



## **Pad-Dry and Pad-Flash Cure Aftertreatments to Improve the Wash Fastness of Sulphur Dyeings on Cotton**

S. M. Burkinshaw & G. W. Collins

Specialty Chemical Group, Department of Colour Chemistry and Dyeing, The University,  
Leeds LS2 9JT, UK

(Received 4 April 1996; accepted 25 April 1996)

### *ABSTRACT*

*The application of two commercial cationic fixing agents using both Pad-Dry and Pad-Flash Cure procedures to the oxidized dyeings of four CI Leuco Sulphur dyes on cotton fabric resulted in improved fastness to the ISOC06/C2 wash test. The extent of the improved wash fastness imparted by the two cationic fixing agents compared favourably with that achieved using a commercial crease resist agent applied by a Pad-Flash Cure procedure. However, while aftertreatment with the two cationic fixing agents did not affect the shade or handle of the dyed fabric, aftertreatment with the crease resist agent imparted a harsh handle to the fabric and dulled the shade in some cases.*  
Copyright © 1997 Elsevier Science Ltd

**Keywords:** cotton, sulphur dyes, aftertreatment, continuous, fastness.

### **INTRODUCTION**

Sulphur dyes remain one of the most popular dye classes used on cellulosic fibres and their blends.<sup>1-3</sup> The dyes are used widely for the production of inexpensive black, blue, brown and green shades in medium to heavy depths.<sup>2-4</sup> The resultant dyeings generally possess poor fastness to bleach but moderate to good fastness to light and wet treatments;<sup>2-4</sup> however, they are less resistant to laundering with detergent/perborate formulations<sup>2,3</sup> that are now common in domestic washing powders.

In a previous paper by the present authors<sup>5</sup> it was reported that the fastness to the ISOC06/C2 wash test of the oxidized dyeings of CI Solubilized Sulphur, CI Leuco Sulphur and CI Sulphur dyes could be markedly improved by the use of polymeric cationic agents when applied using a simple exhaust aftertreatment procedure.<sup>5</sup>

The majority of sulphur dyes are applied using continuous dyeing methods rather than any other dyeing method,<sup>2,3</sup> particularly in the USA.<sup>6</sup> Cotton drill and corduroy are examples of fabric types that are dyed in such long, continuous runs using liquid dye brands (CI Leuco Sulphur dyes) which are highly suitable for this particular dyeing method.<sup>2-4</sup>

The purpose of the work reported in this paper was to assess the effectiveness of two commercial cationic fixing agents in improving the fastness to detergent/perborate washing, of the oxidized dyeings of four CI Leuco Sulphur dyes when applied as an aftertreatment using both Pad-Dry and Pad-Flash Cure application methods. A comparison was also made of the effectiveness of the two cationic aftertreatment agents with that of a commercial crease resist resin.

## EXPERIMENTAL

### **Fabric**

Scoured and bleached, fluorescent brightener-free woven cotton (150 g/m<sup>2</sup>) was used.

### **Dyes**

Commercial samples of four CI Leuco Sulphur dyes (Table 1), generously supplied by James Robinson Ltd, were used.

### **Reducing agent**

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

### **Cationic fixing agents**

Samples of two commercially available cationic products suitable for continuous application, namely Matexil FC-PN<sup>®</sup> and Fixogene CXF<sup>®</sup>,\* were kindly supplied by ICI Surfactants.

\*The words Matexil and Fixogene are trademarks, the property of Imperial Chemical Industries, plc.

**TABLE 1**  
CI Leuco Sulphur Dyes Used

<i>Sulphol Liquid</i>	<i>CI Leuco Sulphur</i>
Black QG	Black 1
Yellow QR	Yellow 23
Green QGCF	Green 2
Dark Blue QL	Blue 5

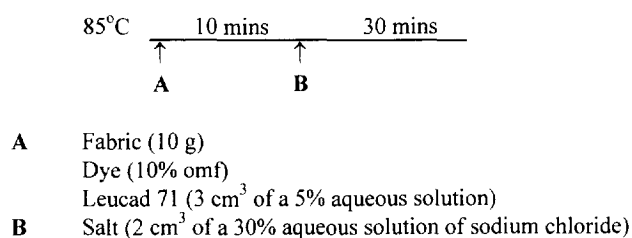
### Crease resist resin

A sample of Finish KKR was kindly supplied by Clariant (UK).

### Dyeing

A typical continuous application of sulphur dyes would be a Pad-Steam process<sup>2,3</sup> which involved padding the dye (usually a leuco sulphur liquid dye), reducing agent and wetting agent followed by steaming for 1 min and then washing-off and oxidation, in 4–14 boxes at speeds of up to 180 m/min.<sup>2,3</sup> However, for the present study, standard oxidized leuco sulphur dyeings were produced using a more convenient laboratory-scale, batchwise dyeing method that resulted in dyeings being produced that were very similar to those produced using a typical, continuous dyeing process.

Stock solutions of 20 g/dm<sup>3</sup> were prepared, using distilled water, of each of the four CI Leuco Sulphur dyes. Each dyebath comprised 50 cm<sup>3</sup> of the stock dye solution (for the 10% omf shade produced on a 10 g fabric sample), together with 3 cm<sup>3</sup> of a 5% aqueous solution of Leucad 71 and 2 cm<sup>3</sup> of a 30% aqueous solution of sodium chloride. Dyeing was carried out in sealed, 100 cm<sup>3</sup> capacity PTFE dyeing tubes housed in a John Jeffries Rota-Dyer laboratory scale dyeing machine using a 7:1 liquor ratio. The dyeing method is shown in Fig. 1.



**Fig. 1.** Dyeing method.

## Oxidation

At the end of dyeing, the dyed sample was thoroughly rinsed in cold water and treated in an aqueous (distilled water) solution (50:1 liquor ratio) containing 1 g/dm<sup>3</sup> hydrogen peroxide (100 vol.) at 40°C for 10 min. At the end of this time the oxidized dyeing was removed, rinsed thoroughly in cold water and allowed to dry in the open air.

## Aftertreatment

The two cationic agents used are currently marketed as aftertreatment agents for direct and reactive dyed cellulosic goods and are suitable for application by continuous application methods.<sup>7</sup> The crease resist resin used during this work can only be applied by a continuous method<sup>8</sup> and is recommended for improving the dimensional stability of dyed cotton goods<sup>8</sup> and, more specifically, as a fastness improver for a range of CI Leuco Sulphur dyes.<sup>8</sup>

The three agents were applied using either a Pad-Dry or a Pad-Flash Cure procedure as outlined in Fig. 2. A Benz laboratory-scale, two-bowl vertical pad-mangle together with a Werner Mathis laboratory-scale steamer/oven were used.

## Colour measurement

The reflectance values and the corresponding CIE  $L^*$ ,  $a^*$ ,  $b^*$ ,  $C$ ,  $h^\circ$  colour coordinates and  $K/S$  values (at the appropriate  $\lambda_{\max}$  for each dyeing) of the dyed samples were measured using the instrument and technique previously described.<sup>5</sup> 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.

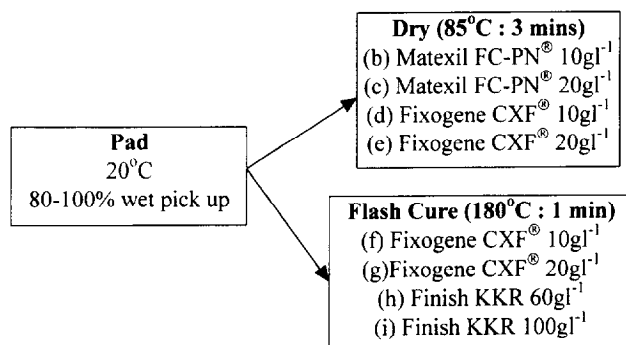


Fig. 2. Pad-Dry/Flash Cure procedures (procedure (a) involved no aftertreatment).

### Fastness determination

The fastness of the dyeings was determined using the ISOC06/C2 test method.<sup>9</sup>

## RESULTS AND DISCUSSION

From Figs 3–6 it is evident that aftertreatment with each of the three agents using both Pad-Dry and Pad-Flash Cure application methods significantly improved the fastness of all four dyes used to the ISOC06/C2 wash test. In

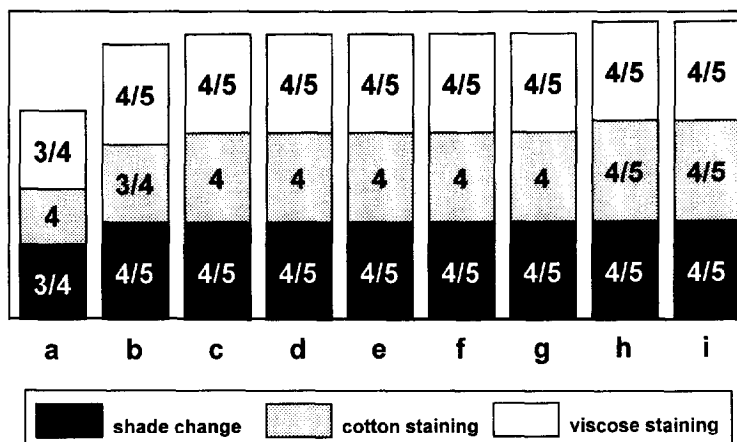


Fig. 3. Wash fastness results for CI Leuco Sulphur Black 1.

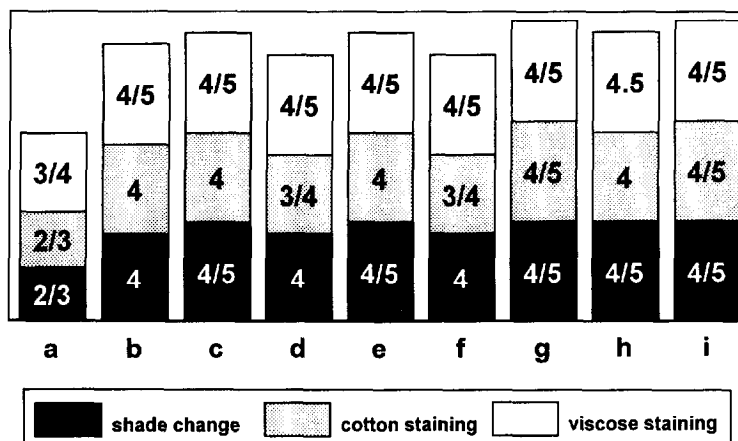


Fig. 4. Wash fastness results for CI Leuco Sulphur Yellow 23.

the cases of Matexil FC-PN<sup>®</sup> and Fixogene CXF<sup>®</sup> it is also clear that an aftertreatment using 20 g/litre of each fixing agent generally imparted slightly higher wash fastness improvement than an aftertreatment using 10 g/litre. Nevertheless, the level of wash fastness improvement imparted by aftertreatment using 10 g/litre Matexil FC-PN<sup>®</sup> and Fixogene CXF<sup>®</sup> was quite marked. It is also evident that Fixogene CXF<sup>®</sup> may be applied by either of the continuous methods employed, namely Pad-Dry or Pad-Flash Cure, with marginally better results being achieved using the latter.

Although it was generally observed that aftertreatment with Finish KKR imparted marginally superior fastness than aftertreatment with the two other

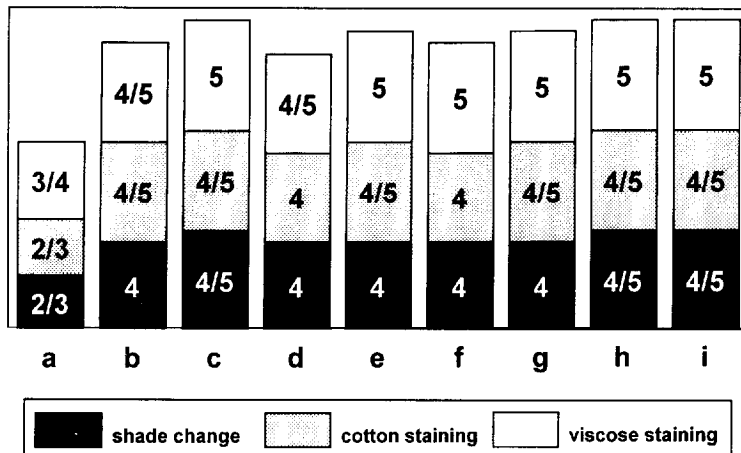


Fig. 5. Wash fastness for CI Leuco Sulphur Green 2.

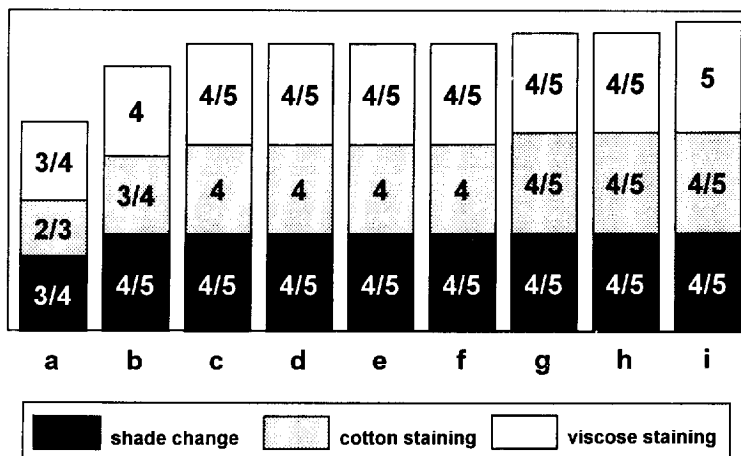


Fig. 6. Wash fastness results for CI Leuco Sulphur Blue 5.

cationic agents, it is evident that this superior wash fastness was achieved using a higher concentration of the crease resist agent. In this context, Figs 3–6 reveal that, in most cases, up to five times more crease resist agent was required to give a level of wash fastness that was either the same or only 0.5 points better than that achieved using 20 g/litre Matexil FC-PN<sup>®</sup> or Fixogene CXF<sup>®</sup>.

Tables 2–5 show that aftertreatment with each of the three agents did not markedly alter the colour of the dyeings although Finish KKR was found to dull the shade in some cases. Manual inspection of the dyeings revealed that the crease resist agent imparted a harsh handle to the fabric.

With regards the mechanism by which the two cationic fixing agents improved wash fastness, two possible explanations can be offered as in the case of the aftertreatment of sulphur dyeings by exhaust methods.<sup>5</sup> First, the enhanced wash fastness could be attributed to the formation of a large molecular-size, dye-cationic agent complex of low aqueous solubility within the fibre and, second, it may be possible that a 'layer' of the polymeric

**TABLE 2**  
Colorimetric Data for CI Leuco Sulphur Black 1

<i>Aftertreatment</i>	L*	a*	b*	C	h°	K/S	ΔK/S
a	19.99	−1.21	−3.00	3.24	248.12	18.02	—
b	20.17	−0.96	−2.91	3.06	251.82	17.40	0.62
c	21.66	−1.13	−3.22	3.41	250.70	16.63	1.39
d	20.27	−1.21	−3.10	3.32	248.74	17.53	0.49
e	20.17	−1.34	−2.96	3.25	245.56	18.02	0.00
f	20.20	−1.11	−2.96	3.16	249.40	17.74	0.28
g	20.23	−1.49	−2.68	3.07	240.87	18.02	0.00
h	19.15	−1.26	−2.54	2.84	243.65	19.26	−1.24
i	20.11	−1.24	−2.55	2.83	244.12	17.46	0.56

**TABLE 3**  
Colorimetric Data for CI Leuco Sulphur Yellow 23

<i>Aftertreatment</i>	L*	a*	b*	C	h°	K/S	ΔK/S
a	69.41	11.80	54.42	55.68	77.76	6.54	—
b	70.54	11.54	54.26	55.47	77.99	6.01	0.53
c	70.64	11.35	54.16	55.33	78.17	5.73	0.81
d	68.60	12.51	54.48	55.90	77.06	6.73	−0.19
e	68.91	12.58	54.22	55.66	76.94	6.51	0.03
f	69.07	12.20	53.72	55.09	77.20	6.34	0.20
g	68.53	12.17	53.47	54.83	77.17	6.51	0.03
h	70.60	10.97	53.79	54.90	78.48	5.84	0.70
i	70.58	10.72	53.24	54.31	78.62	5.74	0.80

**TABLE 4**  
Colorimetric Data for CI Leuco Sulphur Green 2

<i>Aftertreatment</i>	L*	a*	b*	C	h°	K/S	ΔK/S
a	44.85	-21.77	-4.68	22.216	192.13	6.12	—
b	44.96	-21.50	-4.53	21.97	191.40	6.50	-0.38
c	45.74	-21.04	-4.74	21.56	192.70	6.04	0.08
d	44.95	-21.37	-5.13	21.97	193.49	6.23	-0.11
e	45.85	-21.09	-5.44	21.78	194.46	5.70	0.42
f	45.36	-21.35	-5.47	22.04	194.36	6.04	0.08
g	45.65	-21.12	-5.09	21.73	193.54	5.80	0.32
h	45.06	-23.00	-5.32	23.61	193.03	6.57	-0.45
i	44.85	-23.27	-5.54	23.92	193.39	6.80	-0.68

**TABLE 5**  
Colorimetric Data for CI Leuco Sulphur Blue 5

<i>Aftertreatment</i>	L*	a*	b*	C	h°	K/S	ΔK/S
a	31.36	2.35	-20.99	11.12	276.39	8.73	—
b	30.88	2.38	-21.29	11.42	276.37	9.21	-0.48
c	31.06	1.90	-20.44	20.53	275.30	9.07	-0.34
d	31.22	2.56	-21.18	21.33	276.88	8.83	-0.10
e	31.78	2.40	-20.95	21.09	276.52	8.48	0.25
f	31.75	2.31	-20.78	20.91	276.33	8.46	0.27
g	31.48	2.68	-21.05	21.22	277.25	8.62	0.11
h	32.39	3.20	-21.61	21.85	278.41	7.97	0.76
i	32.47	3.41	-21.90	22.16	278.85	7.86	0.87

cationic fixing agent was formed at the periphery of the dyed fibre. Each of these mechanisms would serve to reduce the diffusion of the dye out of the dyed substrate during washing and thus improve wash fastness. Furthermore, as suggested previously in the case of the aftertreatment of sulphur dyeings by exhaust methods<sup>5</sup> there may well be a combination of the above two postulated mechanisms.

## CONCLUSIONS

It has been shown that application of commercial cationic fixing agents as an aftertreatment of the oxidized dyeings of four CI Leuco Sulphur dyes, by continuous methods, significantly enhanced the fastness of the dyeings to the ISOC06/C2 wash test, without affecting the shade or handle of the fabric. The extent of the enhanced wash fastness imparted by 10–20 g/litre of the fixing agents was very similar to that furnished by 60–100 g/litre of a commercial



crease resist agent which also imparted a harsh handle to the fabric and dulled the shade in some cases.

### ACKNOWLEDGEMENTS

The authors thank ICI Surfactants for the provision of a scholarship to G. W. Collins and are grateful to Mr R. Gordon of ICI Surfactants for helpful discussions.

### REFERENCES

1. Luttringer, J. P., Proceedings of the 1992 AATCC International Conference, Atlanta.
2. Clarke, D. & Senior, C. In *The Dyeing of Cellulosic Fibres*, C. Preston (ed.). Society of Dyers and Colourists, Bradford, 1986.
3. Senior, C. In *Cellulosics Dyeing*, J. Shore (ed.). Society of Dyers and Colourists, Bradford, 1995.
4. Burkinshaw, S. M. In *The Chemistry and Application of Dyes*, D. Waring & G. Hallas (eds). New York, 1991.
5. Burkinshaw, S. M. & Collins, G. W., *Dyes and Pigments*, **29** (1995) 323–344.
6. Senior, C. Personal communication.
7. Chemical auxiliaries for the textile industry, CAFT 4(R), ICI Surfactants, Wilton, 1990.
8. Technical information — Finish KKR, Sandoz, Basle, 1986.
9. *Standard Methods for the Determination of the Colour Fastness of Textiles and Leather*, 5th edition. Society of Dyers and Colourists, Bradford, 1990.