figs 3–14) may be due to reduced colour strength of the aftertreated dyeings.

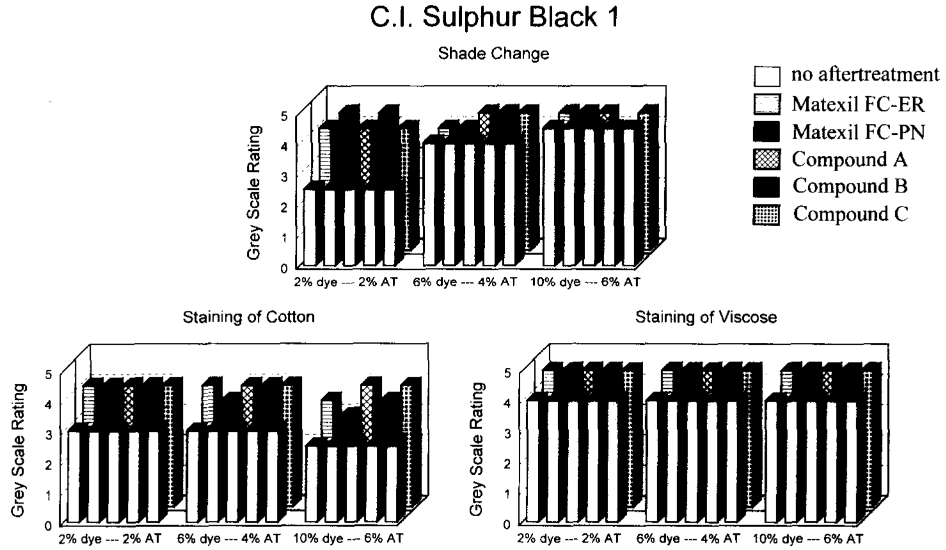

Fig. 11. Wash fastness results for CI Sulphur Black 1.

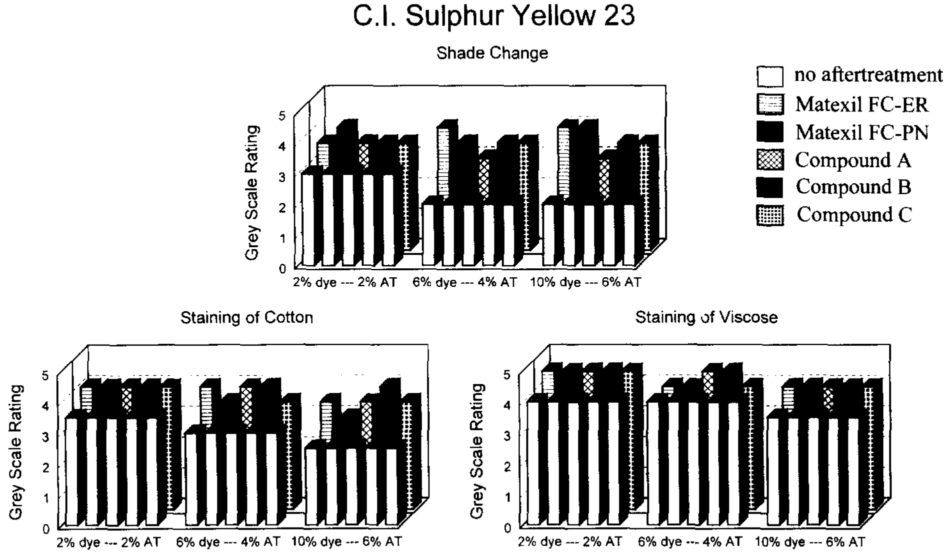

Fig. 12. Wash fastness results for CI Sulphur Yellow 23.

The $\Delta K/S$ results in Tables 4–15 reveal that aftertreatment with each of the five cationic agents had little effect on the colour strength of the dyeings and, therefore, that the observed improvement in wash fastness imparted by the five agents was not due to the aftertreated dyeings being of lower colour strength than the corresponding untreated dyeing. The colorimetric data in Tables 4–15 also show the extent to which aftertreatment

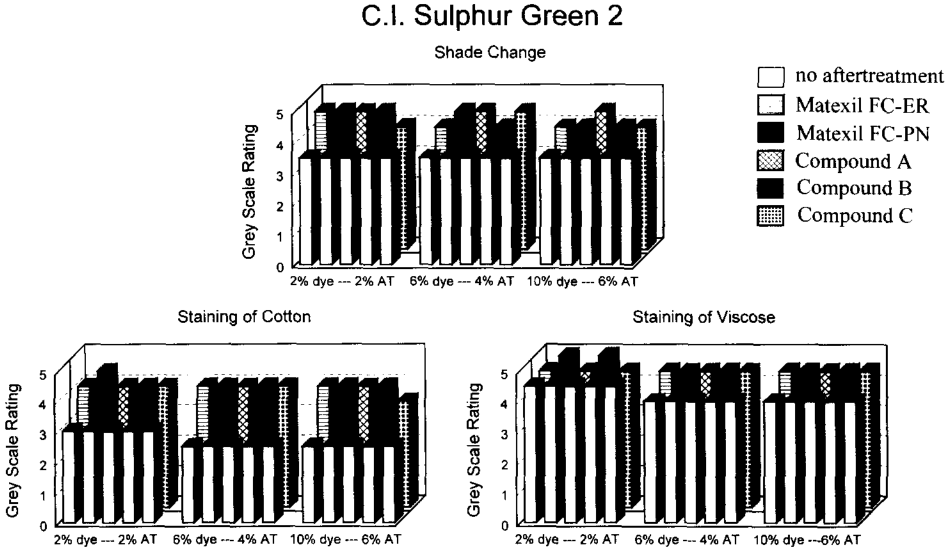

Fig. 13. Wash fastness results for CI Sulphur Green 2.

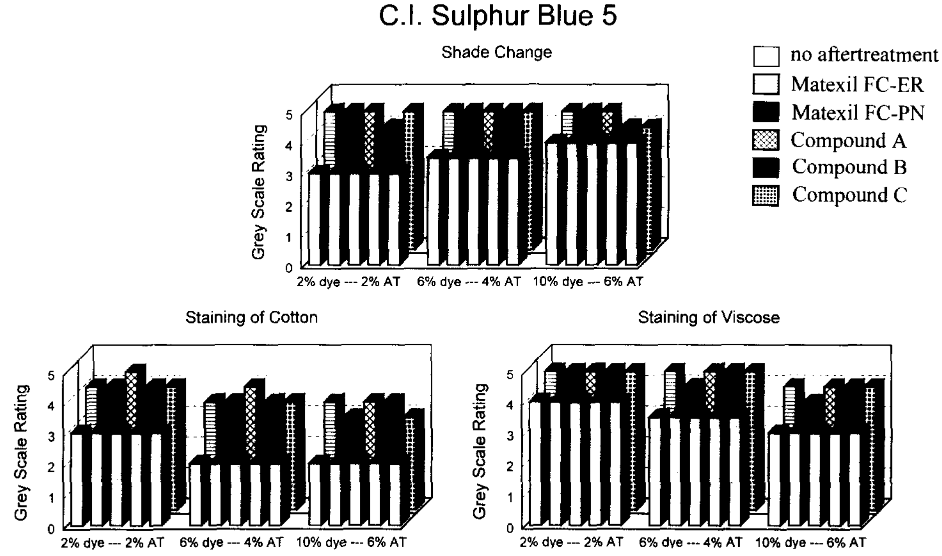

Fig. 14. Wash fastness results for CI Sulphur Blue 5.

altered the shade of the various dyeings; it is evident that whilst aftertreatment caused a flattening of shade of the dyes, this was not marked.

The mechanism by which the improved wash fastness of the dyeings was achieved requires consideration. Each of the five compounds used is a polycation of high molecular mass (M_r); Matexil FC-PN and Matexil FC-ER are currently marketed as cationic fixing agents for the aftertreatment of direct dyes on cellulosic fibres. Initially, the possibility that the improved wash fastness of the dyeings was achieved in a manner analogous to that operating in the case of cationic fixing agents/direct dyes will be discussed.

The aftertreatment of direct dyes with a cationic fixing agent is a commonly used method of improving the wash fastness properties of the dyeings. It is generally considered that the enhanced wash fastness imparted by such high M_r polycationic fixing agents is achieved by the formation of a large molecular size, dye–cationic agent complex of low aqueous solubility. Clearly, this particular mechanism relies upon the presence of anionic (commonly sulphonate) groups in the direct dye. Thus, in order for this mechanism to operate in the case of the observed improvement in wash fastness of sulphur dyes imparted by the five polycationic compounds, then the sulphur dye in the dyed fibre must contain anionic groups.

Although relatively little is known of the structure of sulphur dyes it has been proposed[5] that some dyes may contain sulphonic acid groups and it has been suggested[21] that the suitability of many sulphur dyes for ‘topping’ with basic dyes may be due to oxidation to sulphonic or other

TABLE 4
Colorimetric Data for CI Solubilised Sulphur Black 1

Dye (%)	*AT (% omf)*	*L**	*a**	*b**	*C**	h^0	*K/S*	*ΔK/S*
2		31·76	−0·32	−3·93	3·94	265·35	6·65	—
6	Nil	22·87	0·00	−3·34	3·34	270·06	13·10	—
10		19·53	0·22	−2·35	2·36	275·26	17·13	—
2	2	31·27	−0·27	−3·79	3·80	265·85	6·92	−0·26
6	ER 4	23·19	−0·06	−3·38	3·38	268·91	12·83	0·27
10	6	18·87	0·33	−2·45	2·48	277·75	18·17	−1·04
2	2	31·83	−0·38	−4·13	4·14	264·74	6·69	−0·03
6	PN 4	22·89	−0·06	−3·50	3·50	269·04	13·18	0·08
10	6	19·74	0·28	−2·80	2·81	275·74	16·87	0·26
2	2	33·10	−0·32	−4·43	4·45	265·90	6·15	0·51
6	A 4	23·10	−0·04	−3·80	3·80	269·34	12·98	0·12
10	6	18·95	0·37	−2·87	2·89	277·33	18·17	−1·04
2	2	31·31	−0·33	−4·06	4·07	265·39	6·93	−0·27
6	B 4	22·61	0·08	−3·61	3·61	271·25	13·43	−0·33
10	6	19·19	0·32	−2·71	2·73	276·74	17·67	−0·54
2	2	32·12	−0·24	−4·06	4·07	266·64	6·50	0·16
6	C 4	22·80	0·18	−3·54	3·54	272·92	13·14	−0·04
10	6	19·59	0·42	−2·66	2·70	279·07	17·00	0·13

TABLE 5
Colorimetric Data for CI Solubilised Sulphur Yellow 23

Dye (%)	*AT (% omf)*	*L**	*a**	*b**	*C**	h^0	*K/S*	*ΔK/S*
2		76·81	6·25	51·25	51·63	83·05	4·53	—
6	Nil	68·71	11·05	56·68	57·75	78·96	8·20	—
10		63·04	14·48	57·54	59·33	75·87	10·69	—
2	2	76·28	6·02	46·57	46·96	82·64	3·90	0·63
6	ER 4	67·83	11·42	56·03	57·18	78·48	8·39	−0·19
10	6	64·34	13·54	58·11	54·66	76·89	11·07	−0·38
2	2	75·53	6·38	49·95	50·36	82·72	4·45	0·08
6	PN 4	67·26	11·54	56·58	57·75	78·47	8·81	−0·61
10	6	63·45	13·91	56·11	57·81	76·08	10·08	0·61
2	2	74·53	8·56	46·83	47·61	79·64	4·13	0·40
6	A 4	65·17	14·01	53·29	55·10	75·28	8·81	−0·61
10	6	61·07	16·98	54·98	57·55	72·84	10·81	−0·12
2	2	76·09	5·98	49·42	49·78	83·10	4·32	0·21
6	B 4	67·09	11·33	55·04	56·20	78·37	8·36	−0·16
10	6	64·90	13·07	57·83	59·25	77·26	10·44	0·25
2	2	76·28	5·39	47·98	48·29	83·59	4·14	0·39
6	C 4	68·90	10·45	55·47	56·45	79·33	7·94	0·26
10	6	64·59	13·49	57·92	54·47	76·88	10·76	−0·07

acid groups. Furthermore, hydrogen peroxide was used as oxidant in this work; it has been reported that this particular oxidant can over-oxidise[2,8] thiolate groups in sulphur dyes which imparts a certain degree of water-solubility[8] and reduced wet fastness[2,5] to some dyes. Thus, the improved wash fastness imparted by the five cationic compounds may have been achieved in a similar manner to that operating in the case of cationic fixing agents/direct dyes, namely by the formation of a large molecular size, dye–cationic agent complex of reduced aqueous solubility. In support of this, Heid *et al.*[8] suggest that the aftertreatment of sulphur dyes with peralkylation products of polyamines enhances wash fastness by means of electrostatic interaction operating between anionic groups in the dye and the polycation. Furthermore, although it is claimed[14–17] that the after-treatment of sulphur dyeings with cationic dicyandiamide-formaldehyde condensates improves wash fastness, no explanation is offered as to the mechanism involved. However, in view of the structures of the cationic compounds involved,[14–17] it would appear that ion–ion interactions operating between the compounds and anionic groups in the fibre could result in the claimed enhancement of wash fastness.

Nevertheless, evidence for the formation of large molecular size, dye–cationic agent complex of low aqueous solubility has not, as yet, been secured; indeed, it can be argued that in view of the generally accepted

TABLE 6
Colorimetric Data for CI Solubilised Sulphur Green 2

Dye (%)	*AT (% omf)*	L^*	a^*	b^*	C^*	h^0	K/S	$\Delta K/S$
2		47·16	−21·38	−11·05	24·07	207·33	5·41	—
6	Nil	36·69	−20·44	−10·78	23·11	207·82	11·28	—
10		32·05	−18·50	−10·50	21·27	209·57	14·84	—
2	2	47·43	−20·75	−11·90	23·92	209·85	5·38	0·03
6	ER 4	37·00	−20·05	−11·55	23·14	209·96	11·19	0·09
10	6	32·36	−18·72	−11·11	21·77	210·68	15·30	−0·46
2	2	49·69	−21·29	−11·72	24·30	208·84	4·84	0·57
6	PN 4	37·83	−20·61	−11·50	23·60	209·16	11·04	0·24
10	6	32·32	−18·58	−11·37	21·78	211·47	15·68	−0·84
2	2	47·53	−17·81	−12·60	21·81	215·27	4·72	0·69
6	A 4	36·91	−18·70	−12·96	22·23	215·64	10·54	0·74
10	6	32·25	−17·22	−12·54	21·30	216·08	14·64	0·20
2	2	48·17	−20·91	−11·33	23·78	208·46	5·30	0·11
6	B 4	38·42	−21·15	−11·34	24·00	208·19	10·98	0·30
10	6	34·16	−19·90	−11·05	22·76	209·03	14·31	0·53
2	2	48·52	−19·77	−12·05	23·15	211·37	4·82	0·59
6	C 4	37·77	−19·75	−12·07	23·15	211·43	10·57	0·71
10	6	33·36	−18·56	−12·10	22·15	213·10	14·21	0·63

TABLE 7
Colorimetric Data for CI Solubilised Sulphur Blue 5

Dye (%)	*AT (% omf)*	L*	a*	b*	C*	h^0	*K/S*	*ΔK/S*
2		41·55	4·38	−22·50	22·92	281·01	3·99	—
6	Nil	27·13	6·08	−21·62	22·46	285·69	11·04	—
10		22·93	6·29	−19·96	20·93	287·49	15·20	—
2	2	42·55	3·99	−22·42	22·77	280·10	3·77	0·22
6	ER 4	27·05	6·03	−22·01	22·83	285·32	11·28	−0·24
10	6	23·10	6·61	−21·05	22·06	287·43	15·30	−0·10
2	2	41·27	3·63	−22·77	23·06	279·07	4·19	−0·20
6	PN 4	26·22	5·64	−21·91	22·63	284·44	12·18	−1·14
10	6	22·85	5·99	−20·20	21·07	286·51	15·46	−0·26
2	2	40·73	4·63	−22·22	22·69	281·77	4·19	−0·20
6	A 4	27·09	5·94	−21·75	22·54	285·29	11·19	−0·15
10	6	21·76	6·48	−19·05	20·12	288·77	16·44	−1·24
2	2	40·04	3·07	−22·94	23·14	277·61	4·67	−0·68
6	B 4	27·18	5·58	−23·33	23·99	283·46	11·68	−0·64
10	6	23·19	5·88	−21·19	21·99	285·52	15·46	−0·26
2	2	38·68	4·65	−22·59	23·06	281·62	4·86	−0·87
6	C 4	28·27	5·99	−22·69	23·47	284·78	10·59	0·65
10	6	23·46	6·51	−20·61	21·61	287·53	14·59	0·61

TABLE 8
Colorimetric Data for CI Leuco Sulphur Black 1

Dye (%)	*AT (% omf)*	L*	a*	b*	C*	h^0	*K/S*	*ΔK/S*
2		33·95	−0·73	−4·65	4·71	261·02	5·89	—
6	Nil	22·41	−0·57	−3·85	3·89	261·63	14·62	—
10		18·34	0·06	−2·91	2·91	271·14	19·34	—
2	2	33·93	−0·80	−4·44	4·51	259·76	5·90	−0·01
6	ER 4	23·03	−0·50	−3·89	3·92	262·72	13·47	0·79
10	6	19·00	−0·22	−2·95	2·96	265·68	18·39	0·95
2	2	34·00	−1·05	−4·59	4·71	257·16	5·39	−0·04
6	PN 4	22·89	−0·66	−4·02	4·07	260·65	13·81	0·45
10	6	19·30	−0·44	−3·27	3·30	262·41	18·32	1·02
2	2	33·52	−0·49	−4·51	4·54	263·86	5·98	−0·09
6	A 4	23·04	−0·30	−4·35	4·36	266·11	13·43	0·83
10	6	18·60	−0·05	−3·32	3·33	269·17	19·09	0·25
2	2	33·98	−1·28	−4·71	4·88	254·76	6·04	−0·15
6	B 4	23·40	−0·77	−4·24	4·31	259·67	13·47	0·79
10	6	19·71	−0·33	−3·32	3·34	264·26	17·81	1·53
2	2	32·81	−1·16	−4·53	4·68	255·61	6·52	−0·63
6	C 4	23·19	−0·83	−4·22	4·30	258·92	13·51	0·75
10	6	19·36	−0·46	−3·16	3·19	261·80	18·10	1·24

mechanism of the dyeing of cellulosic fibres with sulphur dyes, namely that at the end of dyeing (i.e. after oxidation), the dye is present in its insoluble form, even if such anionic groups were present in some sulphur dyes, their concentration could be assumed to be relatively low, otherwise, owing to the solubilising effect of the sulphonic acid group, the dyes would display much lower wet fastness than is found in practice. Clearly, further work is required to determine whether the improved wash fastness imparted by the five cationic agents used in this work involves the formation of a dye–cationic agent complex.

The results in Figs 3–14 clearly show that the cationic agents markedly improved the wash fastness of the sulphur dyes which, in turn, indicates that the polycations were adsorbed on to the dyed substrate. As recounted above, it is possible that anionic groups were present in the dye molecules and, therefore, that electrostatic forces operating between these anionic groups and the polycations were responsible for uptake of the cationic agents. Alternatively, adsorption of the polycations on to the sulphur-dyed cotton may also have arisen owing to ion–ion interactions operating between the cationic agent and the substrate in view of the fact that cotton contains anionic carboxylic acid groups[22,23] which, owing to their relatively low pK_a values, will be ionised at the pH values under which the polycations were applied to the dyed fibre. Furthermore, it is

TABLE 9
Colorimetric Data for CI Leuco Sulphur Yellow 23

Dye (%)	*AT (% omf)*	*L**	*a**	*b**	*C**	*h^0*	*K/S*	*ΔK/S*
2		85·21	1·02	33·61	33·63	88·26	1·30	—
6	Nil	75·62	7·73	50·85	51·44	81·35	4·44	—
10		73·16	9·11	55·82	56·56	80·73	6·25	—
2	2	82·46	2·11	35·42	35·48	86·59	1·56	−0·26
6	ER 4	74·74	6·83	48·84	49·31	82·04	4·32	0·12
10	6	73·22	8·28	53·00	53·64	81·12	5·55	0·70
2	2	81·46	3·39	39·41	39·55	85·08	1·91	−0·61
6	PN 4	74·29	7·77	49·14	49·75	81·01	4·37	0·07
10	6	72·75	9·03	54·18	54·93	80·54	5·81	0·44
2	2	83·12	1·82	32·43	32·48	86·79	1·34	−0·04
6	A 4	74·02	8·10	48·42	49·10	80·50	4·34	0·10
10	6	71·46	9·79	52·76	53·66	79·49	6·04	0·21
2	2	83·01	2·31	36·04	36·11	86·33	1·51	−0·21
6	B 4	75·34	7·05	49·37	49·87	81·87	4·16	0·28
10	6	71·84	9·59	54·46	55·30	80·01	6·14	0·11
2	2	84·39	0·39	31·83	31·83	89·30	1·27	0·03
6	C 4	76·35	7·32	50·52	51·03	81·85	4·13	0·31
10	6	73·14	9·04	54·72	55·46	80·62	5·83	0·42

TABLE 10

Colorimetric Data for CI Leuco Sulphur Green 2

Dye (%)	*AT (% omf)*	L^*	a^*	b^*	C^*	h^0	K/S	$\Delta K/S$
2		61·44	−18·63	−6·62	19·77	199·56	1·83	—
6	Nil	48·46	−21·50	−6·20	22·37	196·10	4·78	—
10		41·67	−21·72	−5·68	22·45	194·66	7·72	—
2	2	60·76	−18·92	−6·86	20·13	199·94	1·98	−0·15
6	ER 4	48·77	−21·94	−6·90	23·00	197·46	4·95	−0·17
10	6	43·61	−22·66	−6·69	23·63	196·44	7·32	0·40
2	2	62·14	−19·75	−6·73	20·87	198·82	1·97	−0·14
6	PN 4	47·66	−22·67	−6·23	23·51	195·36	5·80	−1·02
10	6	43·37	−23·12	−6·52	24·02	195·74	7·89	−0·17
2	2	60·88	−18·80	−7·67	20·30	202·19	1·96	−0·13
6	A 4	48·48	−21·73	−7·71	23·05	199·55	5·06	−0·28
10	6	43·31	−22·27	−7·78	23·59	199·26	7·45	0·27
2	2	60·84	−19·94	−6·25	20·90	197·41	2·19	−0·36
6	B 4	49·03	−22·76	−6·44	23·66	195·80	5·18	−0·40
10	6	43·55	−23·57	−6·10	24·35	194·52	8·04	−0·32
2	2	60·67	−19·40	−7·03	20·64	199·91	2·05	−0·22
6	C 4	49·63	−22·59	−7·29	23·73	197·89	4·82	−0·04
10	6	43·76	−22·89	−6·75	23·87	196·42	7·38	0·34

TABLE 11

Colorimetric Data for CI Leuco Sulphur Blue 5

Dye (%)	*AT (% omf)*	L^*	a^*	b^*	C^*	h^0	K/S	$\Delta K/S$
2		51·82	1·70	−19·87	19·94	274·88	2·07	—
6	Nil	36·28	3·72	−22·75	23·06	279·29	6·00	—
10		30·79	4·56	−22·76	23·20	281·22	8·89	—
2	2	52·75	1·51	−19·23	19·29	274·50	1·94	0·13
6	ER 4	34·56	3·72	−22·62	22·93	279·33	6·84	−0·84
10	6	31·67	4·17	−22·97	23·35	280·29	8·48	0·41
2	2	51·23	0·87	−19·77	19·79	272·53	2·22	−0·15
6	PN 4	37·60	2·81	−22·92	23·09	276·99	5·69	1·31
10	6	31·92	3·95	−23·15	23·48	279·68	8·10	0·79
2	2	52·25	1·65	−19·60	19·66	274·82	2·01	0·06
6	A 4	37·35	3·75	−22·53	22·84	279·44	5·54	0·46
10	6	31·52	4·67	−23·21	23·68	281·38	8·46	0·43
2	2	51·95	0·38	−20·42	20·42	271·06	2·19	−0·12
6	B 4	37·22	2·44	−23·70	23·82	275·88	6·07	−0·07
10	6	31·33	3·55	−23·55	23·82	278·58	9·09	−0·20
2	2	50·96	1·37	−20·49	20·54	273·81	2·26	−0·19
6	C 4	37·17	3·54	−23·51	23·78	278·55	5·79	0·21
10	6	31·04	4·40	−23·20	23·61	280·73	8·91	−0·02

well known that during the preparation of cotton, oxidation of the fibre with hydrogen peroxide generates carboxylic acid groups[23] and, as the dyeings were oxidised using this reagent, it is possible that additional anionic carboxyl groups were generated with the dyed fibre during oxidation. Thus, it may be possible that the oxidised, dyed cotton contained a high proportion of anionic carboxyl groups which provide sites for adsorption of the polycations to occur by virtue of ion–ion interaction. Such adsorption could supplement or even replace that occurring between the cationic agents and anionic groups in the dye molecules. If adsorption of the cationic agents on to the dyed fibre was to occur by means of ion–ion interaction involving anionic groups in the fibre, the enhanced wash fastness imparted by the cationic agents could still be attributable to the formation of a dye–cationic agent complex.

An alternative mechanism to that of the formation of a large molecular size, low solubility, dye–cationic agent complex can be proposed, based on the mechanism by which syntans improve the wet fastness of anionic dyes on nylon. Syntans for nylon are, typically, water-soluble, anionic formaldehyde polycondensates of arylsulphonates and sulphonates of dihydroxydiarylsulphones (typically dihydroxydiphenylsulphone[24]). It has been proposed[25] that syntans are adsorbed at the periphery of the dyed polyamide fibre and that their ability to improve the wet fastness properties

TABLE 12
Colorimetric Data for CI Sulphur Black 1

Dye (%)	*AT (% omf)*	*L**	*a**	*b**	*C**	h^0	*K/S*	*ΔK/S*
2	Nil	22·29	−0·14	−4·16	4·16	268·11	14·03	—
6		16·43	0·57	−2·29	2·36	283·94	22·48	—
10		15·39	0·53	−1·08	1·20	296·17	24·39	—
2	2	22·47	−0·03	−4·20	4·20	269·53	13·81	0·22
6	ER 4	16·17	0·41	−2·03	2·07	281·33	22·93	−0·45
10	6	15·35	0·88	−1·75	1·96	296·54	24·92	−0·53
2	2	22·59	−0·12	−4·39	4·39	268·49	13·81	0·22
6	PN 4	17·23	0·32	−2·61	2·63	277·10	21·14	1·34
10	6	15·48	0·38	−1·73	1·77	282·48	24·78	−0·39
2	2	23·17	−0·04	−4·38	4·38	269·51	13·02	1·01
6	A 4	16·66	0·28	−2·50	2·52	276·38	22·48	0·00
10	6	14·75	0·52	−1·74	1·82	286·71	26·63	−2·24
2	2	22·66	−0·18	−4·45	4·45	267·70	13·81	0·22
6	B 4	17·17	0·41	−2·55	2·58	279·24	21·33	1·15
10	6	15·06	0·53	−1·75	1·83	286·70	25·75	−1·36
2	2	23·48	0·04	−4·60	4·60	270·48	12·68	1·35
6	C 4	16·63	0·43	−2·31	2·34	280·51	22·16	0·32
10	6	15·53	0·68	−1·82	1·94	290·35	24·65	−0·26

TABLE 13

Colorimetric Data for CI Sulphur Yellow 23

Dye (%)	*AT (% omf)*	*L**	*a**	*b**	*C**	*h⁰*	*K/S*	*ΔK/S*
2		76·03	6·10	45·86	46·26	82·43	3·76	—
6	Nil	66·78	10·62	53·58	54·63	78·79	7·93	—
10		62·81	11·74	54·69	55·94	77·89	10·57	—
2	2	74·77	7·05	47·22	47·75	81·51	4·02	−0·26
6	ER 4	66·56	10·29	52·61	53·60	78·93	7·77	0·16
10	6	63·54	10·82	54·19	55·26	78·71	9·99	0·58
2	2	75·65	6·34	45·61	46·05	82·08	3·65	0·11
6	PN 4	66·45	10·92	51·82	52·95	78·10	7·46	0·47
10	6	62·92	11·42	53·80	55·00	78·01	10·23	0·34
2	2	76·11	5·46	43·53	43·87	82·85	3·34	0·42
6	A 4	65·72	10·72	51·17	52·28	78·17	7·62	0·31
10	6	62·01	12·08	53·50	54·84	77·28	10·60	−0·03
2	2	76·19	6·02	44·24	44·65	82·25	3·38	0·38
6	B 4	66·06	10·82	51·62	52·74	78·16	7·46	0·47
10	6	63·64	10·91	54·47	55·55	78·67	10·06	0·51
2	2	76·32	5·65	43·59	43·96	82·62	3·32	0·44
6	C 4	66·48	11·13	52·27	53·73	78·04	7·64	0·29
10	6	62·97	11·27	54·34	55·50	78·29	10·28	0·29

TABLE 14

Colorimetric Data for CI Sulphur Green 2

Dye (%)	*AT (% omf)*	*L**	*a**	*b**	*C**	*h⁰*	*K/S*	*ΔK/S*
2		53·35	−15·89	−9·88	18·71	211·88	2·94	—
6	Nil	38·85	−16·56	−10·62	19·67	212·68	8·27	—
10		34·60	−16·08	−10·35	19·13	212·76	11·13	—
2	2	52·83	−15·50	−10·67	18·82	214·55	3·09	−0·15
6	ER 4	38·97	−16·58	−11·24	20·03	214·13	8·53	−0·26
10	6	34·10	−15·91	−11·05	19·37	214·79	12·07	−0·94
2	2	53·56	−15·94	−10·05	18·84	212·24	3·05	−0·11
6	PN 4	40·32	−16·98	−10·70	20·07	212·22	7·99	0·28
10	6	34·21	−15·64	−11·06	19·16	215·26	12·07	−0·94
2	2	52·75	−15·01	−11·27	18·77	216·89	3·06	−0·12
6	A 4	39·54	−16·28	−11·59	19·99	215·45	8·12	0·15
10	6	33·91	−15·50	−11·73	19·44	217·13	12·18	−1·05
2	2	53·73	−16·62	−9·83	19·31	210·62	3·14	−0·20
6	B 4	39·88	−17·45	−10·74	20·49	211·62	8·55	−0·28
10	6	34·37	−16·58	−10·89	19·84	213·28	12·61	−1·48
2	2	53·58	−15·60	−10·35	18·73	213·56	2·95	−0·01
6	C 4	39·35	−16·51	−11·32	20·02	214·44	8·36	−0·09
10	6	34·08	−15·86	−11·29	19·46	215·45	12·18	−1·05

TABLE 15
Colorimetric Data for CI Sulphur Blue 5

Dye (%)	AT (% omf)	L*	a*	b*	C*	h^0	K/S	ΔK/S
2		39·90	4·57	−22·27	22·73	281·60	4·49	—
6	Nil	27·30	6·03	−21·05	21·90	285·99	10·90	—
10		22·71	6·28	−18·97	19·99	288·31	15·30	—
2	2	40·22	4·39	−22·50	22·92	281·05	4·42	0·58
6	ER 4	27·01	6·35	−21·45	22·37	286·48	11·22	0·49
10	6	22·48	6·43	−19·27	20·31	288·46	15·63	−0·33
2	2	42·25	3·56	−22·38	22·66	279·03	3·90	0·59
6	PN 4	26·31	5·74	−21·09	21·86	285·22	11·94	−1·04
10	6	23·13	5·79	−18·71	19·59	287·18	14·84	0·46
2	2	40·98	4·50	−22·29	22·74	281·40	4·17	0·32
6	A 4	27·11	6·35	−21·33	22·25	286·57	11·07	−0·17
10	6	22·65	6·30	−18·73	19·76	288·59	15·30	0·00
2	2	40·89	3·07	−22·53	22·74	277·75	4·34	0·15
6	B 4	27·40	5·34	−22·09	22·73	283·58	11·22	−0·32
10	6	24·08	5·88	−20·47	21·30	286·02	14·21	1·09
2	2	40·07	4·25	−22·32	22·72	280·79	4·46	0·03
6	C 4	28·39	6·05	−21·88	22·70	285·46	10·16	0·74
10	6	23·39	6·29	−19·32	20·32	288·03	14·54	0·76

of non-metallised acid dyes on nylon fibres is attributable to this peripheral ‘layer’ of syntan molecules reducing the diffusion of dye out of the dyed, treated fibre during wet treatments. Syntans are applied to dyed nylon under acidic conditions and ion–ion interaction, operating between the protonated amino groups in the fibre and sulphonate groups in the syntan, as well as hydrogen bonding are considered to contribute towards syntan–fibre substantivity. The importance of ion–ion interaction in syntan–fibre substantivity was demonstrated in the cases of the adsorption of a commercial syntan on nylon 6.6[26,27] as well for the adsorption of several commercial syntans on wool.[28–30] However, the equilibrium adsorption isotherms of a syntan on undyed nylon 6,6 and of various syntans on wool[28–30] revealed that uptake followed a BET mechanism, which implied that uptake involved the formation of multilayers of adsorbed syntan molecules. Further support for the proposal that adsorption of syntans on nylon 6,6 occurs by a combination of both polar and non-polar forces of interaction has been obtained from the observation[26] that a commercial syntan was adsorbed on to basic-dyeable nylon 6,6 and also on to acid-dyeing nylon 6,6, the latter fibre having been chemically modified such that all available amino end groups were replaced by sulphonic acid groups, to an extent that was not substantially different to that secured on regular acid-dyeing nylon 6,6 fibre.

Thus, the results obtained on nylon 6,6 and wool indicate that syntan adsorption on to these two substrates does not occur simply by virtue of ion–ion interaction operating between the anionic syntan molecules and specific sites (namely, the protonated amino groups) in each fibre and, therefore, that other forces of interaction, for example, hydrogen bonding and ion–dipole, contribute towards syntan–fibre interaction. By analogy with this mechanism, in the case of the adsorption of each of the five cationic polymers on to the sulphur-dyed cotton, whilst ion–ion interaction operating between anionic groups in the dye and/or fibre and the polycation will contribute towards adsorption, other forces of interaction may also be responsible for adsorption of the cationic agent. Furthermore, owing to the polymeric nature of the cationic agents, multi-layer adsorption of the polycations may occur which will contribute towards their uptake on to the dyed substrate. By further analogy with syntan/nylon mechanism, the polycations may be adsorbed at the periphery of the sulphur-dyed fibre and their ability to improve the wash fastness of the dyeings may be attributable to this peripheral 'layer' of polycation molecules reducing the diffusion of dye out of the dyed, treated fibre during washing.

From the foregoing, it is evident that further work is required to establish the mechanism by which the cationic agents improve the wash fastness of sulphur dyes on cotton.

CONCLUSIONS

Aftertreatment of cotton which had been dyed with CI Solubilised Sulphur, CI Leuco Sulphur and CI Sulphur dyes with five polycationic agents improved the fastness of the dyeings to the ISOC06/C2 wash test. Whilst aftertreatment caused a slight flattening of shade of some of the dyeings it had little effect on colour strength.

The adsorption of the polycations on to the dyed substrate may have arisen by virtue of electrostatic forces operating between the cationic agents and anionic carboxyl groups in the fibre and/or anionic groups in the dye molecules; alternatively, intermolecular forces other than ion–ion may contribute towards uptake of the polycations. The mechanism by which the improvement in wash fastness was effected may be the formation of a large molecular size, dye–cationic agent complex of reduced aqueous solubility or to the presence of a peripheral 'layer' of polycation molecules having reduced the diffusion of dye out of the dyed, treated fibre during washing.

Further work is required to establish the mechanism by which the observed enhanced wash fastness is achieved.

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