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Investigation into the sequential application of cationic/anionic fixing agents to improve the oxidative washing resistance of C. I. Leuco Sulphur Black 1 dyed cotton fabric

Quratulain Mohtashim¹, Muriel Rigout², Chris Carr²

ABSTRACT

Sulphur dyed cellulosic textiles are susceptible to washing powders containing activated peracid formulations resulting in obvious fading during repeated laundering. This study presents a novel one bath–two stage exhaust finishing process to improve the oxidative wash fastness of C. I. Leuco Sulphur Black 1 dyed cotton fabric. The effect of the combined Tinofix ECO and Bayprotect Cl aftertreatment was to impart better colour fastness to oxidative ISO 105 CO9 washing of the dyed cotton in comparison to the Tinofix ECO alone aftertreated dyed fabrics. In addition, while the dyed fabrics rub and light fastness performances were unchanged by the aftertreatments, some improvement in the tensile strength of the combined Tinofix ECO and Bayprotect Cl aftertreated fabrics was also observed.

Keywords: Cotton, sulphur dye, wash fastness, aftertreatment, tannin, cationic fixing agent.

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INTRODUCTION

Sulphur dyes are a major class of textile dyes that are applied to cellulosic textiles and their blends [1]. The widespread use of sulphur dyeing for cellulosic fibres is based on relatively low cost, good colour strength and acceptable fastness on cellulosic substrates [2]. Another important reason for the popularity of this dye class is the ease of application and the choice of availability for products like garments, furnishings, linings and carpets [3]. These dyes are still useful for producing shades of black, brown, navy, olive and green colour in medium to heavy depths.

Sulphur dyes are widely used on cellulosic fibres and their blends with polyester, nylon and acrylic. Since the 1980s fashion changes have demanded greater usage of Sulphur black dye on denim fabrics. Sulphur dyes also find limited application to paper and silk, and more widely to leather [4]. In recent times, the application of Sulphur dyes on non-cellulosic fibres such as silk [5], nylon [6-9] and wool [10] has been explored and reflects the importance and potential of these dyes. For example with chamois leathers in sports garments, gloves and other personal wear there has been increasing consumer demand for a broader range of colours and an evaluation of the use of water soluble sulphur dyes [11]. The use of solubilized Sulphur dyes for colouring chrome tanned leathers and tone-in-tone dyeing has also been reported recently [12].

Among the dye classes, C.I. Sulphur Black 1 is one of the most popular dyes in the world constituting around 10% by mass of all dyes produced around the globe annually [13, 14].

Historically Sulphur dyes were the most widely consumed dyes for cotton and cotton blends because of their low cost, availability of dark shades, good wet fastness and

moderate to good light fastness. However, with the passage of time, reactive dyes have partially replaced Sulphur dyes due to the latter's low resistance to oxidative laundering and the considerable decrease in reactive dyes' price [15]. Another major reason for their continuing unpopularity is the environmental hazard created by the use of the conventional reducing agent sodium sulphide, which is highly toxic for marine life and sewerage systems. Therefore, attempts have been made to replace this hazardous component of dyeing by more eco-friendly alternatives. In this context, a substantial body of work has been undertaken on the use of reducing sugars for the dyeing of cellulose with sulphur dyes [2, 16, 17].

Furthermore, cellulosic goods dyed with Sulphur dyes are particularly susceptible to perborate bleach-containing washing powders thus exhibiting reduced washfastness against oxidative bleaching. In order to improve the wet fastness of Sulphur dyes, a substantial body of work has been contributed to by various researchers. The use of alkylating agents has been reported to not only replace the conventional oxidation treatment but also to improve the wash fastness of Sulphur dyes against the more severe washing conditions with peroxide-containing detergents [18-21]. Other recommended compounds include quaternary ammonium alkyl compounds [20, 22] dicyandiamide-formaldehyde condensates and crease resist finishing agents [18, 23, 24]. In addition Burkinshaw has explored the exhaust and continuous application treatments with several cationic fixing agents [13, 19, 24-26]. Further, the pad application of lanthanum triacetate for reducing the colour loss of Sulphur dyed cotton during laundering has also been investigated. The method substantially improved the oxidative bleaching resistance of Sulphur dyed textiles which were durable to repeated launderings [27]. However, the

resistance of Sulphur dyes against the action of oxidative bleaching formulations including bleach activators has not been examined in detail.

The aim of this research is to develop a post-treatment method for Sulphur Black 1 dyed cotton fabric (reduced with conventional and biodegradable reductants) which improves the resistance to home laundering processes, in particular ISO 105 CO9, and extends wearer usage and customer satisfaction.

In order to improve the wash fastness of various dyes, the application of two different fixatives in one-bath or two-bath systems has been studied, for example the effect of sequential aftertreatments with tannin/tannic acid, metal salts, polymeric cationic agents and syntan (synthetic tanning agents) on the dye fastness properties has been investigated [27-31].

Recently a preliminary study was reported regarding enhancement of wash fastness of Sulphur Black 1 dyed cotton fabric with an aftertreatment involving the sequential application of a cationic fixative (Tinofix ECO) and tannin (Bayprotect CI) against the oxidative bleaching action of detergent/perborate/bleach activator formulations (ISO 105 C09) [32]. It was found that the extent of wash fastness improvement imparted by the cation-tannin system was greater than that imparted by the cationic fixative alone. The present work continues this investigation for optimising the process parameters of the one-bath system, by varying the application temperatures, treatment times and reagent concentrations. The cotton fabrics were dyed with two reducing agents, namely, sodium sulphide and Diresul Reducing agent D (RAD, Glucose-based reductive agent) and the aftertreated cotton assessed for wash, rub, light fastness and tensile strength.

EXPERIMENTAL

Materials

A plain woven, bleached, 100% cotton fabric, 103 g/m², was used throughout the study and was purchased from Phoenix Calico Limited, UK. Diresul C. I. Leuco Sulphur Black 1 dye and Diresul RAD were kindly donated by Clariant. Hydrogen peroxide (30% vols), sodium perborate tetrahydrate (97% active, Laboratory grade) and sodium bicarbonate (Laboratory grade) were purchased from Aldrich Chemicals Ltd, UK). The ECE non-phosphate detergent and tetraacetythylenediamine (92% active) were purchased from the Society of Dyers and Colourists (SDC), Bradford, UK.

Dyeing with Diresul RAD

All dyeings were carried out in 1000 cm³ capacity sealed stainless steel dye pots in a Mathis Labomat laboratory dyeing machine. Dyeing of cotton with Diresul RAD was performed by the method prescribed by Clariant, Figure 1. The cotton fabric was introduced into a dye bath containing 5% on mass of fabric (omf) Diresul C. I. Leuco Sulphur Black 1 dye liquid, 25 g/L sodium chloride, 13 mL/L of sodium hydroxide (67°Tw), 9 g/L Diresul RAD with a liquor to goods ratio of 10:1. The dye bath was raised to 98°C at a temperature gradient of 4°C/min and maintained at the boil for 60 minutes. The solution was then cooled to 50°C and fabric removed. The dyed fabrics were then washed thoroughly with cold water to remove any unfixed surface dye and then oxidised with 5 g/L hydrogen peroxide and 1 g/L soda ash at 40-45°C for 15 minutes. The fabric was then soaped with 1g/L of non-ionic detergent at the boil for 20 minutes and finally

then rinsed with cold and warm water and air dried. The L:R (liquor to goods ratio) employed for oxidation and soaping was 10:1.

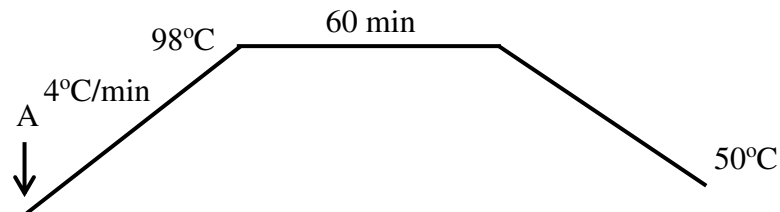


Figure 1 Sulphur dyeing method for cotton using Diresul RAD. A – Dyebath contains fabric, dyestuff, sodium chloride, sodium hydroxide, Diresul RAD and water

Dyeing with sodium sulphide

The dyeing of cotton fabric with sodium sulphide was carried out with 5% omf dye, 5 g/L sodium sulphide, 5 g/L sodium carbonate and 15 g/L sodium chloride with a liquor to goods ratio of 10:1, Figure 2. The initial dyebath with the fabric was heated to a temperature of 40-50°C in the presence of half of the quantities of water, sodium sulphide and soda ash. The liquor was kept at this temperature for 5 minutes and then the dyestuff and balance of water, sodium sulphide and soda ash were added. The dyebath was held for 10 minutes at 50°C and then salt was added. The temperature was then increased to 90°C at a gradient of 2°C/min and treated for 30 minutes. The solution was cooled to 50°C the fabric was then washed thoroughly with cold water to remove any unfixed surface dye and then oxidised with 5 g/L hydrogen peroxide and 1 g/L soda ash at 40-45°C for 15 minutes. The fabric was then soaped with 1g/L of non-ionic detergent at the boil for 20 minutes and finally then rinsed with cold and warm water and air dried. The L:R (liquor to goods ratio) employed for oxidation and soaping was 10:1.

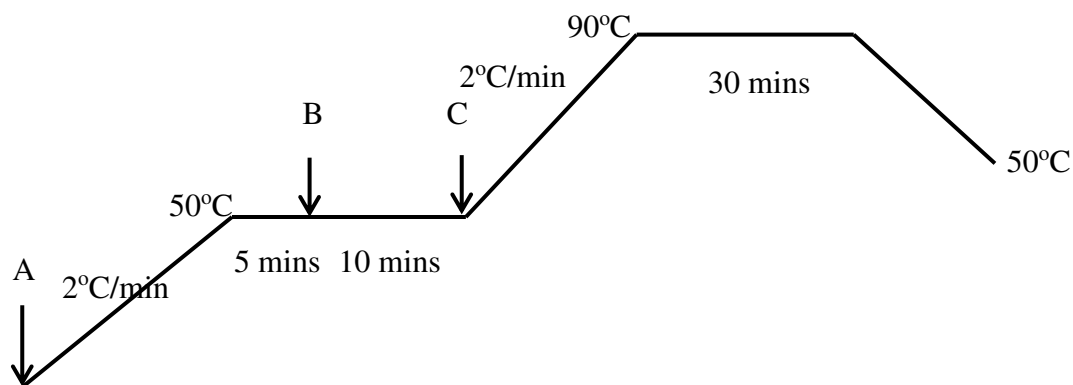


Figure 2 Sulphur dyeing method for cotton using sodium sulphide. A- Initial dyebath contains fabric, half quantities of water, sodium sulphide and soda ash. B – Dyebath additions of dyestuff and balance of water, sodium sulphide and soda ash. C – salt addition.

Aftertreatment with Tinofix ECO

Sulphur dyed fabric was aftertreated with liquor containing either 1, 2, 4, 5, 8 or 10% omf Tinofix ECO in the Mathis Labomat dyeing machine with a liquor to goods ratio of 10:1. The pH of the liquor was 6-7 as recommended by the manufacturer. The fabric was treated at 40°C for either 15, 20 or 30 minutes, rinsed in cold water and finally air dried.

Aftertreatment with Bayprotect Cl

Bayprotect Cl was applied to the 5% omf Tinofix ECO treated Sulphur Black 1 dyed cotton fabric by aftertreating with liquor containing either 1, 2, 3, 5 or 10% omf Bayprotect Cl, with the pH adjusted to 3.5 with citric acid. The fabrics were treated in the liquor solutions at either 40, 60 or 98°C for 10, 15 or 20 minutes with a liquor to goods

ratio of 10:1. The finished fabric was finally rinsed with warm and cold water and air dried.

A one bath/two stage Tinofix ECO + Bayprotect Cl treatment of the Sulphur Black dyed cotton was also assessed and involved an aftertreatment with 5% omf Tinofix ECO (pH 6-7) and 5% omf Bayprotect Cl (pH 3.5) with a liquor to goods ratio of 10:1 for 5, 10, 15 or 20 minutes.

Colour measurement

The colour of the dyed and aftertreated cotton fabrics were measured using a Datacolor Spectroflash 600 spectrophotometer, with a 10° standard observer and D65 illuminant, and were the average of four measurements. The colour strength (K/S) was evaluated using the Kubelka–Munk equation, represented in Equation 1:

$$\left(\frac{K}{S}\right)_{\lambda} = \frac{(1-R_{\lambda})^2}{2R_{\lambda}} \quad \text{Equation 1}$$

Where K is the absorption coefficient, S is the scatter coefficient, R is the reflectance expressed as a fractional value at wavelength of maximum absorption λ .

The % colour loss of the untreated and aftertreated dyed fabrics after laundering were determined with the following equation Equation 2:

$$\% \text{ colour loss} = \frac{\frac{K}{S} \text{ before washing} - \frac{K}{S} \text{ after washing}}{\frac{K}{S} \text{ before washing}} \times 100 \quad \text{Equation 2}$$

Determination of fastness properties

The colour fastness of the untreated and aftertreated sulphur dyeings were tested according to ISO standard methods, including fastness to washing (ISO 105 CO9), rubbing (ISO 105 X12) and light (ISO 105 B02).

Strength Measurement

The tensile strength measurements were performed according to BS EN ISO 13934/1:1999 for textile strips on an Instron 3345 mechanical testing machine, using a 1 kN load cell. Test samples were cut into 300mm×50mm strips, with the warp and weft along the length. The crosshead rate used in the test was 200 mm/min. The textile materials were pre-conditioned under standard conditions for 24 hours prior to measurement and the data is the average of 5 measurements in both the warp and weft directions.

RESULTS AND DISCUSSION

Effect of varying concentration of Tinofix ECO on the washing fastness of Sulphur dyed cotton fabric

Examination of the effect of increasing the concentration of the cationic fixing agent Tinofix ECO on the colour loss of the fabric dyed with Diresul CI Leuco Sulphur Black 1 dye and reduced with Diresul RAD and sodium sulphide, respectively, showed that within the range examined, increasing the concentration of Tinofix ECO up to 5% omf brings about a clear reduction in the colour loss during laundering, from 59% and 71%

for the untreated dyed fabrics to 43% and 41% for Tinofix ECO treated fabrics, respectively, Tables 1 and 2. This effect is presumably due to the formation of large molecular size complexes between the cationic fixative and the anionic Sulphur dye molecules in the cotton fabric. However, on increasing the concentration of Tinofix ECO from 5% to 8-10% omf, the dye fixative did not produce further large reductions in dye loss from the fabric. Accordingly the 5% omf concentration of the cationic Tinofix ECO fixative was selected for further investigations.

Table 1 Colorimetric data for ISO 105 C09 washed C. I. Leuco Sulphur Black 1 dyed cotton fabric reduced with Diresul RAD and aftertreated with Tinofix ECO (30 minutes)

Tinofix ECO (% o.m.f.)	Colour Strength, K/S	% Colour Loss	ΔE	Grey Scale Rating After Laundering
0	9.0 (3.7)*	59	13.0	1
1	8.5 (4.2)*	51	10.1	1/2
2	8.4 (4.3)*	49	9.4	1/2
5	8.8 (5.0)*	43	8.1	2
10	8.5 (5.0)*	41	7.6	2

* Colour strength after laundering

It appeared that the colour strength and percentage colour loss after laundering with the sodium sulphide reduced dyed fabric was marginally higher than for the comparably dyed fabric reduced with Diresul RAD. The Diresul RAD is a commercial product based on glucose and is identified as a biodegradable reducing system. Glucose is expected to

produce sulphur dyeings with comparable colour strength and wash fastness to the conventional sulphide system when applied under suitable temperature and concentrations of reducing agent and alkali [16]. Dyeing of cellulosic fabric with sulphur dyes at the optimum redox potential (-650 mV) was found to offer the highest colour strength dyeings and minimum fading after washing for sodium sulphide as well as reducing sugars. The fabric dyeings produced at this reduction potential achieve maximum dye uptake, since above and below this value the dye molecule is either too large or too fragmented for maximum adsorption and subsequent diffusion [2].

Table 2 Colorimetric data for ISO 105 C09 washed C. I. Leuco Sulphur Black 1 dyed cotton fabric reduced with sodium sulphide and aftertreated with Tinofix ECO (30 minutes)

Tinofix ECO (% o.m.f.)	Colour Strength, K/S	% Colour Loss	ΔE	Grey Scale Rating After Laundering
0	10.2 (3.0)*	71	17.6	1
1	9.5 (3.2)*	66	15.8	1/2
2	9.2 (4.5)*	51	10.9	1/2
5	9.5 (5.6)*	41	7.8	2
10	9.0 (5.6)*	38	7.1	2

* Colour strength after laundering

It is known that large dye molecules have higher affinity for cellulosic fibre owing to extensive hydrophobic interactions and hydrogen bonding [4]. However, larger dye

molecules may also have lower adsorption and subsequent penetration, diffusion and colour strength. In contrast, smaller molecules can easily diffuse but their affinity for cellulose would be lower due to a lesser degree of dye-fibre interaction, hence would display lower levels of wash fastness in relation to the larger dye chromophores [2]. It was proposed that upon oxidation, smaller dye molecules would be likely to display lower levels of wash fastness in relation to larger fragments because larger crystallites of the dye molecules will form in situ when larger reduced dye molecules reform into the polymeric parent structure [2].

Therefore the decrease in the wash fastness of fabric dyed with sodium sulphide may possibly be attributed to the formation of smaller dye fragments in comparison to Diresul RAD reduced dye molecules, resulting in higher colour strength but reduced wash fastness.

On comparing the effects of Tinofix ECO on the two systems, it was observed that treating Diresul RAD reduced fabric with 5% omf Tinofix ECO decreased the percentage colour loss by 16%, while for sodium sulphide reduced dyed fabric colour loss was 30%. This suggests the cationic fixative offers greater protection to ISO 105 C09 fading with the sodium sulphide reduced dyed fabric.

Effect of varying concentrations of Bayprotect Cl on the wash fastness of 5% omf Tinofix ECO treated Sulphur dyed fabrics

The effect of applying the tannin-based Bayprotect Cl to the Tinofix ECO treated Sulphur Black dyed cotton was to further improve the colour fastness to ISO 105 C09 laundering, Tables 3 and 4. Again similar to the 5% omf application Tinofix ECO the optimum

application level for the Bayprotect CI was also 5% omf for both the sodium sulphide and Diresul RAD reduced Sulphur Black Dyed cottons. The two-bath sequential application of the two reagents was initially studied due to the differing pH application conditions, that is Bayprotect CI requires an acidic pH (<3.5) while Tinofix ECO needs a pH range of 6-7.

Table 3 Colorimetric data for ISO 105 C09 washed C. I. Leuco Sulphur Black 1 dyed cotton fabric reduced with Diresul RAD and aftertreated with 5% omf Tinofix ECO (30 minutes) and varying levels of Bayprotect CI at 40°C for 20 minutes

Bayprotect CI (% o.m.f.)	Colour Strength, K/S	% Colour Loss	ΔE	Grey Scale Rating After Laundering
0 ⁺	9.0 (3.7) [*]	59	13.0	1
0 [#]	8.8 (5.0) [*]	43	8.1	2
1 [#]	8.2 (5.8) [*]	29	5.8	2/3
2 [#]	8.3 (6.0) [*]	28	5.3	2/3
3 [#]	8.1 (6.0) [*]	26	5.1	2/3
5 [#]	7.8 (6.0) [*]	23	4.2	2/3
10 [#]	7.8 (6.0) [*]	23	4.5	2/3

⁺ 0% omf Tinofix ECO & 0% Bayprotect CI

[#] 5% omf Tinofix ECO & x% Bayprotect CI

^{*} Colour strength after laundering

As part of this study the effect of application temperature for the Bayprotect Cl was also investigated and it was found that there was little benefit in increasing the temperature from 40°C to either 60°C or 98°C and again 5% omf of Bayprotect Cl was found to provide the “best” combination treatment for protection against dye fading with ISO 105 C09 laundering. (Data not presented). The mechanism for the improved wash fastness is probably based on the increased molecular size of the cationic/anionic complex but also due to the antioxidant effect of the Bayprotect Cl.

Table 4 Colorimetric data for ISO 105 C09 washed C. I. Leuco Sulphur Black 1 dyed cotton fabric reduced with sodium sulphide and aftertreated with 5% omf Tinofix ECO (30 minutes) and varying levels of Bayprotect Cl at 40°C for 20 minutes

Bayprotect Cl (% o.m.f.)	Colour Strength, K/S	% Colour Loss	ΔE	Grey Scale Rating After Laundering
0 ⁺	10.2 (3.0) [*]	71	17.6	1
0 [#]	9.5 (5.6) [*]	41	7.8	2
1 [#]	8.7 (5.3) [*]	39	8.1	2
2 [#]	8.8 (5.5) [*]	38	7.5	2
3 [#]	8.9 (5.7) [*]	36	7.1	2
5 [#]	8.5 (5.9) [*]	31	6.3	2
10 [#]	8.5 (6.0) [*]	29	6.0	2

⁺ 0% omf Tinofix ECO & 0% Bayprotect Cl

[#] 5% omf Tinofix ECO & x% Bayprotect Cl

^{*} Colour strength after laundering

Development of a one bath/two stage wash protection process

As highlighted in the previous section, the substantial loss in colour during ISO 105 C09 laundering can be reduced by sequentially treating C. I. Leuco Sulphur Black 1 dyed cotton fabric with 5% omf Tinofix ECO and 5% omf Bayprotect Cl at 40°C for 30 and 20 minutes, respectively. The reduction in percentage colour loss for the two bath/two stage aftertreated fabric reduced with Diresul RAD was 59% (untreated) down to 25% (aftertreated), while for the sulphide reduced fabric the decrease was 71% (untreated) to 31% (aftertreated). However in this study a one-bath process has been evaluated with a view to sequentially apply both finishes in order to reduce the consumption of water and heating treatment bath costs. Examination of Tables 5 shows that for the Diresul RAD reduced dyed cotton the one bath/two finish treatment offers comparable performance to the sequential two bath process. In contrast for the sulphide reduced dyed cotton the one bath/two finish treatment offers marginally better performance in comparison to the sequential two bath process, Table 6.” The reason for the improvement may again be due to chromophore size effect previously discussed.

- Therefore the optimized Tinofix ECO/Bayprotect Cl one bath process which reduce costs and minimise processing time, temperature and water usage would be based on:
 - Application temperature of Tinofix ECO: 40°C;
 - Application temperature of Bayprotect Cl: 40°C;
 - Application time of Tinofix ECO: 15 minutes;
 - Application time of Bayprotect Cl: 15 minutes;
 - pH of Tinofix ECO: 6-7;
 - pH of Bayprotect Cl: 3-3.5;
 - Liquor to goods ratio: 10:1.

Table 5 Colorimetric data for ISO 105 C09 washed C. I. Leuco Sulphur Black 1 dyed cotton fabric reduced with Diresul RAD and aftertreated with 5% o.m.f. Tinofix ECO and 5% o.m.f. Bayprotect Cl at 40°C for varying time periods in one bath

Bayprotect Cl (% o.m.f.)	Application Time (mins)	Colour Strength, K/S	% Colour Loss	ΔE	Grey Scale Rating After Laundering
0 ⁺	-	8.8 (5.0) [*]	43	8.1	2
5	20 [#]	7.8 (6.0) [*]	23	4.2	2/3
5	5	7.4 (4.9) [*]	34	6.4	2
5	10	7.1 (4.8) [*]	32	6.2	2
5	15	7.1 (5.3) [*]	25	4.9	2/3
5	20	7.9 (5.9) [*]	25	4.7	2/3

⁺ 5% omf Tinofix ECO & 0% Bayprotect Cl

^{*} Colour strength after laundering

[#] Sequential two bath Tinofix ECO and Bayprotect Cl treatments

Effect of Tinofix ECO and Bayprotect Cl aftertreatments on the rubbing and light fastness of C. I. Leuco Sulphur Black 1 dyed cotton fabric

The aftertreatments with the cationic fixing agent Tinofix ECO and the tannin-based product Bayprotect Cl did not produce any significant improvements on the rubbing and light fastness of CI Leuco Sulphur Black 1 dyed and aftertreated cotton fabrics. The dry rub fastness was rated 4/5 for both sulphide and Diresul Rad reduced Sulphur dyed cottons. In contrast the wet rub fastness was 3/4 for the Diresul Rad reduced dyed cotton

while it was rated marginally lower at 3 for the sulphide reduced dyed cotton. This slightly lower rating again may be due to the lower chromophore size of the sulphide reduced Sulphur dyed cotton and the associated lower wet fastness [2].

The light fastness of the untreated dyed fabric and the Tinofix ECO/Bayprotect Cl treated dyed cottons were similar with a light fastness rating of 4 achieved with both coloured materials

Table 6 Colorimetric data for ISO 105 C09 washed C. I. Leuco Sulphur Black 1 dyed cotton fabric reduced with sodium sulphide and aftertreated with 5% o.m.f. Tinofix ECO and 5% o.m.f. Bayprotect Cl at 40°C for varying time periods in one bath

Bayprotect Cl (% o.m.f.)	Application Time (mins)	Colour Strength, K/S	% Colour Loss	ΔE	Grey Scale Rating After Laundering
0 ⁺	-	9.5 (5.6) [*]	41	7.8	2
5	20 [#]	8.5 (5.9) [*]	31	6.3	2
5	5	8.9 (6.1) [*]	31	5.9	2
5	10	8.5 (6.2) [*]	27	5.3	2/3
5	15	8.5 (6.6) [*]	22	4.7	2/3
5	20	8.7 (6.9) [*]	21	4.3	2/3

⁺ 5% omf Tinofix ECO & 0% Bayprotect Cl

^{*} Colour strength after laundering

[#] Sequential two bath Tinofix ECO and Bayprotect Cl treatments

Effect of Tinofix ECO and Bayprotect Cl aftertreatments on the tensile strength of C. I. Leuco Sulphur Black 1 dyed cotton fabric

Analysis of the dyed fabric treated with Tinofix ECO and Bayprotect Cl indicates an increase in the tensile strength of the fabric, Table 7. A previous study on the effect of cationic fixing agents on the tensile strength of cotton fabric has also shown that Tinofix ECO increased the tensile strength of the cotton fabric, although no explanation for the behaviour was provided [34]. However, it is likely that the cationic reagent provides increased ionic bonding with the bleached anionic cellulosic polymer backbone.

Table 7 Effect of different aftertreatments on the tensile strength of Sulphur Black dyed cotton fabrics

Fixing Agent Aftertreatment (% omf)	Warp direction	Weft direction
	Tensile strength (N)	Tensile strength (N)
Untreated	4.6	3.8
5% omf Tinofix ECO	5.6	3.7
10% omf Tinofix ECO	4.9	4.9
5% omf Bayprotect Cl	5.6	4.4
10% omf Bayprotect Cl	5.3	4.7
5% omf Tinofix ECO & 5% omf Bayprotect Cl	5.8	4.7
10% omf Tinofix ECO & 10% omf Bayprotect Cl	6.2	4.1

CONCLUSIONS

This study indicates that the cationic fixing agent Tinofix ECO had a beneficial effect on the ISO 105 C09 wash fastness of C. I. Leuco Sulphur Black 1 dyed cotton fabric. A subsequent addition of the anionic tannin-based Bayprotect Cl further increased the wash fastness and it is likely this improvement is based both on the formation of larger dye/fixing agent complexes with lower water solubility but also due to the antioxidant nature of the Bayprotect Cl. Sequential treatment of the dyed cotton with the fixing agents either in a two bath application or as a one bath process imparts greater wash fastness benefits. The one bath process also being commercially attractive in terms of lower water usage and heating costs. While rub fastness and light fastness performance of the dyed fabric was little changed after the fixing agent application, there were observed benefits in the tensile strength following Tinofix ECO and Bayprotect Cl application.

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REFERENCES

1. TA Nguyen and RS Juang, *Chem. Eng. J.*, **219** (2013) 109.
2. RS Blackburn and A Harvey, *Environ. Sci. Technol.*, **38** (2004) 4034.
3. M Parvinzadeh, *J. Surfactants Deterg.*, **10** (2007) 219.
4. J Shore, *Cellulosics Dyeing* (Bradford: Society of Dyers and Colourists, 1995) 280.
5. S Burkinshaw and M Paraskevas, *Dyes Pigm.*, **88** (2011) 156.
6. SM Burkinshaw, SN Chevli, and DJ Marfell, *Dyes Pigm.*, **45** (2000) 65.
7. SM Burkinshaw, K Lagonika, and DJ Marfell, *Dyes Pigm.*, **56** (2003) 251.
8. SM Burkinshaw, K Lagonika, and DJ Marfell, *Dyes Pigm.*, **58** (2003) 157.
9. SM Burkinshaw and K Lagonika, *Dyes Pigm.*, **69** (2006) 185.
10. JY Cai, JA Rippon, J McDonnell and AE Parnell, *Color. Technol.*, **128** (2012) 9.
11. AJ Prakash, R Aravindhana, NN Fathimaa and JR Rao, *J. Am. Leather Chem. Assoc.* , **111** (2016) 383.
12. R Venba, M Jawahan, G Jothi, D Dakshinamoorthy, NC Babu, and A Deepika, *J. Am. Leather Chem. Assoc.*, **110** (2015)177.
13. SM Burkinshaw and GW Collins, *J. Soc. Dyers Colour.*, **114** (1998) 165.
14. H Zollinger and P Rys, *Fundamentals of the Chemistry and Application of Dyes* (John Wiley & Sons Canada, Limited, 1972).
15. W Zhou and Y Yang, *Ind. Eng. Chem. Res.*, **49** (2010) 4720.
16. A Madhu, G Singh, A Sodhi, S Malik and Y Madotra, *JTATM*, **7**(2012) 1.
17. R Zouhaier, D Sofiène and S Faouzi, *Eur. Sci. J.*, **10** (2014) 436.
18. C Preston, *The Dyeing of Cellulosic Fibres* (Dyers' Company Publications Trust, 1986).
19. SM Burkinshaw and GW Collins, *Dyes Pigm.*, **29** (1995) 323.

20. CC Cook, *Rev. Prog. Color. Relat. Top.*, **12** (1982) 73.
21. WE Wood, *Rev. Prog. Color. Relat. Top.*, **7** (1976) 80.
22. C Heid, K Holoubek and R Klein, *Melliand Textilber. Int.*, **54** (1973) 1314.
23. K Venkataraman, *The Chemistry of Synthetic Dyes* (Elsevier, 2012).
24. SM Burkinshaw and GW Collins, *Dyes Pigm.*, **33** (1997) 1.
25. SM Burkinshaw, FE Chaccour and A Gotsopoulos, *Dyes Pigm.*, **34** (1997) 227.
26. SM Burkinshaw and GW Collins, *Book of Papers: 1996 International Conference & Exhibition - AATCC* (1996) 296.
27. R Blackburn and S Burkinshaw, *J. Soc. Dyers Colour*, **114** (1998) 96.
28. R Blackburn and S Burkinshaw, *Color. Technol.*, **115** (1999) 102.
29. S Burkinshaw and N Kumar, *Dyes Pigm.*, **79** (2008) 48.
30. SM Burkinshaw and M Paraskevas, *Dyes Pigm.*, **88** (2011), 156.
31. S Burkinshaw and K Maseka, *Dyes Pigm.*, **30** (1996) 21.
32. Q Mohtashim and M Rigout, *NED Univ. J. Res.*, **14** (2017) 93.
33. WD Schindler and PJ Hauser, *Chemical Finishing of Textiles* (Woodhead Publishing Limited, 2004).
34. M El-Molla, N Badawy, A Abdel-Aal, A El-Bayaa and H El-Shaimaa, *Indian J. Fibre Text. Res.*, **36** (2011) 88.