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The Pre-treatment of Cotton to Enhance its Dyeability—I. Sulphur Dyes

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ABSTRACT

Three commercial cationic agents, each marketed as a fixing agent to improve the wash fastness of direct dyes on cellulosic fibres, were used to pre-treat cotton fabric. The pre-treated fabric was dyed using four C.I. Solubilised Sulphur dyes and the effects of pre-treatment on the colour strength and wash fastness properties of the dyeings were investigated. It was found that pre-treatment increased the colour strength of the dyeings and also improved wash fastness. Copyright © 1996 Elsevier Science Ltd

Keywords: Cotton, dyeability, sulphur dyes, pre-treatment, colour yield, wash fastness.

INTRODUCTION

Considerable interest has attended techniques for enhancing the dyeability of cotton with direct and reactive dyes by pre-treating the fibre with cationic products. Shore[1] has concisely reviewed more recent excursions by workers in this area and discusses the varied approaches that have been explored. In essence, the most widely researched strategy has been the introduction of cationic sites, usually based on nitrogen, within the fibre and the terms cationisation and amination have been used in this context. Essentially, the objective in pre-treating cotton and other cellulosic fibres prior to their dyeing with direct and reactive dyes is to enhance the substantivity of the anionic dye for the substrate through the operation of ion–ion forces of interaction between the anionic (commonly sulphonate) groups in the dye and the cationic groups in the pre-treated fibre. In the case of reactive dyes, pre-treatment with an appropriate compound can also introduce within the fibre sites for the covalent attachment of the dye.

Although a plethora of pre-treatment compounds have been examined, these tend to be of two basic types, namely monomeric or polymeric; with relatively few exceptions, the cationic compounds examined have tended to be scientifically interesting rather than commercially available products. Despite the very large amount of research that has attended this area, few of these pre-treatments enjoy widespread commercial use; one of these is discussed below.

Sulphur dyes are one of the most popular of all dye classes used on cellulosic fibres.[2,3] On such fibres, the dyes characteristically furnish inexpensive medium to heavy depth shades of moderate to good light fastness, good wet fastness but poor fastness to bleaching.[3,4] Each of the three commercially important types of sulphur dye (C.I. Sulphur, C.I. Leuco Sulphur and C.I. Solubilised Sulphur dyes) are commonly applied to cellulosic fibres from alkaline reducing solutions as water-soluble, thiolate ($D\text{-}S^- \; Na^+$) anions that are subsequently oxidised to the insoluble, parent C.I. Sulphur dye, *in situ* in the fibre. Thus, the pre-treatment of cellulosic fibres with cationic compounds prior to their dyeing with the anionic, thiolate form of sulphur dyes should enhance the substantivity of the dyes for the substrate through the operation of ion–ion forces of interaction between the anionic ($D\text{-}S^-$) groups in the dye and the cationic groups in the pre-treated fibre. Surprisingly, despite the immense interest in techniques for enhancing the dyeability of cotton with direct and reactive dyes by pre-treating the fibre with cationic products, very little interest has been shown in the effect of such pre-treatment on the dyeability of cotton with reduced sulphur dyes. However, a non-reductive dyeing system has recently gained commercial importance in which the cellulosic fibre is pre-treated with a suitable cationic resin and the pre-treated substrate then dyed using non-reduced, C.I. Solubilised Sulphur dyes.[3]

The work reported in this first part of the paper comprised an examination of the effect of pre-treating cotton fabric with three readily available proprietary polymeric cationic fixing agents on the uptake of reduced C.I. Solubilised Sulphur dyes.

EXPERIMENTAL

Materials

Fabric

Scoured and bleached, fluorescent brightener-free woven cotton (156.5 g m^{-2}) was used.

Dyes

Four commercial C.I. Solubilised Sulphur dyes, namely *Sulphosol Black SG* (C.I. Solubilised Sulphur Black 1), *Sulphosol Blue SL* (C.I. Solubilised Sulphur Blue 5), *Sulphosol Yellow SR* (C.I. Solubilised Sulphur Yellow 23) and *Sulphosol Bordeaux SB* (C.I. Solubilised Sulphur Red 6) were used, each generously supplied by J. Robinson Ltd.

Reducing agent

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

Cationic fixing agents

Commercial samples of *Matexil FC-PN* and *Matexil FC-ER* were kindly supplied by ICI Surfactants; a commercial sample of *Solfix E* was generously provided by Ciba-Geigy (UK).

All other reagents were of general purpose grade.

Procedures

Pre-treatment

All pre-treatment (0.5%, 1%, 2% or 5% omf) was carried out using fabric (10 g) which had been wetted out in cold tap water, in sealed, stainless steel dyeing tubes of 300 cm^3 capacity housed in a Zeltex Polycolor laboratory-scale dyeing machine, using a 20:1 liquor ratio. The pre-treatment methods employed to apply the cationic agents are shown in Fig. 1. At the end of pre-treatment, the samples were removed from the treatment bath, rinsed in cold tap water and allowed to dry in the open air.

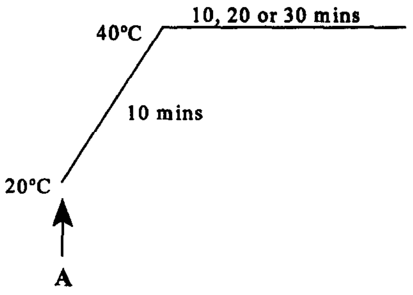
Dyeing

All dyeings (6% omf) were carried out using fabric which had been wetted out in cold distilled water, in sealed, stainless steel dyeing tubes of 300 cm^3 capacity, housed in a Zeltex Polycolor laboratory-scale dyeing machine, using a 7:1 liquor ratio. The dyeing method used is shown in Fig. 2 and the additions made to the dyebaths are displayed in Table 1.

Oxidation

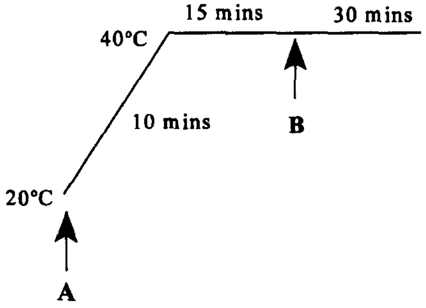
At the end of dyeing, the dyed sample was removed, rinsed thoroughly in cold water and then in hot water and treated in a stirred, aqueous (distilled water) solution (50:1 liquor ratio) containing 1 g litre^{-1} hydrogen peroxide (30% w/v) and 1 g litre^{-1} glacial acetic acid at 60°C for 15 min. At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

Matexil FC-PN and Matexil FC-ER



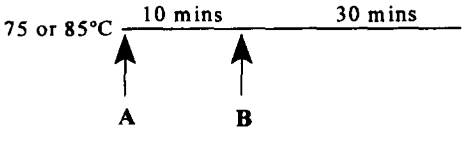
A 0.5, 1, 2 or 5% omf Matexil FC-PN or Matexil FC-ER

Solfix E



A 0.5, 1, 2 or 5% omf Solfix E
B 2 cm^3 l^{-1} 36°Bé NaOH

Fig. 1. Application methods for cationic fixing agents.



A Dye (6% omf)
Fabric (10g)
Leucad 71
B 2.5 cm^3 or 3.5cm^3 of 300 gl^{-1} NaCl

Fig. 2. Dyeing method.

TABLE 1
Dyebath Additions

C.I. Solubilised	Dyeing temperature (°C)	NaCl addition (cm^3 of 300 g $litre^{-1}$ aqueous solution)	Leucad 71 (cm^3 of 5% aqueous solution)
Sulphur Black 1	85	3.5	9.0
Sulphur Blue 5	85	2.5	4.5
Sulphur Yellow 23	85	3.5	12.0
Sulphur Red 6	75	3.5	6.0

Colour measurement
The reflectance values of the dry, dyed samples were measured using a Colorgen reflectance spectrophotometer interfaced to a Digital personal computer, under illuminant D_{65} using a 10° standard observer with specular component excluded and UV component included, from which the corresponding *K*/*S* values and CIE L*, a*, b*, C* and h° coordinates 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.

Determination of wash fastness
The fastness of the dry, dyed samples to the ISO C06/C2 wash test was determined using the standard method.[5]

RESULTS AND DISCUSSION

Pre-treatment with Matexil FC-PN

The colour strength (*K*/*S* values) and colorimetric parameters of cotton fabric which had been pre-treated with Matexil FC-PN and dyed using 6% omf C.I. Solubilised Sulphur Black 1, C.I. Solubilised Sulphur Blue 5, C.I. Solubilised Sulphur Yellow 23 and C.I. Solubilised Sulphur Red 6 are presented in Tables 2–5, respectively. The *K*/*S* values and colorimetric parameters of dyed, untreated cotton fabric are also given. The results clearly demonstrate that pre-treatment using Matexil FC-PN enhanced the colour strength of the dyeings carried out in both the absence and presence of electrolyte. Also, it is apparent that the enhancement in colour strength imparted by pre-treatment generally increased with increasing concentration of the cationic fixing agent used, but was little influenced by the duration of pre-treatment.

Electrolyte, commonly sodium chloride, is added to C.I. Solubilised Sulphur dyebaths to increase dye–fibre substantivity and thus colour strength. The effect of the addition of NaCl to the 6% omf dyeings is clearly demonstrated by the results in Tables 2–5. For each of the four dyes used, a pair of dyed, untreated samples were produced; in Tables 2–5 it is obvious that the *K*/*S* value of the untreated dyeing carried out in the presence of electrolyte was higher than the corresponding untreated dyeing carried out in the absence of NaCl. For each dye, the difference in colour strength between the two *K*/*S* values reflects the increased dye–fibre substantivity imparted by the added electrolyte.

From the foregoing, the finding (Tables 2–5) that the colour strength of the pre-treated dyeings which had been carried out in the presence of electrolyte

TABLE 2
Colorimetric Data for Dyeings Pre-treated using Matexil FC-PN
(C.I. Solubilised Sulphur Black 1)

Pre-treatment	*K*/*S*	L*	a*	b*	C*	h°
Dyeing in the absence of NaCl						
None	2.62	45.63	−0.42	−4.99	5.01	265.19
FC-PN 0.5% 10 min	3.09	43.13	−0.30	−5.34	5.35	266.78
FC-PN 1.0% 10 min	3.29	42.12	0.05	−5.50	5.50	269.48
FC-PN 2.0% 10 min	3.94	39.40	−0.23	−4.91	4.92	267.32
FC-PN 5.0% 10 min	4.20	38.46	−0.19	−5.05	4.95	267.80
FC-PN 0.5% 20 min	3.12	42.88	−0.20	−5.00	5.00	267.71
FC-PN 1.0% 20 min	3.70	40.42	−0.36	−5.16	5.07	265.93
FC-PN 2.0% 20 min	4.07	38.99	−0.36	−4.96	4.97	265.85
FC-PN 5.0% 20 min	4.43	41.64	−0.39	−5.34	5.35	265.82
FC-PN 0.5% 30 min	3.06	43.28	−0.21	−5.36	5.36	267.76
FC-PN 1.0% 30 min	3.33	42.00	−0.31	−5.23	5.24	266.61
FC-PN 2.0% 30 min	4.12	38.74	−0.14	−5.13	5.13	268.44
FC-PN 5.0% 30 min	4.56	37.32	−0.23	−5.10	5.11	267.42
Dyeing in the presence of NaCl						
None	3.50	41.21	−0.26	−5.09	5.10	267.08
FC-PN 0.5% 10 min	4.35	37.87	0.15	−5.32	5.32	271.62
FC-PN 1.0% 10 min	4.98	35.80	0.31	−5.06	5.07	273.51
FC-PN 2.0% 10 min	5.26	34.96	0.35	−4.79	4.80	274.18
FC-PN 5.0% 10 min	4.10	38.76	0.11	−5.45	5.45	271.16
FC-PN 0.5% 20 min	3.86	39.67	0.01	−5.35	5.35	270.11
FC-PN 1.0% 20 min	4.22	38.36	0.01	−5.44	5.44	270.11
FC-PN 2.0% 20 min	3.99	39.27	0.01	−5.57	5.57	270.10
FC-PN 5.0% 20 min	3.40	37.22	−0.06	−5.50	5.50	269.37
FC-PN 0.5% 30 min	3.60	40.74	−0.09	−5.34	5.34	269.03
FC-PN 1.0% 30 min	3.38	41.68	0.03	−5.52	5.52	270.31
FC-PN 2.0% 30 min	4.22	38.40	−0.03	−5.33	5.33	269.68
FC-PN 5.0% 30 min	3.97	39.30	0.01	−5.52	5.52	270.10

was generally higher than that of the corresponding dyeings which had been carried out in the absence of NaCl was expected. From Tables 2 to 5, it is apparent that pre-treatment with the cationic fixing agent can be considered as an alternative to the use of salt in dyeing in that in many cases, the colour strength of pre-treated fabric which had been dyed in the absence of electrolyte was similar to or even higher than that of untreated fabric which had been dyed in the presence of salt.

It was observed that for all the dyeings, pre-treatment did not result in unlevelness. The findings displayed in Tables 2–5 also reveal that the colour of the dyed, pre-treated samples was very similar to that of the corresponding dyed, untreated dyeing as shown by the a*, b* and h° values of the dyeings.

TABLE 3
Colorimetric Data for Dyeings Pre-treated using Matexil FC-PN
(C.I. Solubilised Sulphur Blue 5)

Pre-treatment	*K/S*	L*	a*	b*	C*	h°
Dyeing in the absence of NaCl						
None	2.98	46.01	3.74	−21.55	21.87	279.85
FC-PN 0.5% 10 min	3.64	43.65	2.81	−22.75	22.92	277.04
FC-PN 1.0% 10 min	3.66	43.64	2.40	−22.59	22.72	276.06
FC-PN 2.0% 10 min	4.04	42.15	2.89	−22.96	23.14	277.17
FC-PN 5.0% 10 min	4.31	41.26	2.63	−22.72	22.87	276.60
FC-PN 0.5% 20 min	2.98	46.72	2.15	−22.42	22.52	275.48
FC-PN 1.0% 20 min	3.79	43.00	2.89	−22.66	22.84	277.27
FC-PN 2.0% 20 min	3.90	42.71	2.88	−23.16	23.34	277.09
FC-PN 5.0% 20 min	4.54	40.15	3.33	−22.31	22.56	278.49
FC-PN 0.5% 30 min	3.33	44.95	2.42	−22.30	22.43	276.19
FC-PN 1.0% 30 min	3.36	44.51	3.18	−22.17	22.40	278.16
FC-PN 2.0% 30 min	3.66	43.56	2.74	−22.78	22.94	276.86
FC-PN 5.0% 30 min	5.04	38.77	3.10	−22.29	22.50	277.92
Dyeing in the presence of NaCl						
None	3.76	42.60	4.23	−22.00	22.90	280.67
FC-PN 0.5% 10 min	3.65	43.59	2.85	−22.90	23.08	277.09
FC-PN 1.0% 10 min	3.96	42.39	3.40	−23.51	23.75	278.23
FC-PN 2.0% 10 min	4.03	42.10	3.38	−23.42	23.66	278.21
FC-PN 5.0% 10 min	4.57	40.17	3.51	−23.18	23.44	278.61
FC-PN 0.5% 20 min	3.93	42.45	3.28	−23.21	23.44	278.04
FC-PN 1.0% 20 min	3.90	42.67	3.16	−23.33	23.54	277.71
FC-PN 2.0% 20 min	4.33	41.07	3.82	−23.90	24.20	279.08
FC-PN 5.0% 20 min	4.53	40.40	3.65	−23.70	23.98	278.76
FC-PN 0.5% 30 min	3.66	43.46	3.65	−23.66	23.94	278.77
FC-PN 1.0% 30 min	3.91	42.58	3.76	−23.96	24.25	278.92
FC-PN 2.0% 30 min	3.71	43.38	3.41	−23.77	24.01	278.16
FC-PN 5.0% 30 min	4.52	40.48	3.57	−23.71	23.98	278.56

Tables 2–5 reveal that in general the four dyes varied in the extent to which their adsorption was modified by pre-treatment. Of the four dyes used, the behaviour of C.I. Solubilised Sulphur Yellow 23 (Table 4) differed to that of its three counterparts insofar as the extent to which its adsorption was enhanced by pre-treatment was generally much lower than that of the three other dyes used.

Pre-treatment with Matexil FC-ER and Solfix E

The colour strength and colorimetric parameters of cotton fabric which had been pre-treated, both with Matexil FC-ER and Solfix E, and then dyed

TABLE 4
Colorimetric Data for Dyeings Pre-treated using Matexil FC-PN
(C.I. Solubilised Sulphur Yellow 23)

Pre-treatment	*K/S*	L*	a*	b*	C*	h°
Dyeing in the absence of NaCl						
None	6.02	71.06	11.33	53.81	54.99	78.11
FC-PN 0.5% 10 min	5.51	69.92	10.33	49.61	50.67	78.24
FC-PN 1.0% 10 min	5.92	67.70	10.88	47.59	48.82	77.12
FC-PN 2.0% 10 min	6.34	67.34	11.43	49.63	50.93	77.03
FC-PN 5.0% 10 min	6.41	66.85	11.44	49.10	50.42	76.88
FC-PN 0.5% 20 min	6.43	67.29	11.28	49.50	50.77	77.16
FC-PN 1.0% 20 min	6.47	66.21	11.78	48.51	49.92	76.35
FC-PN 2.0% 20 min	6.52	68.50	11.69	51.64	52.95	77.24
FC-PN 5.0% 20 min	6.68	66.61	11.11	49.36	50.59	77.32
FC-PN 0.5% 30 min	6.36	69.74	11.31	52.42	53.63	77.82
FC-PN 1.0% 30 min	6.53	67.73	11.13	50.41	51.62	77.55
FC-PN 2.0% 30 min	6.71	66.10	11.57	48.86	50.21	76.68
FC-PN 5.0% 30 min	6.86	66.24	11.83	49.45	50.85	76.55
Dyeing in the presence of NaCl						
None	6.81	68.25	12.77	53.48	54.98	76.57
FC-PN 0.5% 10 min	6.91	67.62	12.74	52.76	54.28	76.42
FC-PN 1.0% 10 min	7.02	66.17	12.95	51.32	52.93	75.84
FC-PN 2.0% 10 min	6.91	66.62	11.82	50.63	51.99	76.86
FC-PN 5.0% 10 min	6.83	66.86	12.30	50.90	52.37	76.41
FC-PN 0.5% 20 min	6.75	67.13	12.13	51.41	52.82	76.72
FC-PN 1.0% 20 min	7.11	66.34	12.93	51.91	53.50	76.01
FC-PN 2.0% 20 min	6.45	67.96	11.68	51.35	52.66	77.19
FC-PN 5.0% 20 min	6.70	66.55	12.44	50.12	51.64	76.06
FC-PN 0.5% 30 min	7.07	67.90	12.33	53.63	55.03	77.05
FC-PN 1.0% 30 min	7.02	66.93	11.41	50.85	52.11	77.35
FC-PN 2.0% 30 min	6.76	67.34	12.25	52.27	53.69	76.81
FC-PN 5.0% 30 min	7.17	67.05	12.20	52.95	54.34	77.03

using 6% omf of each of the four C.I. Solubilised Sulphur dyes, are presented in Tables 6–9 and Tables 10–13, respectively.

It is evident that pre-treatment with each cationic fixing agent markedly enhanced colour strength, when dyeing had been carried out in both the absence and presence of sodium chloride. Close similarities exist between the effects, on the uptake of the four dyes, imparted by pre-treatment using Matexil FC-ER and using Solfix E, as revealed by a comparison of the results presented in Tables 6–9 and Tables 10–13, respectively. These include the findings that the enhancement in colour strength imparted by pre-treatment generally increased with increasing concentration of the cationic fixing agent used. For each of the four dyes used, the colour strength of the pre-treated

TABLE 5
Colorimetric Data for Dyeings Pre-treated using Matexil FC-PN
(C.I. Solubilised Sulphur Red 6)

Pre-treatment	*K/S*	L*	a*	b*	C*	h°
Dyeing in the absence of NaCl						
None	4.57	41.53	20.62	−2.64	20.79	352.70
FC-PN 0.5% 10 min	5.40	39.29	21.62	−4.43	22.07	348.42
FC-PN 1.0% 10 min	6.24	37.35	22.06	−5.58	22.75	345.80
FC-PN 2.0% 10 min	7.59	34.22	20.71	−5.52	21.43	345.08
FC-PN 5.0% 10 min	8.39	32.62	20.04	−5.28	20.72	345.24
FC-PN 0.5% 20 min	6.03	37.36	20.79	−3.07	21.02	351.60
FC-PN 1.0% 20 min	6.74	35.48	19.43	−2.63	19.61	352.29
FC-PN 2.0% 20 min	7.47	34.74	21.68	−6.14	22.53	344.19
FC-PN 5.0% 20 min	7.49	34.97	22.46	−7.29	23.61	342.02
FC-PN 0.5% 30 min	5.37	39.59	22.41	−5.20	23.01	346.94
FC-PN 1.0% 30 min	5.65	38.37	21.05	−3.53	21.34	350.48
FC-PN 2.0% 30 min	6.47	36.13	19.73	−2.87	19.94	351.72
FC-PN 5.0% 30 min	6.61	35.67	19.53	−3.09	19.77	351.01
Dyeing in the presence of NaCl						
None	6.36	37.00	21.19	−1.57	21.25	355.76
FC-PN 0.5% 10 min	6.08	37.57	21.54	−2.29	21.66	353.93
FC-PN 1.0% 10 min	6.47	36.60	20.91	−1.33	20.95	356.36
FC-PN 2.0% 10 min	7.21	35.04	20.10	−0.31	20.10	359.12
FC-PN 5.0% 10 min	7.28	34.60	19.59	−1.47	19.65	355.71
FC-PN 0.5% 20 min	6.23	37.35	21.85	−2.10	21.95	354.51
FC-PN 1.0% 20 min	6.75	36.14	21.18	−1.46	21.23	356.06
FC-PN 2.0% 20 min	7.01	34.65	19.76	−1.55	19.82	355.51
FC-PN 5.0% 20 min	7.32	34.43	18.92	−0.41	18.92	358.76
FC-PN 0.5% 30 min	5.90	37.85	20.81	−1.80	20.89	355.06
FC-PN 1.0% 30 min	6.53	36.02	19.92	−1.08	19.95	356.90
FC-PN 2.0% 30 min	7.06	34.73	19.39	−1.56	19.45	355.40
FC-PN 5.0% 30 min	7.39	34.38	18.02	−0.26	18.02	359.17

dyeings which had been carried out in the presence of electrolyte was generally higher than that of the corresponding dyeings which had been carried out in the absence of NaCl. Also, pre-treatment did not cause any uneveness and the colorimetric parameters displayed in Tables 6–13 reveal that the colour of the dyed, pre-treated samples was not greatly affected by pre-treatment.

Tables 6–13 also show that, in general, the four dyes varied in the extent to which their adsorption was modified by pre-treatment. The behaviour of C.I. Solubilised Sulphur Yellow 23 (Tables 8 and 12) differed to that of its three counterparts, insofar as, when dyeing was carried out in the absence of NaCl, pre-treatment with each of the two cationic fixing agents imparted only a very small increase in colour strength and, when dyeing had been

TABLE 6

Colorimetric Data for Dyeings Pre-treated using Matexil FC-ER
(C.I. Solubilised Sulphur Black 1)

Pre-treatment	K/S	L*	a*	b*	C*	h°
Dyeing in the absence of NaCl						
None	2.62	45.63	−0.42	−4.99	5.01	265.19
FC-ER 0.5% 10 min	5.17	35.33	0.05	−4.84	4.84	270.59
FC-ER 1.0% 10 min	5.30	34.88	0.31	−4.96	4.97	273.58
FC-ER 2.0% 10 min	5.37	34.70	0.20	−4.83	4.83	272.37
FC-ER 5.0% 10 min	5.44	34.50	0.25	−4.79	4.80	272.99
FC-ER 0.5% 20 min	5.16	35.31	0.12	−4.78	4.78	271.44
FC-ER 1.0% 20 min	5.18	35.19	0.35	−4.82	4.83	274.15
FC-ER 2.0% 20 min	5.31	34.85	0.35	−5.01	5.02	274.00
FC-ER 5.0% 20 min	5.42	34.76	−0.09	−4.91	4.91	268.95
FC-ER 0.5% 30 min	4.86	36.10	0.35	−5.02	5.03	273.99
FC-ER 1.0% 30 min	4.84	36.22	0.15	−4.81	4.81	271.79
FC-ER 2.0% 30 min	5.07	35.66	0.02	−4.93	4.93	270.23
FC-ER 5.0% 30 min	5.92	33.37	0.01	−4.64	4.64	270.12
Dyeing in the presence of NaCl						
None	3.50	41.21	−0.26	−5.09	5.10	267.08
FC-ER 0.5% 10 min	6.02	32.86	0.73	−4.59	4.65	279.04
FC-ER 1.0% 10 min	6.01	32.91	0.67	−4.61	4.66	278.27
FC-ER 2.0% 10 min	6.10	32.70	0.59	−4.44	4.48	277.57
FC-ER 5.0% 10 min	6.60	31.62	0.57	−4.32	4.36	277.52
FC-ER 0.5% 20 min	5.47	34.36	0.40	−4.68	4.70	274.89
FC-ER 1.0% 20 min	6.07	32.79	0.60	−4.51	4.55	277.58
FC-ER 2.0% 20 min	5.91	33.06	0.73	−4.24	4.30	279.77
FC-ER 5.0% 20 min	6.16	32.58	0.59	−4.40	4.44	277.64
FC-ER 0.5% 30 min	5.97	32.97	0.01	−4.29	4.29	270.13
FC-ER 1.0% 30 min	6.57	31.55	0.81	−4.22	4.30	280.87
FC-ER 2.0% 30 min	6.92	30.92	0.60	−4.24	4.28	278.05
FC-ER 5.0% 30 min	7.04	30.58	0.63	−3.89	3.94	279.20

carried out in the presence of electrolyte, pre-treatment lowered colour strength. This anomalous behaviour of C.I. Solubilised Sulphur Yellow 23 agrees with that observed earlier in the case of pre-treatment using Matexil FC-PN.

Wash fastness results

Representative dyeings were selected for wash fastness evaluation. Each of the untreated dyeings was subjected to the ISO C06/C2 wash fastness test; the selection of dyed, pre-treated samples for wash fastness was carried out with reference to their colour strength (*K*/*S* value) in that dyeings of very high *K*/*S* together with dyeings with, as far as possible, similar *K*/*S* were

TABLE 7
Colorimetric Data for Dyeings Pre-treated using Matexil FC-ER
(C.I. Solubilised Sulphur Blue 5)

Pre-treatment	*K*/*S*	L*	a*	b*	C*	h°
Dyeing in the absence of NaCl						
None	2.98	46.01	3.74	−21.55	21.87	279.85
FC-ER 0.5% 10 min	5.92	35.63	3.99	−20.24	20.63	281.15
FC-ER 1.0% 10 min	6.09	35.43	3.91	−20.86	21.22	280.62
FC-ER 2.0% 10 min	6.11	35.40	3.73	−20.71	21.04	280.21
FC-ER 5.0% 10 min	6.38	34.56	4.10	−20.17	20.58	281.49
FC-ER 0.5% 20 min	5.54	36.92	3.73	−21.35	21.67	279.91
FC-ER 1.0% 20 min	6.14	35.36	4.09	−21.31	21.70	280.86
FC-ER 2.0% 20 min	6.31	34.91	3.98	−20.92	21.30	280.77
FC-ER 5.0% 20 min	6.36	34.90	4.02	−21.34	21.72	280.67
FC-ER 0.5% 30 min	5.43	36.94	4.04	−20.85	21.24	280.97
FC-ER 1.0% 30 min	5.90	35.82	3.85	−20.75	21.10	280.51
FC-ER 2.0% 30 min	6.24	35.03	4.14	−21.05	21.45	281.13
FC-ER 5.0% 30 min	6.45	34.75	3.97	−21.37	21.74	280.52
Dyeing in the presence of NaCl						
None	3.76	42.57	4.23	−22.45	22.85	280.67
FC-ER 0.5% 10 min	7.27	32.41	5.05	−19.84	20.47	284.28
FC-ER 1.0% 10 min	7.31	32.46	4.74	−20.05	20.60	283.30
FC-ER 2.0% 10 min	7.19	32.63	4.63	−19.60	20.14	283.29
FC-ER 5.0% 10 min	7.36	32.23	4.71	−19.45	20.01	283.61
FC-ER 0.5% 20 min	7.13	32.67	4.79	−19.67	20.24	283.69
FC-ER 1.0% 20 min	8.15	30.79	4.62	−19.05	19.60	283.63
FC-ER 2.0% 20 min	8.04	31.12	4.83	−19.58	20.17	283.86
FC-ER 5.0% 20 min	7.94	31.03	4.99	−18.89	19.54	284.80
FC-ER 0.5% 30 min	7.86	31.34	4.85	−19.49	20.08	283.97
FC-ER 1.0% 30 min	8.04	31.15	4.91	−19.94	20.54	283.83
FC-ER 2.0% 30 min	8.64	29.98	4.95	−18.93	19.57	284.65
FC-ER 5.0% 30 min	8.91	29.57	5.07	−19.25	19.91	284.76

chosen. The results are displayed in Tables 14–17, from which it is evident that for each of the four dyes used, the wash fastness of the dyed, pre-treated samples was either very similar to or superior to that of the corresponding dyed, untreated samples. This finding is of even greater significance when it is considered that each of the dyed, pre-treated samples was of higher colour strength than the corresponding dyed, untreated sample.

General discussion

The enhanced colour strength imparted by pre-treatment with each of the three cationic fixing agents can be ascribed to a corresponding increase in substantivity of the reduced (thiolate; D-S$^-$ Na$^+$) form of the dye resulting

TABLE 8
Colorimetric Data for Dyeings Pre-treated using Matexil FC-ER
(C.I. Solubilised Sulphur Yellow 23)

Pre-treatment	*K/S*	L*	a*	b*	C*	h°
Dyeing in the absence of NaCl						
None	6.02	71.06	11.33	53.81	54.99	78.11
FC-ER 0.5% 10 min	6.55	68.68	12.53	53.63	55.07	76.85
FC-ER 1.0% 10 min	6.52	68.60	12.70	53.51	55.00	76.65
FC-ER 2.0% 10 min	6.54	68.37	12.18	52.94	54.32	77.04
FC-ER 5.0% 10 min	6.49	68.89	11.84	53.16	54.46	77.44
FC-ER 0.5% 20 min	6.77	68.05	12.60	52.86	54.34	76.59
FC-ER 1.0% 20 min	6.55	69.11	12.38	53.79	55.20	77.04
FC-ER 2.0% 20 min	6.70	67.83	12.94	53.02	54.58	76.28
FC-ER 5.0% 20 min	6.84	68.15	12.63	53.51	54.98	76.72
FC-ER 0.5% 30 min	6.75	68.67	12.94	54.11	55.64	76.55
FC-ER 1.0% 30 min	6.94	68.06	12.70	53.79	55.27	76.72
FC-ER 2.0% 30 min	6.84	68.13	12.92	53.60	55.14	76.45
FC-ER 5.0% 30 min	6.80	68.38	12.27	53.48	54.87	77.08
Dyeing in the presence of NaCl						
None	6.81	68.25	12.77	53.48	54.98	76.57
FC-ER 0.5% 10 min	6.60	65.52	12.13	48.69	50.18	76.01
FC-ER 1.0% 10 min	6.45	66.31	11.61	48.43	49.80	76.52
FC-ER 2.0% 10 min	6.51	66.20	11.25	48.54	49.83	76.95
FC-ER 5.0% 10 min	6.59	66.47	11.20	49.02	50.28	77.13
FC-ER 0.5% 20 min	6.43	66.83	11.45	49.50	50.81	76.98
FC-ER 1.0% 20 min	6.46	66.32	11.38	48.41	49.73	76.77
FC-ER 2.0% 20 min	6.54	66.41	11.34	48.94	50.24	76.95
FC-ER 5.0% 20 min	6.62	66.26	11.37	49.05	50.35	76.95
FC-ER 0.5% 30 min	6.38	67.04	11.50	49.36	50.68	76.89
FC-ER 1.0% 30 min	6.59	66.19	11.57	49.07	50.42	76.73
FC-ER 2.0% 30 min	6.44	67.12	10.99	49.41	50.62	77.46
FC-ER 5.0% 30 min	6.71	66.83	11.06	49.79	51.00	77.48

from the presence of the cationic compound within the fabric. The increased dye–fibre substantivity can be attributed to ion–ion forces of interaction operating between anionic groups in the dye and cationic groups in the pre-treated fibre.

A comparison of the results obtained for pre-treatment using Matexil FC-PN (Tables 2–5), Matexil FC-ER (Tables 6–9) and Solfix E (Tables 10–13) shows that the extent to which the three fixing agents enhanced colour strength increased in the order: Matexil FC-PN < Matexil FC-ER < Solfix E.

An explanation of this finding is required. However, details of the composition of Matexil FC-PN, Matexil FC-ER and Solfix E are not publicly available, but instead public domain information describes the three fixing agents as, respectively, *a nitrogenous condensation product*,[6] *an aqueous*

TABLE 9
Colorimetric Data for Dyeings Pre-treated using Matexil FC-ER
(C.I. Solubilised Sulphur Red 6)

Pre-treatment	*K/S*	L*	a*	b*	C*	h°
Dyeing in the absence of NaCl						
None	4.57	41.53	20.62	−2.64	20.79	352.70
FC-ER 0.5% 10 min	6.87	34.64	17.01	−0.77	17.03	357.41
FC-ER 1.0% 10 min	7.82	32.99	17.81	−2.79	18.03	351.10
FC-ER 2.0% 10 min	8.66	31.83	18.30	−2.59	18.48	351.94
FC-ER 5.0% 10 min	9.17	31.20	18.65	−2.92	18.88	351.10
FC-ER 0.5% 20 min	6.81	34.71	17.06	−0.73	17.08	357.55
FC-ER 1.0% 20 min	7.76	32.67	17.67	−2.59	17.86	351.66
FC-ER 2.0% 20 min	9.02	31.21	18.17	−2.90	18.40	350.93
FC-ER 5.0% 20 min	9.89	29.94	18.01	−2.79	18.22	351.19
FC-ER 0.5% 30 min	6.74	35.45	18.77	−0.93	18.79	357.16
FC-ER 1.0% 30 min	7.62	33.56	17.91	−1.06	17.94	356.61
FC-ER 2.0% 30 min	8.97	31.24	18.02	−3.02	18.27	350.49
FC-ER 5.0% 30 min	9.53	30.44	17.95	−2.59	18.14	351.79
Dyeing in the presence of NaCl						
None	6.36	37.00	21.19	−1.57	21.25	355.76
FC-ER 0.5% 10 min	9.40	30.82	18.00	−0.64	18.01	357.96
FC-ER 1.0% 10 min	8.66	31.91	17.81	−0.20	17.81	359.36
FC-ER 2.0% 10 min	8.55	32.07	17.33	0.69	17.34	2.28
FC-ER 5.0% 10 min	9.53	30.53	17.46	−0.36	17.46	358.82
FC-ER 0.5% 20 min	9.13	31.27	17.77	0.18	17.77	0.58
FC-ER 1.0% 20 min	9.17	31.04	17.37	0.02	17.37	0.07
FC-ER 2.0% 20 min	9.88	29.87	17.08	−0.65	17.09	357.82
FC-ER 5.0% 20 min	9.53	30.44	17.91	−2.04	18.03	353.50
FC-ER 0.5% 30 min	9.96	30.06	18.38	−2.29	18.52	352.90
FC-ER 1.0% 30 min	9.73	30.23	17.51	−0.98	17.54	356.80
FC-ER 2.0% 30 min	9.00	31.29	17.49	−0.53	17.50	358.26
FC-ER 5.0% 30 min	9.17	31.09	16.65	1.53	16.72	5.25

solution of a low M_r *resin*[6] and *an aqueous preparation of a modified polyamine derivative.*[7] Thus, although the three compounds differ chemically, it is not possible to characterise these differences in terms of chemical structure, degree of cationicity, M_r, proportion of active ingredient, etc., and therefore, no meaningful explanation of the relative effectiveness of the three fixing agents can be furnished. Nevertheless, this study has clearly shown that pre-treating cotton fabric with three, readily available, chemically different, proprietary polymeric cationic fixing agents markedly enhanced the uptake of reduced C.I. Solubilised Sulphur dyes.

TABLE 10

Colorimetric Data for Dyeings Pre-treated using Solfix E (C.I. Solubilised Sulphur Black 1)

Pre-treatment	*K/S*	L*	a*	b*	C*	h°
Dyeing in the absence of NaCl						
None	2.62	45.63	−0.42	−4.99	5.01	265.19
Solfix E 0.5%	4.26	38.39	−0.23	−5.38	5.38	267.55
Solfix E 1.0%	4.78	36.82	−0.35	−5.51	5.52	266.37
Solfix E 2.0%	5.43	34.98	−0.18	−5.75	5.75	268.21
Solfix E 5.0%	6.61	32.24	−0.12	−5.78	5.78	268.81
Dyeing in the presence of NaCl						
None	3.50	41.21	−0.26	−5.09	5.10	267.08
Solfix E 0.5%	5.84	33.60	0.16	−5.03	5.03	271.82
Solfix E 1.0%	5.75	33.78	0.33	−5.18	5.19	273.65
Solfix E 2.0%	6.06	33.09	0.23	−5.02	5.03	272.62
Solfix E 5.0%	7.23	30.59	0.40	−4.84	4.86	274.72

TABLE 11

Colorimetric Data for Dyeings Pre-treated using Solfix E (C.I. Solubilised Sulphur Blue 5)

Pre-treatment	*K/S*	L*	a*	b*	C*	h°
Dyeing in the absence of NaCl						
None	2.98	46.01	3.74	−21.55	21.87	279.85
Solfix E 0.5%	3.99	42.43	3.57	−24.23	24.49	278.38
Solfix E 1.0%	5.21	38.70	3.93	−24.89	25.20	278.97
Solfix E 2.0%	6.76	34.93	4.82	−25.16	25.62	280.84
Solfix E 5.0%	7.96	32.79	4.85	−25.05	25.52	280.96
Dyeing in the presence of NaCl						
None	3.76	42.57	4.23	−22.45	22.85	280.67
Solfix E 0.5%	5.80	36.84	4.35	−24.18	24.57	280.20
Solfix E 1.0%	6.19	36.01	4.32	−24.26	24.64	280.10
Solfix E 2.0%	7.91	32.55	4.86	−24.01	24.50	281.44
Solfix E 5.0%	9.73	29.67	5.33	−23.81	24.40	282.62

An explanation is also required for the finding that the wash fastness of the dyed, pre-treated samples was either very similar to or superior to that of the corresponding dyed, untreated fabric even though the dyed, pre-treated samples were of higher colour strength than the corresponding dyed, untreated sample. A possible explanation is offered on the basis 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.

Each of the three cationic compounds used are currently marketed as fixing agents for the aftertreatment of direct dyes on cellulosic fibres. It is

TABLE 12

Colorimetric Data for Dyeings Pre-treated using Solfix E (C.I. Solubilised Sulphur Yellow 23)

Pre-treatment	*K/S*	L*	a*	b*	C*	h°
Dyeing in the absence of NaCl						
None	6.02	71.06	11.33	53.81	54.99	78.11
Solfix E 0.5%	6.02	69.88	10.61	51.21	52.30	78.29
Solfix E 1.0%	6.39	70.24	9.95	52.20	53.14	79.21
Solfix E 2.0%	6.05	71.37	8.83	51.89	52.64	80.34
Solfix E 5.0%	6.17	70.84	9.07	51.59	52.38	80.03
Dyeing in the presence of NaCl						
None	6.81	68.25	12.77	53.48	54.98	76.57
Solfix E 0.5%	6.48	68.19	11.46	51.29	52.55	77.40
Solfix E 1.0%	6.43	68.45	10.87	50.80	51.95	77.92
Solfix E 2.0%	6.56	68.18	10.46	50.55	51.62	78.31
Solfix E 5.0%	6.91	68.42	10.65	52.80	53.86	78.60

TABLE 13

Colorimetric Data for Dyeings Pre-treated using Solfix E (C.I. Solubilised Sulphur Red 6)

Pre-treatment	*K/S*	L*	a*	b*	C*	h°
Dyeing in the absence of NaCl						
None	4.57	41.53	20.62	−2.64	20.79	352.70
Sofix E 0.5%	7.02	35.63	21.65	−3.17	21.88	351.67
Sofix E 1.0%	9.85	31.00	21.23	−4.91	21.79	346.98
Sofix E 2.0%	7.83	33.81	20.55	−1.82	20.63	354.94
Sofix E 5.0%	9.64	30.94	20.01	−1.50	20.07	355.71
Dyeing in the presence of NaCl						
None	6.36	37.60	21.19	−1.57	21.25	355.76
Sofix E 0.5%	6.80	35.97	21.07	−2.30	21.20	353.77
Sofix E 1.0%	8.73	32.47	20.29	−1.07	20.32	356.98
Sofix E 2.0%	10.28	29.93	18.94	−0.81	18.96	357.55
Sofix E 5.0%	10.81	29.20	18.61	−0.72	18.62	357.78

generally accepted that in the case of the aftertreatment of direct dyes with cationic fixing agents, enhanced wash fastness is achieved by the formation of a large molecular size, dye–cationic agent complex of low aqueous solubility. Earlier in this paper, it was proposed that pre-treatment with the cationic fixing agents increased the substantivity of the anionic thiolate (D-S^- Na^+) form of the dye because of ion–ion forces of interaction operating between anionic groups in the dye and cationic groups in the pre-treated fibre. Thus, initially at least, it seems reasonable to propose that such electrostatic interaction could result in the formation of a large molecular

TABLE 14
Wash Fastness Results (ISO C06/C2) for C.I. Solubilised Sulphur Black 1

Pre-treatment	*K/S*	Ch.	Cot.	Visc.
Dyeing in the absence of NaCl				
None	2.62	2–3	4	5
FC-PN 5.0% 30 min	4.56	3	4	5
FC-ER 5.0% 30 min	5.92	3	4	5
Solfix E 5.0%	6.61	3–4	4–5	5
Dyeing in the presence of NaCl				
None	3.50	2–3	4	5
FC-PN 1.0% 10 min	4.98	2–3	3–4	4–5
FC-ER 5.0% 30 min	7.04	3	4	5
Solfix E 5.0%	7.23	3	4	5

Ch, change in shade of original sample; Cot, staining of cotton adjacent; Visc., staining of viscose adjacent.

TABLE 15
Wash Fastness Results (ISO C06/C2) for C.I. Solubilised Sulphur Blue 5

Pre-treatment	*K/S*	Ch.	Cot.	Visc.
Dyeing in the absence of NaCl				
None	2.98	2	3	3–4
FC-PN 5.0% 30 min	5.04	2–3	3–4	4
FC-ER 2.0% 30 min	6.24	3	3	3–4
Solfix E 5.0%	7.96	3	4	4
Dyeing in the presence of NaCl				
None	3.76	2	3	3–4
FC-PN 0.5% 10 min	3.65	2–3	2–3	3
FC-ER 5.0% 30 min	8.91	3	2	3
Solfix E 5.0%	9.73	3	3	4

Legend as for Table 14.

size, low solubility, dye–cationic agent complex in the fibre that would be responsible for the observed improved wash fastness imparted by the three cationic agents.

However, although such a mechanism may be plausible during dyeing, in which the anionic, water-soluble, thiolate form of the dye can interact with the cationic agent in the fibre, the mechanism cannot, theoretically at least, apply to the completed (i.e. oxidised) dyeing. This is because the generally accepted mechanism of the dyeing of cellulosic fibres with C.I. Solubilised Sulphur dyes contends that at the end of dyeing (i.e. after oxidation), the dye is present in its insoluble (non-ionic) form. Consequently, in the context of

TABLE 16

Wash Fastness Results (ISO C06/C2) for C.I. Solubilised Sulphur Yellow 23

Pre-treatment	*K/S*	Ch.	Cot.	Visc.
Dyeing in the absence of NaCl				
None	6.02	2–3	2–3	3–4
FC-PN 1.0% 20 min	6.47	2–3	3	3–4
FC-ER 5.0% 30 min	6.80	3	3	3
Solfix E 1.0%	6.39	3	3–4	4
Dyeing in the presence of NaCl				
None	6.81	2–3	3	3–4
FC-PN 0.5% 10 min	6.91	2–3	2–3	3–4
FC-ER 0.5% 30 min	6.38	2–3	3	3–4
Solfix E 5.0%	6.91	3	3–4	4

Legend as for Table 14.

TABLE 17

Wash Fastness Results (ISO C06/C2) for C.I. Solubilised Sulphur Red 6

Pre-treatment	*K/S*	Ch.	Cot.	Visc.
Dyeing in the absence of NaCl				
None	4.57	2	2–3	3
FC-PN 1.0% 20 min	6.74	2	2–3	3
FC-ER 2.0% 30 min	8.97	2	2	2–3
Solfix E 5.0%	9.64	2	3	3–4
Dyeing in the presence of NaCl				
None	6.36	2	2–3	3–4
FC-PN 1.0% 10 min	6.47	1–2	2–3	3
FC-ER 1.0% 10 min	8.66	2	2–3	3
Solfix E 5.0%	10.81	2	2–3	3

Legend as for Table 14.

the improved wash fastness imparted by the three cationic agents, at the end of dyeing (i.e. after oxidation), the dye is no longer anionic and cannot, therefore, interact electrostatically with the cationic agent to form a large molecular size, low solubility, dye–cationic agent complex in the fibre.

However, recent work[8] has demonstrated that Matexil FC-PN and Matexil FC-ER improved the wash fastness of C.I. Solubilised Sulphur dyes on cotton when the two compounds were applied as aftertreatments of oxidised dyeings. In this particular study,[8] it was postulated that the enhanced wash fastness imparted by the two cationic compounds may have been secured in a similar manner to that operating in the case of cationic fixing agents/direct dyes, namely through the formation of a large molecular size, low solubility, complex between the oxidised dye and the cationic agents. Although direct evidence for the formation of such a dye–cationic agent complex was not secured, support for the proposed mechanism was elicited from the results of other workers and it was suggested that whilst very little is known of the structure of sulphur dyes, some dyes may, at the end of dyeing (after oxidation), contain anionic (e.g. sulphonic acid) groups that are capable of undergoing ion–ion interactions with the cationic agents.[8]

Clearly, further work is required to determine whether the improved wash fastness imparted by pre-treatment with the three cationic agents involves the formation of a dye–cationic agent complex.

Finally, it was considered pertinent to comment on the observation that, of the three cationic fixing agents used in the work, Solfix E imparted not only the greatest enhancement of colour strength but also the highest wash fastness. Solfix E is recommended for the aftertreatment of selected direct dyes on cellulosic fibres and it is the only reactive cationic fixing agent of the three used in the present study.[9] It is in the context of this reactivity that comment shall be made.

Exploratory work has been carried out in the author's laboratory into the manner in which the reactivity of Solfix E is utilised in the aftertreatment of direct dyes on cotton. Results obtained suggest that under the alkaline application conditions used to apply Solfix E to dyed cotton, the cationic polyamine self-reacts to produce a larger molecular size, cationic polymer within the dyed fibre. Although reaction of the agent with the cellulosic substrate is also possible under the particular application conditions employed, exploratory studies intimate that the extent of such reaction is small in comparison to the self-reaction of the product.

However, as explained, these findings into the manner in which the reactivity of Solfix E is utilised during the aftertreatment of direct dyes on cotton were obtained during exploratory work and need to be confirmed by more detailed and thorough investigations. Nevertheless, based on these initial findings, it can be proffered that in the case of cotton which had been pre-treated with Solfix E and subsequently dyed with the reduced (thiolate) dye, if any reactive groups were present in the pre-treated cotton, these would be susceptible to attack by the highly nucleophilic thiolate groups in the reduced dye resulting in the dye becoming covalently bound to the Solfix E in the substrate. If such a reaction did occur, the ensuing dye–Solfix E product would be of very large molecular size and, therefore, could be expected to display high fastness to washing owing to its corresponding low diffusional power within the fibre. Whilst this mechanism may explain the fact that Solfix E imparted the highest wash fastness to the dyeings of the three cationic compounds used, it does of course rely upon the presence, within the Solfix E pre-treated cotton, of reactive groups; in turn, this presupposes that not all the reactive groups in the cationic agent were consumed during pre-treatment and subsequent rinsing and drying.

None the less, whilst further work is clearly required to examine the feasibility of such a proposal, the possibility that Solfix E can react with the nucleophilic thiolate groups in reduced sulphur dyes when the cationic fixing agent is used as an aftertreatment, has been investigated in the author's laboratory and will be the subject of future publications.

CONCLUSIONS

It has been demonstrated that the pre-treatment of cotton with three commercially available cationic polymers that are marketed as fixing agents for direct dyes on cellulosic fibres, was generally very effective in enhancing the colour strength of dyeings achieved using four reduced forms of C.I. Solubilised Sulphur dyes. The pre-treated dyeings were generally of higher colour strength than the corresponding untreated dyeings when dyeing had been carried out in either the absence or presence of sodium chloride. The enhanced colour strength imparted by pre-treatment can be ascribed to a corresponding increase in substantivity of the thiolate form of the dye resulting from the presence of the cationic compound within the fabric. In turn, the increased dye–fibre substantivity can be attributed to ion–ion forces of interaction operating between anionic groups in the dye and cationic groups in the pre-treated fibre.

The results imply that the dyeing of cotton with C.I. Solubilised Sulphur dyes could be carried out in the absence of electrolyte if the fabric was pre-treated prior to dyeing.

The pre-treated dyeings exhibited very similar or slightly higher wash fastness than the corresponding untreated dyeings even though the colour strength of the dyed, pre-treated samples was greater than that of the dyed, untreated samples. It was postulated that the improved wash fastness imparted by pre-treatment with the cationic compounds may have been secured in a similar manner to that operating in the case of cationic fixing agents/direct dyes, namely the formation of a large molecular size, low solubility, complex between the oxidised dye and the cationic agent. Further work is required to establish the mechanism by which pre-treatment with the cationic agents improved the wash fastness of the dyes on cotton.

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