Surface chemical analysis of the effect of extended laundering on C. I. sulphur black 1 dyed cotton fabric

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ABSTRACT

The colour resulting from the laundering of cotton fabric is influenced by the nature of the dye, the detergent formulation and the physical structure of the fibre surface. In this study the effect of ISO (International Organisation for Standardization) 105 C06 and ISO 105 C09 wash fastness testing, with and without oxidant, and with and without stainless steel abrasive balls, on the colour of C.I. Sulphur Black 1 dyed cotton fabric was evaluated. The surface sensitive X-ray Photoelectron Spectroscopy (XPS) was used to probe the nature of the outer 3–10 nm of the cotton surface, characterise the surface functionalities and elemental composition and establish the durability of the surface dye to different washing regimes. In addition the effect of laundering and modification to the surface sulphur dye was related to colour through K/S and L^* analysis.

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1. Introduction

Sulphur dyes are one of the most popular colourants used on cellulosic fibres and their blends [1–4]. C. I. Sulphur Black 1 in particular represents a substantial portion (20–25%) of the dyestuff market for cotton and has been reported to have the highest consumption of any single textile dyestuff in the world [5]. Sulphur dyes are characterised by their moderate cost and acceptable fastness for medium to heavy depths, especially black, blue and brown [3,4,6]. In spite of sulphur dyes offering excellent light fastness and good wash fastness to non-perborate based detergents, their commercial application in recent years has declined due to the availability of relatively dull colours, limited colour gamut, relatively poor wet rub fastness, the possibility of over-oxidation of the leuco form back to the colourant and the environmental impact associated with the presence of sulphides in the effluent [7,8]. However the environmental impact of sulphur dyeing can be significantly reduced with the use of “greener” reducing agents, such as sugars [3,5,9].

The application of the water insoluble sulphur dyes to cotton involves an initial alkaline reduction to the water soluble leuco

form and the subsequent absorption of the dye into the fibres. After exhaustion the leuco dye is re-oxidised using an oxidant, such as hydrogen peroxide, back to the original water insoluble form within the fibre and any surface dye is removed with after-soaping [1,2]. The fastness and cross-staining performance of sulphur dyed cellulosic fibres on exposure to severe washing conditions, especially those that use peroxide-containing detergent, has been typically characterised using the standard ISO 105 C06 benchmark [10–12]. However, recently a more representative ISO 105 C09 test method, reflecting modern detergent formulations and laundering practice, has been developed using a standard detergent incorporating a low temperature tetraacetylenediamine (TAED) bleach activator, incorporating either a single or multiple wash cycles [11–13].

In this study the relative effect of ISO 105 C06 [10] and ISO 105 C09 [13] washing, with and without oxidant and with and without stainless steel abrasive balls, on the colour of C. I. Sulphur Black 1 dyed cotton fabric has been evaluated and their chemical and physical effect on the outer surface of the Sulphur Black dyed fibres investigated for the first time. The surface sensitive X-ray Photoelectron Spectroscopy (XPS) technique [14,15] was used to probe the nature of the outer 3–10 nm of the cotton's surface and in order to characterise the surface functionalities, establish the elemental composition and assess the durability of the surface sulphur dye to different washing regimes. Wet laundering of cellulosic fibres can also produce mechanical damage to the fibre resulting in fibrillation and a loss in colour intensity due to diffuse reflection of light at

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the fibre surface [16–21]. Therefore by fully understanding the nature of the fibre surface interface on exposure to chemically and physically aggressive media improved laundering processes and extended garment lifetime may be achieved.

2. Experimental

2.1. Materials

A plain woven, bleached, 100% cotton fabric, 135 g/m², supplied by Phoenix Calico Ltd., UK, was used throughout this study and dyed with 5% o.w.f. (on mass of fabric) C. I. Sulphur Black 1. The ECE non-phosphate detergent, ECE phosphate detergent and tetraacetythylenediamine (92% active) were purchased from the Society of Dyers and Colourists (SDC), Bradford, UK. Sodium perborate tetrahydrate (97% active) was purchased from Aldrich Chemicals Ltd., UK.

2.2. Methods and procedures

2.2.1. Dyeing procedure [20]

The cotton fabric was introduced into a dyebath containing 50 g/L Diresul Black B (C. I. Sulphur Black 1), 25 g/L sodium chloride, 13 ml/L sodium hydroxide (67° Tw), 9 g/L Diresul Reducing agent D and 1 g/L of Sandopan CBN at 20 °C and a liquor:goods ratio of 10:1. The dyebath was raised to 98 °C over 20 min and maintained at the boil for 60 min. The fabric was then rinsed in cold water and oxidised with 40 g/L Sandopur DSC (oxidant and soaping agent) and 20 g/L sodium carbonate at 98 °C for 20 min. The fabric was then soaped in 1 g/L non-ionic detergent solution for 5 min at 60 °C, rinsed in water and dried at room temperature.

2.2.2. Laundering conditions

The C. I. Sulphur Black 1 dyed fabric was washed as described in the ISO 105 C06 C1S/C2S [10] procedures. The wash fastness test involved treating the dyed fabric in a solution containing 4 g/L ECE detergent, with or without 1 g/L sodium perborate, with or without 25 stainless steel balls, adjusted to pH 10.5, at 60 °C for 30 min. The fabric was finally rinsed in running water at 40 °C and air dried at room temperature.

Dyed fabric was also washed in accordance with the ISO 105 C09 [13] procedure, again with or without the perborate. The wash fastness test involved introducing the black dyed fabric into a solution containing 10 g/L ECE non-phosphate detergent, 1.8 g/L TAED, with or without 12 g/L sodium perborate, with or without 25 stainless steel balls, at 25 °C and raising the temperature to 60 °C at 2 °C/min and maintaining at 60 °C for 30 min. The fabric was finally rinsed in running water at ambient temperature and air dried at room temperature prior to further analysis.

2.2.3. Colour analysis

The colour strength (K/S) was calculated from reflectance measurements using the Kubelka–Munk equation (Equation (1)):

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

where K is the absorption coefficient, S is the scatter coefficient, R is reflectance expressed as a fractional value.

K/S and CIE $L^*a^*b^*$ values were calculated using a Datacolor Spectroflash 600 and the mean value was an average of four measurements. The K/S values in Table 2 were calculated at a $\lambda_{\max}$ of 580 nm.

Table 1

XPS surface elemental composition of ISO 105 C06/C09 washed sulphur black dyed cotton fabrics.

Washing treatment	XPS atomic %			
	Carbon	Nitrogen	Oxygen	Sulphur
None	73.5	2.6	21.0	3.0
ISO 105 C06				
With perborate ^a	68.9	2.1	26.3	2.7
With perborate ^b	71.2	2.6	23.5	2.8
Without perborate ^a	72.0	2.8	21.9	3.0
Without perborate ^b	70.0	2.4	24.9	2.7
With perborate ^{a,c}	69.3	1.7	27.3	1.6
Without perborate ^{b,c}	72.2	2.6	22.0	3.2
ISO 105 C09				
With perborate ^a	69.0	0.7	30.0	0.6
With perborate ^b	68.3	0.4	30.5	0.8
Without perborate ^a	70.2	2.3	24.5	3.0
Without perborate ^b	71.5	2.9	22.7	2.9

^a With stainless steel balls.

^b Without stainless steel balls.

^c Triplicate washing cycles.

2.2.4. XPS analysis

XPS analysis was performed using a Kratos Axis system spectrometer. The fabric samples were cut from the middle of the specimen and attached to the sample holder using a double sided tape. Monochromatic Al K α X-rays (1486.6 eV) with a power of 150 W were used to irradiate the samples and wide scan spectra were recorded with a pass energy of 160 eV from which the surface composition (C, O, S and N) was determined. High resolution Carbon (1s) and Sulphur (2p) spectra were recorded with pass energy of 40 eV and the binding energy (BE) values were calculated relative to Carbon (1s) photoelectron peak at 285.0 eV. Charge compensation for the samples was achieved using a 4–7 eV beam at a flood current of approximately 0.1 mA, with an electrically ground 90% transmission nickel mesh screen. All samples were analysed in duplicate and data analysed using the CASA XPS software [22].

2.2.5. SEM analysis

A Hitachi S3000N variable pressure instrument was used throughout the study. A magnification of 2000:1, a 5 kV accelerating voltage and a working distance of 10 mm were typically found to be the most appropriate analysis conditions and the samples were gold coated prior to analysis.

Table 2

Effect of ISO 105 C06/C09 washing on the colour of sulphur black dyed cotton fabrics.

Washing treatment	K/S	L^*
None	23.2	16.1
ISO 105 C06		
With perborate ^a	21.1	17.1
With perborate ^b	22.8	16.4
Without perborate ^a	21.5	17.0
Without perborate ^b	22.4	16.5
With perborate ^{a,c}	19.2	18.3
Without perborate ^{b,c}	21.3	17.0
ISO 105 C09		
With perborate ^a	8.8	28.4
With perborate ^b	8.4	29.0
Without perborate ^a	21.6	16.9
Without perborate ^b	21.6	16.8

^a With stainless steel balls.

^b Without stainless steel balls.

^c Triplicate washing cycles.

Fig. 1. S(2p) XP spectrum of unlaundred sulphur black dyed cotton fabric.

3. Results and discussions

3.1. ISO 105 CO6 washing

Examination of the S(2p) XP spectrum of C. I. Sulphur Black 1 dyed cotton fabric demonstrates the presence of sulphur at the surface of the cotton fibres, with the major peak intensity at 164.0 eV indicating it is predominately in the unoxidised S^{2+} form ($-S-$, $-S-S-$), Fig. 1. The smaller peak intensity at 168.0 eV suggests that re-oxidation of the alkali reduced sulphur dye thiols to reform the insoluble disulphide bond-based sulphur dye has resulted in over-oxidation to S^{6+} species. The S^{6+} oxidised dye derivatives may be assigned to $-SO_3$, $-S-SO_2-$ or $-S-SO_3$ species and are most likely the precursors to loss of dye from the fibre. Interestingly there is little spectral intensity at 166.0 eV which could be attributed to any intermediate oxidised S^{4+} species.

The effect of the ISO 105 CO6 washing with perborate was to increase the amount of higher binding energy spectral component at 168.0 eV, Fig. 2, indicating an increase in the oxidised S^{6+} dye species. This oxidised sulphur species spectral intensity was further increased with repeated ISO 105 CO6 washings with perborate,

Fig. 2. S(2p) XP spectrum of sulphur black dyed cotton laundered with sodium perborate and stainless steel balls (ISO 105 CO6).

Fig. 3. S(2p) XP spectrum of sulphur black dyed cotton laundered with sodium perborate and stainless steel balls (ISO 105 CO6 – triplicate wash cycles).

Fig. 3. The XP spectral difference between perborate-based washing with or without the stainless steel balls was minimal in terms of any increased surface oxidation. It can therefore be concluded that the addition of steel balls into the washing procedure does not directly affect the formation of oxidised dye sulphur species at the fibre surface.

The effect of individual and repeated ISO 105 CO6 washing of the sulphur dyed cotton without perborate was also to increase the level of oxidised sulphur at 168.0 eV in the S(2p) XP spectra, Figs. 4 and 5. However the oxidative effect was not as great as that observed with the perborate-based laundings. In particular the loss of sulphur from the fibre surface is minimal in the case of the non-perborate based laundering regimes, while it is significant in the presence of perborate (3.2% and 1.6% Atomic Sulphur, respectively, Table 1) It is presumed that oxidation of the dye disulphide bonds leads to the formation of water-soluble sulphonated short chain dye fragments which are lost into solution.

3.2. ISO 105 CO9 washing

Examination of the S(2p) XP spectrum of the ISO 105 CO9 washed C. I. Sulphur Black 1 dyed cotton fabric demonstrated that

Fig. 4. S(2p) XP spectrum of sulphur black dyed cotton laundered without sodium perborate and with stainless steel balls (ISO 105 CO6).

Fig. 5. S(2p) XP spectrum of sulphur black dyed cotton laundered without sodium perborate and without stainless balls (ISO 105 C06 – triplicate wash cycles).

Fig. 7. S(2p) XP spectrum of sulphur black dyed cotton laundered without sodium perborate and with stainless steel balls (ISO 105 C09).

the effect of the much more aggressive TAED catalysed perborate treatment was to convert most of the surface sulphur to the oxidised S^{6+} form, Fig. 6, in addition significant concomitant reduction of the surface sulphur concentration (from 3.0% to 0.6% Atomic Sulphur, Table 1) probably due to loss of the sulphonated dye fragments into solution was observed. In contrast the S(2p) XP spectrum of the ISO 105 C09 washed without perborate fabric, Fig. 7, mirrored the low level of oxidation and minimal loss of sulphur observed for the comparable ISO 105 C06, without perborate, washed cotton fabric, Fig. 4.

Examination of the C(1s) XP spectrum of C. I. Sulphur Black 1 dyed cotton fabric demonstrates the presence non-cellulosic carbon species at the fibre surface, Fig. 8; specifically the major peak intensity at 285.0 eV assigned to C–C and C–H species. If the fibre surface were purely cellulosic the expected carbon spectral peak intensities would occur at 286.6 and 288.0 eV, with an intensity ratio of 5:1 respectively, and could be assigned to:

286.6 eV $\text{C}-\text{OH}$
288.0 eV $\text{O}-\text{C}-\text{O}$

However evidence of oxidised functionalities at the fibre surface is also observed; these other C(1s) species can be attributed to:

288.8 eV $\text{C}=\text{O}$
289.0 eV $\text{O}=\text{C}-\text{OH}$

The effect of the ISO 105 C09 laundering with perborate on C(1s) spectral intensities was to reduce the hydrocarbon signal intensity at 285.0 eV and to increase the oxidised species intensities at 286.6, 288.0 and 289.0 eV, Fig. 9. The surface carbon, nitrogen and sulphur content also decreased while the surface oxygen content clearly increased indicating exposure of the cotton to a highly oxidative environment, Table 1. The effect of comparable laundering without perborate present was also to reduce the hydrocarbon signal intensity at 285.0 eV but to a much lesser extent, Fig. 10, reflecting the far less oxidative and degradative environment.

3.3. Influence of ISO 105 C06/9 washing on fabric colour

The effect of ISO 105 C06 washing with and without perborate was to marginally reduce the colour strength and increase fabric

Fig. 6. S(2p) XP spectrum of sulphur black dyed cotton laundered with sodium perborate and stainless steel balls (ISO 105 C09).

Fig. 8. C(1s) XP spectrum of unlaunched sulphur black dyed cotton fabric.

Fig. 9. C(1s) XP spectrum of sulphur black dyed cotton laundered with sodium perborate and stainless steel balls (ISO 105 CO9).

lightness, Table 2. With repeated (triplicate) ISO 105 CO6 washing with perborate however the fabric colour strength clearly decreased and the fabric lightness increased. These results are in good agreement with the XPS analysis data where increased oxidation of dye sulphur S^{2+} to S^{6+} species and the concomitant decrease in surface atomic % sulphur content were observed. In contrast, the fabric subjected to triplicate ISO 105 CO6 washing *without* perborate the colour and lightness change was greater than the single washed fabric, but as expected this change was however far smaller in magnitude than that observed with the fabric that had been triplicate washed with the oxidative perborate solution.

For the single ISO 105 CO9 washing with perborate, a much larger colour strength and lightness change was observed (K/S and L^* values in Table 2) probably due to the catalysed perborate/TAED bleaching of the dyed fabric causing oxidation of the sulphur dye to water soluble S^{6+} dye fragments. In contrast the ISO 105 CO9 washing without perborate showed a similar decrease in colour strength to that observed to the ISO 105 CO6 washing without perborate procedure.

The effect of introducing stainless steel balls into the washing process was to increase abrasion of the fibre/fabric surface. This process may remove surface dye and potentially increase fibrillation of the fibres. The fibrillation of cellulosic fibres can be an

important physical process in the fading of dyed textiles where the specular light reflectance at smooth fibre surfaces is replaced by diffuse reflectance resulting in an apparent loss in colour strength and an increase in fabric lightness [16–21]. Examination of the ISO 105 CO6 washing treatments of the dyed fabrics with and without the abrasive stainless steel balls indicates that the balls tended to further increase the fabric lightness and decrease the colour strength, Table 2, while XPS analysis suggests little additional dye is lost through the addition of steel balls in the washing process, Table 1.

Scanning Electron Microscopic analysis of the fabrics washed with the steel balls indicates there is significantly more fibrillation of the cotton fibres. Coupled with associated dye loss through washing, the fibrillation at the fibre surface is the likely cause of increased lightness and colour strength loss.

4. Conclusions

The surface sensitive XPS technique has demonstrated the presence of the sulphur-based colourant within the outer 3–10 nm of the fibre surface of C. I. Sulphur Black 1 dyed cotton fabric. The sulphur atoms attributed to the surface sulphur dye are predominantly in the S^{2+} form, occurring as $-S-$ or $-S-S-$, with a lesser amount of oxidised S^{6+} possibly occurring as $-SO_3^-$, $-S-SO_2-$ or $-S-SO_3^-$ species. These oxidised surface species have probably arisen due to over-oxidation of the dye during the dyeing process.

The effect of ISO 105 CO6 washing with perborate was to increase the higher oxidation state S(2p) signal intensity at 168 eV and the concomitant visual loss in colour, as indicated by decreased colour strength K/S and increased lightness L^* values. The effect of ISO 105 CO6 washing without perborate was also to increase the higher oxidation state S(2p) signal intensity at 168 eV but to a significantly smaller extent. The effect of including stainless steel balls in the washing test was to increase surface fibrillation and increase the fabric lightness by introducing greater diffuse reflectance at the fibre/fabric surface.

Laundering the sulphur dyed cotton using the ISO 105 CO9 protocol resulted in far greater surface oxidation, surface dye loss and colour change due to the activated bleaching environment. There was no evidence for the formation of S^{4+} dye species at the fibre surface but it is probable that dye loss occurs through conversion of the disulphide bonds in the sulphur dye to water-solubilising sulphonate species and the subsequent loss of short chain dye fragments into solution.

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Fig. 10. C(1s) XP spectrum of sulphur black dyed cotton laundered without sodium perborate and with stainless steel balls (ISO 105 CO9).

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