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Investigation into the Removal of Pigment, Sulphur and Vat Colorants from Cotton Textiles and Implications for Waste Cellulosic Recycling

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Abstract

Cotton can be coloured by dyeing and printing using either dye or pigment colorants. Pigments are insoluble in water but can be dispersed in a polymer print binder and heat fixed to the fabric. Vat and Sulphur dyes similarly have low solubility in water but through alkali/reduction can be solubilised and exhausted onto the cotton fibre. Following their re-oxidation, the dyes are insolubilized in the fibre and like pigment prints, in general, exhibit good wash fastness.

In this study sequential acid/alkali/peroxide or acid/dithionite/peroxide treatments were investigated as a means of removing pigment/polymer prints and common sulphur and vat dyes from coloured cotton fabric. Using the sequential acid/dithionite/peroxide treatment up to 97% of both sulphur and vat colorants could be "stripped" from dyed cotton producing a white cellulosic feedstock material that could be used for 'new' fibre regeneration. In contrast the "stripping" of the pigment/polymer binder colorant system was less predictable and less complete and is probably a reflection of the different chemical nature of the polymer binder and pigments. This contrasting behaviour highlights the range of chemistries applied to cotton and that developing a universal single treatment to strip out all finishes may be problematic.

Keywords: Waste cotton, Recycling, Pigment prints, Vat dyes, Sulphur dyes, Dye stripping

Introduction

Over the past few years the amount of textile waste has increased significantly, resulting in the perception that the textile industry is one of the most significant waste-generating industrial sectors. This problem is being exacerbated by population growth, the increasing number of short fashion seasons and the affordability of fashion for many consumers (Wang, 2006; Barnes, 2006). The main disposal routes for waste textiles are reuse and recycling, with a significant amount of waste being landfilled or incinerated (Wang, 2006). In the United Kingdom for example an estimate of 0.62 million tonnes were discarded through landfill and incineration for energy recovery in the year 2014 (WRAP, 2016). In addition, a more recent study (Labfresh, 2021) sourced from information from the Statistical Office of the European Union (Eurostat) in 2016 indicated that 81.4% of the EU generated textile waste is either incinerated or goes to landfill. Similarly, the United States discarded approximately 13.6 million tonnes of textile through the same routes in the year 2014, according to the US Environmental Protection Agency (USEPA, 2016).

Although reuse seems to be the best option, the ever-increasing amount of waste and its decreasing quality, due to the nature of fast fashion (Morley et al. 2009), point to a decline in reusability and therefore the need for alternative disposal routes such as recycling, landfill or incineration. Both landfill and incineration cause environmental pollution, while most of the mechanically recycled waste textiles yields low value non-woven products (Wang, 2006; Morley et al. 2009; Ütebay et al. 2019) with small amounts of waste materials collected from cut, make and trim (CMT) factories being successful converted into new textile garments (Pure Waste, accessed 2020). Nevertheless, the process is still limited by the overall poor quality of the yarns produced in terms of colour consistency and yarn strength (Wang, 2006; Payne, 2015). Therefore, the increased application of chemical recycling of waste garments, involving either dissolution or melting of the material and re-extrusion to obtain new fibres or depolymerisation and polymerisation of the fibre polymers and re-extrusion to generate new fibres through spinneret seems inevitable. Worn Again in the United Kingdom and Teijin in Japan are examples of chemical recycling technologies have reported that new yarns from waste textiles can be used to manufacture new textiles and clothing (WRAP, 2016).

However chemical recycling of waste garments is currently limited by the presence of colorants and crosslinks introduced during the processing of the cellulose. These colorants and the crosslinks between hydroxyl groups of the cellulose may impair not only the dissolution of the generated cellulosic feedstock, but also subsequent spinning efficiency of the recycled materials and the final properties and colour of the regenerated cellulosic fibres (Haule et al. 2014; Bigambo et al. 2018; Wedin et al. 2018). Therefore, the removal of colorants and crosslinking chemicals is essential, prior to any chemical recycling of waste cotton garments through new "white" fibre regeneration. The production of white fibre-based yarns offers greater creative flexibility for designers and manufacturers, as distinct from accepting that the colour of the regenerated yarns is prescribed by the waste feedstock, hence limiting the ability of the designer to specify product colour.

Pigment printing is an important fashion coloration technique that is relatively simple, economical and used to produce multi-coloured effects and designs on textile substrates (Miles, 2003). The main difference between pigments and dyes is that pigments have no solubilising groups making them effectively water-insoluble (Miles, 2003). They are therefore applied on the surface of the fabric in the presence of a thickening agent and a polymeric binder. On heat curing the surface print formulation the polymer binder matrix attaches the pigment to the fibre surface, thereby imparting durability in terms of both wet and dry fastness.

A range of dyes are currently used to colour cellulosic fibres including reactive dyes, direct dyes, vat dyes and sulphur dyes. While reactive dyes are the most commonly used (Broadbent, 2001; Kulandainathan, 2007), sulphur dyes and vat dyes are also important in cellulosic dyeing. Sulphur dyes offer a wide range of hues such as blacks, navy, brown, olives and greens in medium to heavy depths and at relatively low cost (Shore, 2002; Soliman, 2013). Vat dyes offer the best overall fastness properties based on light, wash and chlorine fastness, surpassing the performance of all the other cellulosic dye classes (Broadbent, 2001).

In this paper, pigments prints, sulphur and vat dyes were stripped from the cotton fabrics either using the combined effects acid and alkali hydrolysis treatments, alkaline hydrogen peroxide oxidative treatment or alkaline dithionite reduction treatment (Bigambo et al. 2019). The acid and alkaline treatments were used as they have previously been reported to strip easy care crosslinking agents from cotton fabrics (Abyankar et al. 1985; Abyankar et al. 1987; Haule, 2014). While the alkaline sodium dithionite treatment was selected as the reducing agent due to its widespread use in industrial scale reduction and decolorisation processing (Shore 2002). The agent is also relatively cheap and has high effectiveness/cost ratio (Oğulata and Balci, 2007). The dye scavenging agent, polyvinylpyrrolidone (PVP), was also added into the alkaline dithionite stripping liquor to prevent any redeposition of the stripped colorants on the fabrics (Walles 1963). The reusability of the pigment printed and vat and sulphur dyed waste cotton in the production of new “white” cellulosic fibres was also evaluated.

Experimental

Materials

A bleached, mercerised, plain woven, 100 % cotton fabric, (135 g/m^2) was supplied by Phoenix Calico Limited, Cheshire, UK. Printofix Binder 83, Printofix thickener, Printofix Fixing Agent and the pigments: Printofix Black T-M, Printofix Blue T-P and Printofix Red T-N01 were supplied by Archroma, UK. C. I. Vat Blue 4 (Duranthrene Blue RS) and C. I. Vat Black 27 (Duranthrene Olive R) were supplied by Town End (Leeds) Ltd., Leeds, UK and C. I. Vat Blue 1

(Indigo) was obtained from Sigma Aldrich Ltd. C. I. Sulphur Black 1 (Diresul Black RDT-LS) and C. I. Sulphur Blue 7 (Diresul Blue RDT-G) were obtained from Archroma, UK. All other chemicals were of laboratory grade obtained from various chemical suppliers. Table 1 presents the information on the dyes used in this study.

INSERT TABLE 1

Application of Pigment Print Formulation

Printofix Binder 83, Printofix thickener and Printofix Fixing Agent were incorporated into the base formulation as shown in Table 2. After mixing of the stock paste, 8% of the specified pigment (Printofix Black T-M, Printofix Blue T-P or Printofix Red T-N01) was added to 92% of the stock paste to make a print paste which was then manually applied to the cotton fabric using a conventional print screen. The printed fabrics were then air dried prior to curing for 5 minutes at 150°C temperature in a Mathis Baker. The printed cured samples were then washed with warm water to remove any chemical residues and then air-dried.

INSERT TABLE 2

Dyeing Treatments

The cotton fabric was dyed with C. I. Sulphur Black 1, C. I. Sulphur Blue 7, C. I. Vat Blue 4 and C. I. Vat Black 27, respectively, using recommended commercial exhaust dyeing methods.

All long liquor dyeings were carried out in sealed stainless steel dye pots of 1000 cm^3 capacity, housed in a Mathis Labomat laboratory dyeing machine. The sulphur dyeing of cotton fabric was performed with 4% o.m.f. (on mass of fabric) dye, 5 g/L sodium sulphide, 5 g/L sodium carbonate and 15 g/L sodium chloride, with liquor to goods ratio of 10:1.

The fabric was first heated to a temperature of 40-50^{o}C in the presence of half of the quantities of water, sodium sulphide and sodium carbonate. The liquor was kept at this temperature for 5 minutes, then the dyestuff and balance of water, sodium sulphide and sodium carbonate were added. The dyebath was further kept for 10 minutes at the same temperature and then the sodium chloride was added. The temperature was then increased to 90^{o}C at a gradient of 2^{o}C/min and kept at 90^{o}C for 30 minutes. The solution was then cooled to 50^{o}C at a gradient of 5^{o}C/min.

The dyed fabrics were then washed thoroughly with cold water to remove any unfixed surface dye. The dyed fabric was then oxidised with 5 g/L hydrogen peroxide and 1 g/L sodium carbonate at 40-45^{o}C for 15 minutes. The fabric was then finally soaped with 1g/L of non-ionic detergent at the boil for 20 minutes, then rinsed with cold and warm water and air dried. The liquor to goods ratio employed for oxidation and soaping was 10:1.

For C. I. Vat Blue 1, the fabric was dyed by immersing in the leuco dye liquor (the leuco vat dyebath contained: 5 ml/l caustic soda (27% by weight); 1.5 g/l sodium hydrosulphite; 62.5 ml/l stock vat. The stock vat consisted of: 80 g/l C.I. Vat Blue 1; 4 g/l dispersing agent; 1 g/l wetting agent; 130 ml/l caustic soda (27% by weight); 60 g/l sodium hydrosulphite; 2 g/l sequestering agent), 4% o.m.f. for 10 seconds, squeezing to 100% wet pick-up between padding machine roller sets and skied for about 2 minutes to partially oxidise the dye (Shore, 1995; Choudhury, 2006). The process was repeated five times to obtain the required depth. Dyed fabrics were then air-oxidised for 30 minutes prior to washing in 1 mL/L hydrochloric acid (37% Vols) followed by cold water rinsing. The dyed fabric was then soaped for 15 minutes at 100°C in a liquor containing 2 g/L sodium carbonate and 2 mL/L non-ionic washing detergent. Fabrics were then thoroughly rinsed in water prior to air drying.

Acid/Alkali treatment of the pigment printed and dyed cotton

All treatments were performed in a Pyrotec Infra-red laboratory scale dyeing machine using a liquor: goods ratio of 30:1. Fabrics were initially soaked for 2 hours in 10 mL/L sulphuric acid (96% Vols) at room temperature, before raising the liquor temperature to 60°C and further treating the fabrics for 1 hour. The fabric was then rinsed in warm water, neutralised in 0.2 mL/L sodium hydroxide (NaOH) followed by further rinsing in warm water and air dried (***Acid Treated Cotton***).

The *Acid Treated Cotton* was then treated in a boiling solution of 23% (w/v) NaOH for 10 minutes followed by rinsing in warm water for 10 minutes. The alkali treated sample was then neutralised in 0.2 mL/L acetic acid prior to warm rinsing and air drying (***Acid/Alkali Treated Cotton***).

Acid/Dithionite treatment of the pigment printed and dyed cotton

The *Acid Treated Cotton* was then treated further in an alkaline dithionite solution containing 30 g/L sodium dithionite, 40 g/L NaOH, 2.5 g/L PVP and 2 mL/L non-ionic detergent. The bath temperature was raised to 80°C and fabrics were treated at this temperature for 30 minutes, before raising the temperature to 100°C and further treating for 1 hour. The treatment bath was then cooled to 50°C and the stripped fabrics rinsed in hot water for 5 minutes. The dithionite treated sample was then neutralised in 0.2 mL/L acetic acid prior to warm water rinsing and air drying (***Acid/Dithionite treated fabric***).

Hydrogen Peroxide treatment of the pigment printed cotton and dyed cotton

The *Acid/Alkali* and *Acid/Dithionite* treated fabrics were further treated for 60 minutes at 85°C in a bath containing 1M hydrogen peroxide (35%Vols), 1.2 g/L sodium hydroxide, 1.8 g/L sodium carbonate and 7 g/L sodium silicate, followed by water rinsing and air drying to produce the ***Acid/Alkali/Peroxide*** or ***Acid/Dithionite/Peroxide*** treated fabrics.

Colorimetric Analysis

The colorimetric data presented was obtained using a Datacolor Spectroflash 600 spectrophotometer, under illuminant D65 using a 10° standard observer and is the mean of four reflectance measurements. Each fabric sample was folded twice to achieve opacity and the K/S values were calculated at the λ_{max} of the treated fabrics. The K/S values of fabrics were calculated from the Kubelka-Munk equation, which relates the reflectance of the dyed fabric to its absorbance and scattering at a specific wavelength (Bigambo et al. 2019). The ISO brightness values, defined as the intrinsic reflectance factor measured at a specific wavelength of 457 nm and a half bandwidth of 44 nm (British Standards, 2009), of both stripped and unstripped fabrics were measured at 460 nm wavelength using a Datacolor SF600 spectrophotometer.

The percentage of dye stripped from the fabric was calculated by relating the K/S values of treated fabrics and that of untreated dyed fabrics using Equation 1.

$$\% \, Stripping = \frac{K/S_{\text{unstripped fabric}} - K/S_{\text{stripped fabric}}}{K/S_{\text{unstripped fabric}}} \text{ x } 100 \qquad \text{(Equation 1)}$$

Scanning Electron Microscopy (SEM) Analysis

A Hitachi S-2600N SEM was used to assess the change in surface topography of the pigment printed fabrics and samples were gold sputtered prior to examination in the analysis chamber. Microscopic images were collected at 1000x magnifications, using a 5kV accelerating voltage and an average working distance of 5.3 mm.

Results and Discussion

Effect of Sequential Stripping Treatments on Pigment Printed Cotton

The effect of the sequential acid/alkali/peroxide and acid/dithionite/peroxide “stripping” treatments on the colour strength and brightness of the pigment printed cotton fabrics is presented in Tables 3 and 4, where it is clear that both sequential acid/alkali/peroxide and acid/dithionite/peroxide treatments significantly reduced the colour strength, *K/S*, and increased the ISO brightness of the treated printed fabrics. However, of the two processes the acid/alkali/peroxide appears to be the most effective in reducing colour strength and increasing fabric brightness of the non-crosslinked pigment printed cotton, which is in contrast to our previous study where the acid/dithionite/peroxide treatment was better at decolourising reactive dyes on cotton (Bigambo et al. 2019). This difference in stripping efficiency may be related to the relative greater sensitivity of the pigment/polymer binder system to alkali whereas the reactive dye azo chromophore was more susceptible to reductive bleaching. All three pigments in this study appear equally sensitive to the acid/alkali/peroxide treatment with high levels of colour loss observed, Table 3.

However, with the addition of the Printofix Fixing Agent to the polymer binder formulation the efficiency of the acid/alkali/peroxide treatment was reduced due to the formaldehyde-based crosslinking of the polymer matrix and increasing chemical resistance. Although in general the acid/alkali/peroxide treatment had greater effect over the three non-crosslinked pigment print systems evaluated, for the red pigment formulation it was apparent the acid/dithionite/peroxide "stripping" treatment was most efficient and was effective even with the crosslinked formulation. It is worth noting that the effect of the acid/dithionite/peroxide treatment on the Red pigment formulation was much clearer on the ISO brightness values of the stripped materials (Table 4) which increased to 84.9% and 85.8% for the red pigment printed fabric, without and with fixing agent respectively, compared to 82.4% for original unprinted (untreated). The small increase in the baseline brightness may be due to incomplete bleaching of the original cotton fabric and the combined oxidative and reductive treatments removing this original residual coloured impurity.

The observed varying level of decolourisation of the three pigments used in this study suggests that the red pigment had an azo chromophore, the black pigment was based on a carbon black chromophore while the blue pigment was based on a copper phthalocyanine chromophore. The carbon black structure is reported to withstand both high temperature and chemical treatment, while the copper phthalocyanine has highly stable molecular structure that is resistant to chemical attack (Shore, 2002). In contrast, the azo structure is reported to be sensitive to reductive chemical agents (Choudhury, 2006). Therefore, the variable decolourisation effect observed on the stripped printed fabric was thought to be related to the chemical nature of the pigment, with the red pigment being most sensitive and the black pigment most resistant to the dithionite reducing agent.

INSERT TABLES 3 & 4

SEM analysis of the printed fabrics clearly shows the polymer binder distributed over the cotton fibre surface and also evidence of interfibre bonding, Figure 1a and 1b. Following the sequential stripping processes the SEM micrographs indicate surface polymer is still evident, but much reduced, Figure 1c and 1d, and the varying levels of removal of the surface polymer correlates with their associated colour strengths and ISO brightness values, Tables 3 & 4.

INSERT FIGURE 1

Effect of Sequential Stripping Treatments on Sulphur Dyed Cotton fabrics

C. I. Sulphur Black 1 and C. I. Sulphur Blue 7 dyes were selected for this study due to their wide commercial usage and importance in textile dyeing as they offer heavy depths and excellent fastness properties at reasonable cost. Figure 2 shows the effect of the sequential acid/dithionite/peroxide treatment on the colour strength of the sulphur dyed fabrics. Although the acid treatment included in both stripping methods was not effective in removing colorants from the cotton materials, its inclusion was essential due to its ability to break crosslinks associated with easy care finishes applied to the coloured cotton (Haule, 2014). Subsequent alkaline dithionite treatment significantly decreased the K/S values to 0.7 and 0.1 on the C. I. Sulphur Black 1 and C. I. Sulphur Blue 7 dyed fabrics, respectively. The alkaline dithionite can reduce the disulphide bond of the sulphur dyes into the water-soluble (thiol) form (Aspland, 1997), which coupled with the addition of the polyvinylpyrrolidone (PVP) polymer in the stripping liquor can effectively prevent redeposition of the water-soluble sulphur dyes back onto the fibre (Laing et al.1991; Sheth, 1985; Boardman and Jarvis, 2000). Thus, the high reducing power of the alkaline dithionite solution combined with the dye binding capacity of the PVP polymer is responsible for the high colour removal from the two sulphur dyed cottons.

INSERT FIGURE 2

A further peroxide treatment clearly removed residual colourant from the C. I. Sulphur Black 1 dyed fabric by degrading any remaining coloured species/byproducts, however, the oxidative treatment had relatively little effect on the C. I. Sulphur Blue 7 fabric although the K/S value was already very low, Figure 2. Nevertheless Figure 3 shows that both the dithionite and final peroxide treatments significantly increased the ISO brightness for the C. I. Sulphur Black 1 and C. I. Sulphur Blue 7 dyed fabrics up to 74% and 83%, respectively. Again, this was thought to be due to the removal of any residual coloured species remaining on the stripped fabric after the initial treatments.

INSERT FIGURE 3

Earlier in this paper we indicated that the sequential acid/alkali/peroxide treatment was less successful in decolorising reactive dyed cotton than the alternative acid/dithionite/peroxide treatment, and that the converse was evident for the Printofix pigment printed cotton fabrics. On comparing the effect of the two stripping treatments on the sulphur dyed fabrics in this study it is apparent that the acid/dithionite/peroxide treatment is more effective in decolorising the dyed fabrics, Figure 4. This contrasting behaviour highlights the distinctive coloration chemistries available for cotton textiles and that a single stripping treatment effective for removing all the dye ranges (and associated fixing agents), pigment prints (and associated fixing agents), easy care finishes and fluorescent whitening agents may not be possible.

INSERT FIGURE 4

Effect of Sequential Stripping Treatments on Vat Dyed Cotton fabrics

The three vat dyes were selected based on their distinct chemical classes (anthraquinone and indigoid), and the fact that C. I. Vat Blue 1 is also widely used in the coloration of denim fabrics. Figure 5 shows the effect of the sequential acid/dithionite/peroxide treatment on the colour strength of the vat dyed fabrics. The acid treatment had the least effect indicating the stability of the vat dye chromophores to acidic hydrolysis. Subsequent alkaline dithionite treatment significantly decreased the K/S values to 0.1, 0.9 and 0.4 with the C. I. Vat Black 27, Vat Blue 4 and Vat Blue 1 treated cottons, respectively. As with the sulphur dyes, the alkaline sodium dithionite reduced the water-insoluble vat dye present on the fibre into its water-soluble form (Shore, 1995; Broadbent, 2001). Furthermore, the PVP polymer (a dye transfer inhibitor) present in the stripping liquor complexed with the water-soluble leuco vat dye preventing it from redepositing back on the fibre surface. Finally, oxidative peroxide bleaching removed additional colour from all fabrics resulting in K/S of 0.07, 0.49 and 0.05 on C. I. Vat Black 27, Vat Blue 4 and Vat Blue 1 fabrics, respectively. The effect of the final oxidative bleaching is relatively small in comparison to the effect of the precursor dithionite treatment, nevertheless it does have an obvious effect in raising the base brightness of the cotton fabric and possibly also degraded adsorbed residual vat colorant/byproducts.

INSERT FIGURE 5

Similar to the sulphur dyed study the effect of the acid/dithionite/peroxide stripping treatment was to increase the ISO brightness of the treated vat dyed fabrics, Figure 6. However, while the C. I. Vat Black 27 and C. I. Vat Blue 1 treated fabrics increased their brightness values to 70% and 84%, respectively, the C.I. Vat Blue 4 only increased its brightness value to 50%. The lowest brightness observed on the C.I. Vat Blue 4 fabric could be explained as a result of the greater chemical resistant and lower water solubility anthraquinone chromophore of the C. I. Vat Blue 4 dye.

INSERT FIGURE 6

Figure 7 illustrates the relative effect of the acid/alkali/peroxide and acid/dithionite/peroxide on the stripping treatments on the vat dyed fabrics assessed in this study and it is apparent that the acid/dithionite/peroxide treatment is more effective in decolorising the fabrics. With both sequential treatments the C. I. Vat Blue 4 dyed fabric was the most resistant to stripping, however the acid/dithionite/peroxide treatment was also relatively ineffective against the C. I. Vat Black 27 and Vat Blue 1.

INSERT FIGURE 7

Conclusions

This study evaluated the effect of sequential acid/alkali/peroxide or acid/dithionite/peroxide stripping processes in stripping pigment/polymer prints, sulphur and vat dyes from coloured cotton fabrics. Results indicated that the acid/dithionite/peroxide stripping process could strip over 97% of the vat and sulphur dyes applied to the coloured cotton fabrics. This was attributed to the strong reducing nature of the alkaline dithionite solutions together with the dye transfer inhibiting properties of the PVP polymer. Hydrogen peroxide bleaching further removed dye residues remaining after the dithionite treatment also contributing to the high stripping efficiency of the sequential acid/dithionite/peroxide treatment. In contrast the sequential acid/alkali/peroxide treatment was less effective in dye removal and maybe less useful in preparing a "white feedstock" for new fibre generation.

In terms of pigment prints, the acid/alkali/peroxide treatment was observed to be more effective in stripping the polymeric binder with incorporated black and blue pigments, which contrasts the behaviour of sulphur and vat dyed cotton. However, on incorporating crosslinking fixing agent into the polymer binder formulation the decolourisation efficiency visibly decreased. While the polymeric binder clearly influenced the colour loss, it was evident that the Printofix Red T-N01 pigment was particularly sensitive to the acid/dithionite/peroxide treatment with the crosslinker having no protective effect. SEM analysis also demonstrated the loss of the surface polymer binder with chemical stripping which correlated with the increase in fabric colour strength and brightness.

In conclusion it is evident the development of universal stripping process for the removal of colorants from dyed and printed cotton fabrics in order to provide a "white feedstock" for the regeneration of "new" cellulosic fibres is challenging and reflects the range of chemistries applied to cotton apparel. Although the current paper did not include the stripping of easy care finishes or fluorescent whitening agents from cotton garments, our long term approach to delivering a commercial stripping treatment for all dyed and finished cotton garments was to recognise that the waste material feedstock will be mixed and the likelihood that it will be pre-separated into different types of processed and dyed cotton is low. Accordingly, in endeavouring to establish a universal stripping sequence we assumed the "worst feedstock mixture" and part of that scenario was to assume a crease resist finish was present. And for that reason, the acid treatment was included in the stripping sequence to ensure wider processing coverage and that crosslinking agents would also be removed.

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Table 1 Structure of dyes used for the study

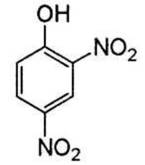
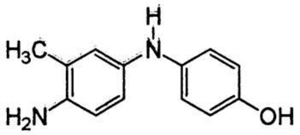
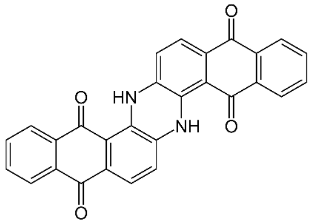
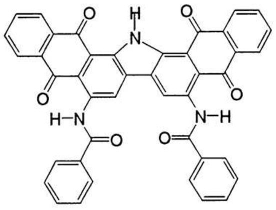
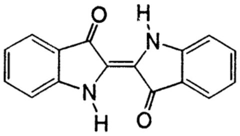
Generic name; Commercial name	**Chemical Class**	**Molecular structure (monomer unit)**
C. I. Sulphur Black 1; Diresul Black RDT-LS	Unknown	 [World dye variety, 2012a]
C. I. Sulphur Blue 7; Diresul Blue RDT-G	Unknown	 [World dye variety 2012b]
C. I. Vat Blue 4; Cibanone Blue RS	Anthraquinone	 [Shore, 1995]
C. I. Vat Blue 27; Solanthrene Olive R	Anthraquinone	 [Shore, 1995]
C. I. Vat Blue 1	Indigo	 [Shore, 1995]

Table 2 Stock paste recipes used in study

Chemical	**Formulation Composition (% component)**	
	Printofix Without Fixing Agent	**Printofix With Fixing Agent**
Ammonium Hydroxide	1	1
Printofix Binder 83	24	24
Printofix Fixing Agent	-	1.5
Printofix Thickener	1.2	1.2
Water	73.8	72.3
Total	100	100

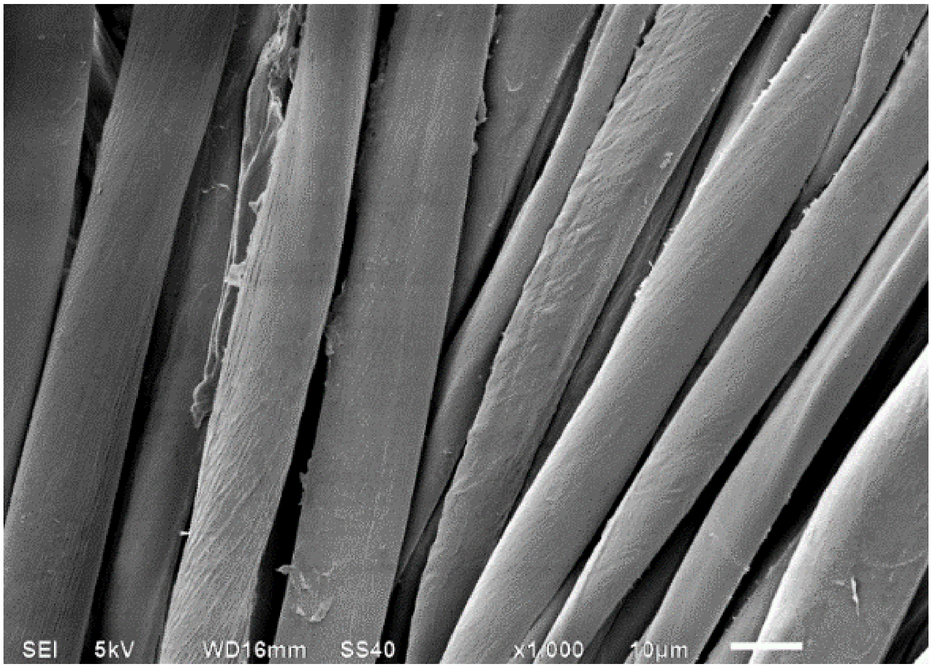
Table 3 Colour strength values for Printofix pigment printed fabrics stripped by either sequential acid/alkali/peroxide or acid/dithionite/peroxide treatments.

Print System	**Colour Strength, K/S**		
	Original Print	**Acid/Alkali/Peroxide Strip Treatment**	**Acid/Dithionite/Peroxide Strip Treatment**
Printofix Black T-M without Fixing Agent	16.7	0.7	5.4
Printofix Black T-M with Fixing Agent	16.3	5.2	9.8
Printofix Blue T-P without Fixing Agent	16.8	0.2	2.0
Printofix Blue T-P with Fixing Agent	19.5	5.3	4.0
Printofix Red T-N01 without Fixing Agent	16.6	0.3	0.02
Printofix Red T-N01with Fixing Agent	14.6	5.4	0.02

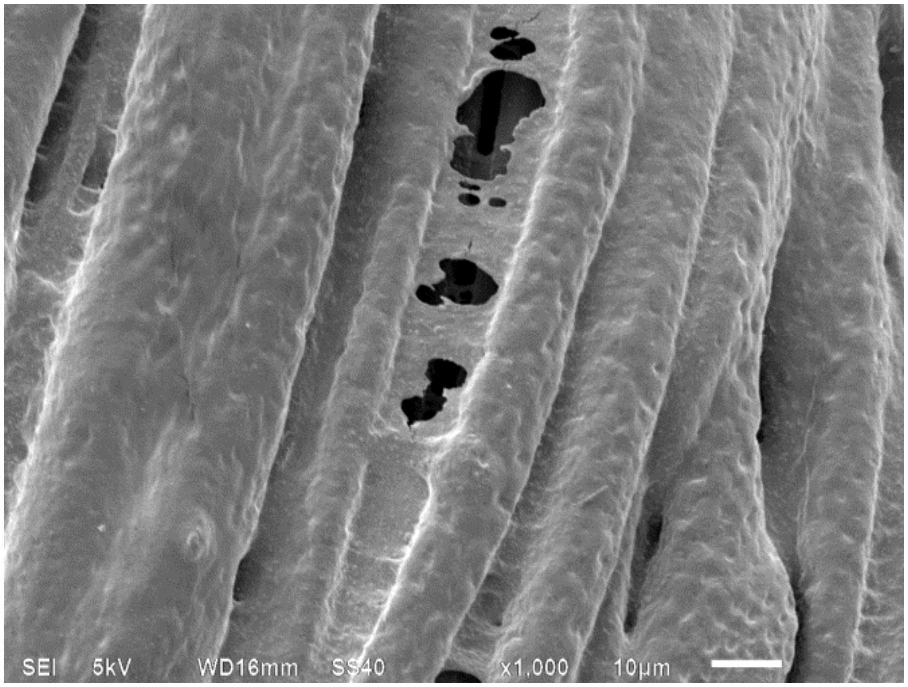
Table 4 ISO brightness for the Printofix pigment printed cotton fabrics stripped by either sequential acid/alkali/peroxide or acid/dithionite/peroxide treatments.

Pigment Print System	**ISO Brightness, %**		
	Original Print	**Acid/Alkali/Peroxide Strip Treatment**	**Acid/Dithionite/Peroxide Strip Treatment**
Untreated Fabric	82.4		
Printofix Black T-M without Fixing Agent	2.9	32.3	7.9
Printofix Black T-M with Fixing Agent	2.9	8.1	4.6
Printofix Blue T-P without Fixing Agent	26.7	78.9	43.3
Printofix Blue T-P with Fixing Agent	21.9	29.6	34.1
Printofix Red T-N01 without Fixing Agent	3.5	50.5	84.9
Printofix Red T-N01 with Fixing Agent	4.7	9.9	85.8

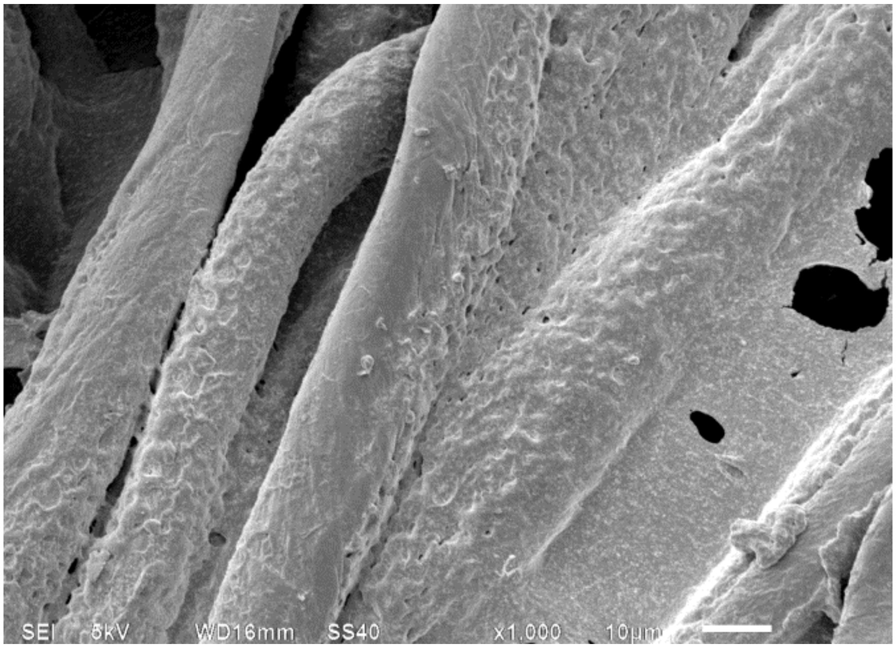
Figure 1 SEM micrographs of (a) untreated cotton fabric; (b) Printofix Black T-M pigment printed fabric; (c) pigment printed fabric sequentially stripped with acid/dithionite/peroxide solutions (d) Printofix Red T-N01 pigment printed fabric sequentially stripped with acid/dithionite/peroxide solutions.



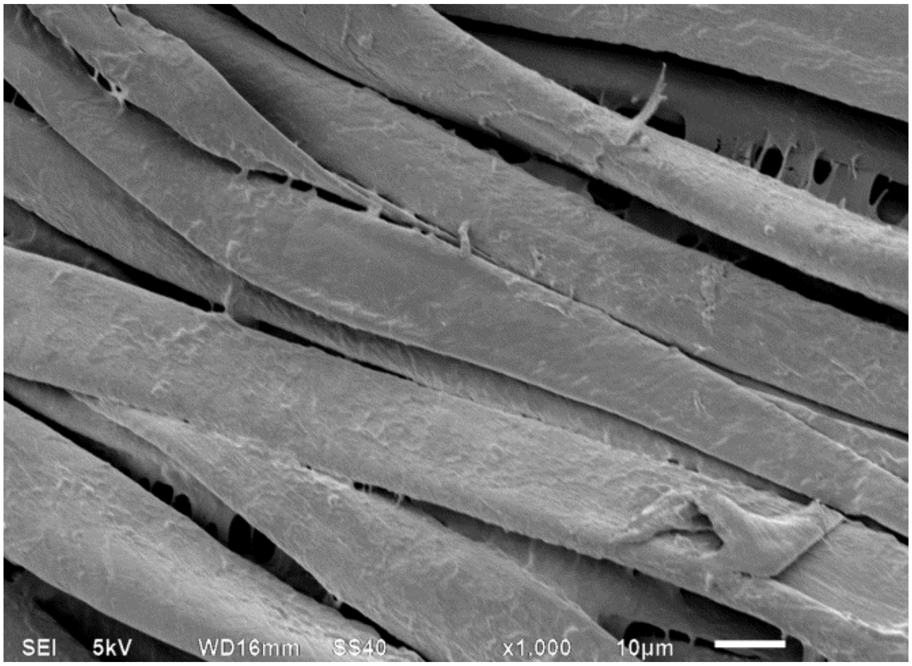
(a) Untreated cotton fabric.



(b) Printofix Black T-M pigment printed fabric



(c) Printofix Black T-M pigment printed fabric sequentially stripped with acid/dithionite/peroxide solutions.



(d) Printofix Red T-N01 pigment printed fabric sequentially stripped with acid/dithionite/peroxide solutions.

Figure 2 Colour strength for Sulphur dyed fabrics stripped with the sequential acid/dithionite/peroxide treatment.

■ Original dyed fabric; ■ Acid Treated Fabric; ☐ Acid/Dithionite Treated Fabric; ☐ Acid/Dithionite/Peroxide Treated Fabric.

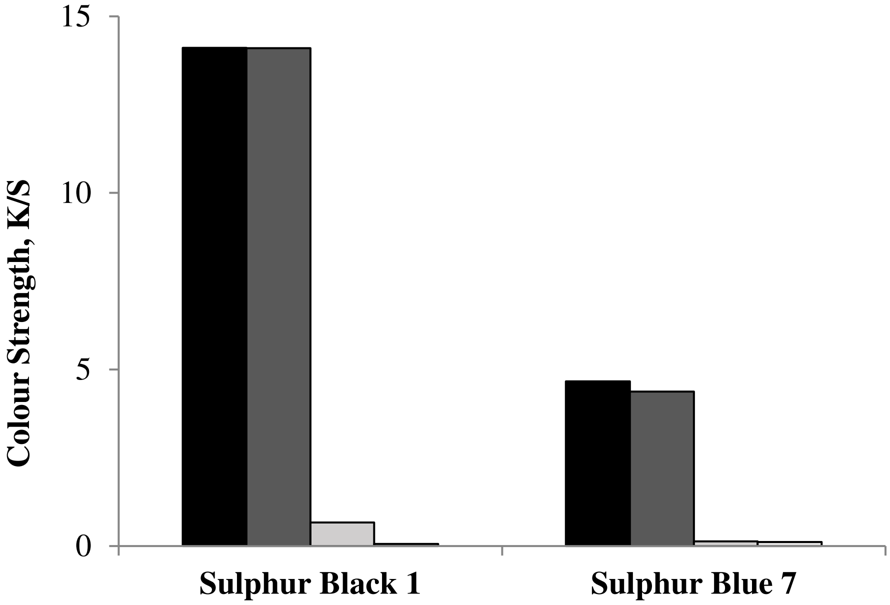


Figure 3 ISO Brightness Values for Sulphur dyed fabrics stripped with the sequential acid/dithionite/peroxide treatment.

■ Original dyed fabric; ■ Acid Treated Fabric; □ Acid/Dithionite Treated Fabric; □ Acid/Dithionite/Peroxide Treated Fabric.

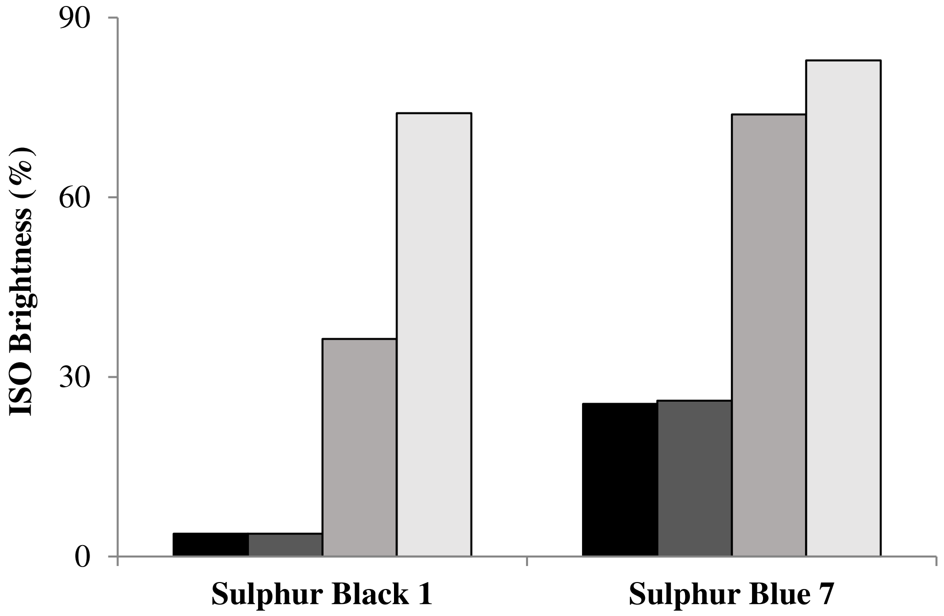


Figure 4 Visual appearance of Sulphur dyed cotton fabrics following stripping with the sequential acid/dithionite/peroxide or acid/alkali/peroxide treatments.

Colorant	**Dyed fabric**	**Acid treated**	**Acid/Dithionite treated**	**Acid/Dithionite/ Peroxide**	**Undyed fabric**
Sulphur Black 1					
Sulphur Blue 7					
Colorant	**Dyed fabric**	**Acid treated**	**Acid/Alkali treated**	**Acid/Alkali/ Peroxide**	**Undyed fabric**
Sulphur Black 1					
Sulphur Blue 7					

Figure 5 Colour strength for Vat dyed fabrics stripped with the sequential acid/dithionite/peroxide treatment.

■Original dyed fabric; ■Acid Treated Fabric; □ Acid/Dithionite Treated Fabric; □ Acid/Dithionite/Peroxide Treated Fabric.

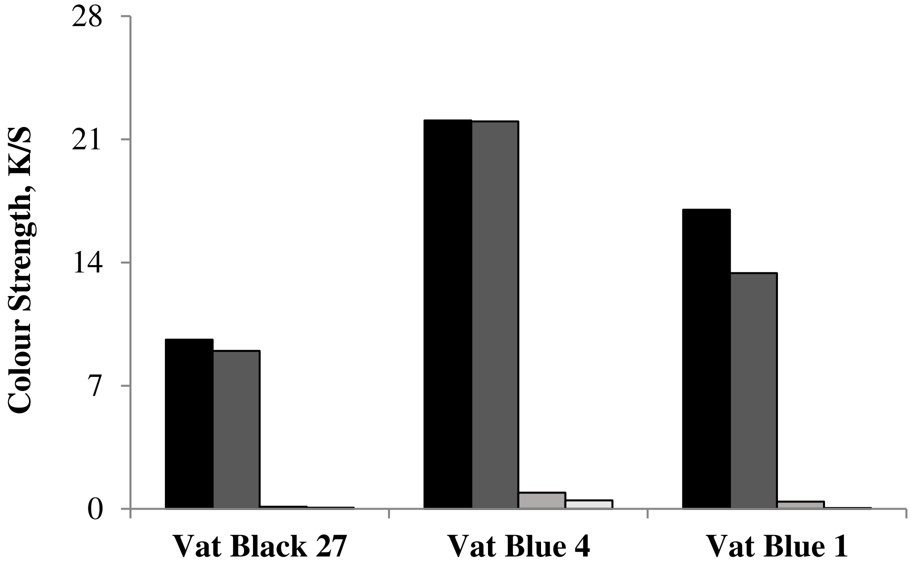


Figure 6 ISO Brightness Values for Vat dyed fabrics stripped with the sequential acid/dithionite/peroxide treatment.

■ Original dyed fabric; ■ Acid Treated Fabric; □ Acid/Dithionite Treated Fabric; □ Acid/Dithionite/Peroxide Treated Fabric.

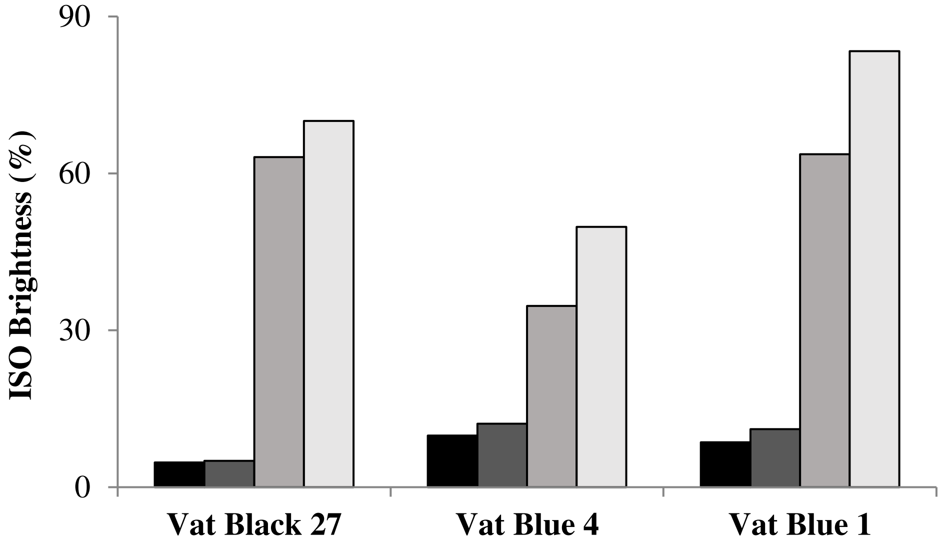
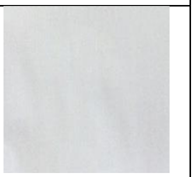


Figure 7 Visual appearance of Vat dyed cotton fabrics following stripping with the sequential acid/dithionite/peroxide or acid/alkali/peroxide treatments.

Colorant	Dyed fabric	Acid treated	Acid/Dithionite treated	Acid/Dithionite/ Peroxide	Undyed fabric
Vat Black 27					
Vat Blue 4					
Vat Blue 1					

Colorant	Dyed fabric	Acid treated	Acid/Alkali treated	Acid/Alkali/ Peroxide	Undyed fabric
Vat Black 27					
Vat Blue 4					
Vat Blue 1