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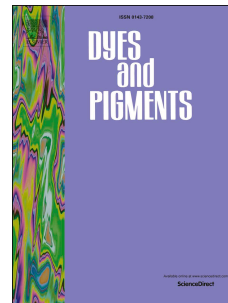


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1 **Surface Chemical and Colorimetric Analysis of Reactively Dyed Cellulosic Fabric. The**
2 **Effect of ISO 105 C09 Laundering and the Implications for Waste Cellulosic Recycling**

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10
11 **ABSTRACT**

12 Previous studies have established that the application of crosslinking dyes and easy care
13 finishes to cotton can significantly reduce the dissolution of waste cotton in solvents, such as
14 N-Methylmorpholine oxide, and limit the potential recycling of cellulosic materials through
15 the Lyocell fibre regeneration process. In this investigation the surface chemical
16 compositions of three reactive dyed Tencel fabrics were studied using X-ray Photoelectron
17 Spectroscopy (XPS) and the presence of the dye at the fibre surface demonstrated. The effect
18 of the ISO 105 C09 oxidative-bleach fading test on the azo and anthraquinone chromophoric
19 species was established by both surface chemical and colorimetric analyses. At low dye
20 application levels the C. I. Reactive Black 5 and C. I. Reactive Red 228 dyed fabrics (azo
21 chromophore) exhibited obvious colour fade while the anthraquinone-based C. I. Reactive
22 Blue 19 dyed fabric was resistant to colour fade. However it is apparent that although some

1 of the covalently bound dye will be removed during “first life” usage, most of the reactive
2 colorant will remain bound to the cotton and will therefore need to be stripped from the waste
3 garments to produce a white cellulosic feedstock prior to reprocessing through Lyocell fibre
4 regeneration. A sequential acid, alkali and peroxide treatment completely removed the azo-
5 based C. I. Reactive Black 5 and C. I. Reactive Red 228 colorants from the dyed cotton,
6 however, the anthraquinone-based C. I. Reactive Blue 19 was highly resistant to removal and
7 will require alternative chemical processing to remove the colorant.

8
9 **Keywords:** Cellulose, reactive dyes, x-ray photoelectron spectroscopy, recycling, dye
10 stripping, waste cotton garments.

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15 1. INTRODUCTION

16 Lyocell is a regenerated cellulose fibre, which has been developed in response to technical,
17 environmental and economic challenges [1]. It is the first commercially solvent-spun
18 cellulosic fibre which negates the necessity for the xanthate derivatisation step in viscose
19 manufacturing, with the added benefit of the amine oxide solvent being recyclable [2].

20 Reactive dyes are reported to have a high affinity for Lyocell/Tencel and can form covalent
21 bonds, particularly the polyfunctional dyestuffs, with the cellulosic substrate [3-5]. Reactive
22 dye systems can be classified as mono-functional, bi-functional and tri-functional, with the
23 extent of substrate fixation, hydrolysis and durability influenced by the nature of the reactive

1 functionality and the application conditions [3-5]. With the multi-functional reactive dyes,
2 there is also the opportunity for crosslinking reactions which can enhance the physical
3 properties of the Lyocell fabric by reducing wet fibrillation, maintain the colour strength by
4 more durable fixation and minimise diffuse reflectance at the fibre/fabric surface resulting
5 from wet laundering [6-11].

6 The surface sensitive X-ray Photoelectron Spectroscopy (XPS) technique has been used to
7 investigate the nature of the outer cellulosic fibre surface, characterising the surface
8 functionalities and elemental composition [12-14]. In this study the application of three
9 reactive dyestuffs was investigated in order to assess dye fixation in the fibre bulk and at the
10 fibre surface and the build-up of dye within the outer 10 nm surface. In addition the dyed
11 Tencel fabrics were washed under ISO 105 C09 test conditions with a view to establishing
12 the durability of the surface bound dye to different washing regimes through the colour
13 strength (K/S) and lightness (L*) measurements, and exploring the dye fading mechanism.
14 This diagnostic ISO 105 C09 oxidative-bleach fading test has now gained wide acceptance
15 and can be used to predict the potential fading due to colorant destruction in domestic use
16 [15-17].

17 Previous studies have established that the application of crosslinking dyes and easy care
18 finishes to cotton can significantly reduce the dissolution of waste cotton in swelling solvents
19 and accordingly can limit the potential recycling of cellulosic materials through the Lyocell
20 fibre regeneration process [18-22]. Therefore it is vital in any commercial processing of
21 waste cotton that colourless crosslinking easy care finishes and coloured dyestuffs are
22 effectively removed prior to dissolution. This study investigated a method to 'strip'
23 colourants from reactive dyed cotton in order to prepare the materials for new fibre
24 regeneration. The relative efficiencies of sequential acid, alkali and oxidative hydrogen

1 peroxide dye stripping treatments were assessed subjectively and quantified by determining
2 the fabric colour strength (K/S) and lightness (L*).

3 **2. EXPERIMENTAL**

4 **2.1 Materials**

5 Scoured plain woven Tencel fabric (150 g/m²), generously donated by Lenzing, Austria, was
6 further treated with deionised water twice at 90°C for 20 minutes and then washed in acetone,
7 rinsed in deionised water and finally air-dried prior to use in the laboratory. A bleached,
8 mercerised, plain woven, 100 % cotton fabric, (135 g/m²) was supplied by Phoenix Calico
9 Limited, Cheshire, United Kingdom and was used as received.

10 The ECE phosphate detergent and tetraacetylenediamine (92% active) were purchased
11 from the Society of Dyers and Colourists (SDC) enterprise, Bradford, UK. Sodium perborate
12 tetrahydrate (97% active) was purchased from Aldrich Chemicals Ltd., UK.

13 C. I. Reactive Blue 19 and C. I. Reactive Black 5 were kindly supplied by Dystar, Germany
14 and C. I. Reactive Red 228 was kindly supplied by Ciba, UK. The dye structures are
15 illustrated in Figure 1.

16 **INSERT FIGURE 1**

17 **2.2 Methods**

18 **2.2.1 *Application of Reactive Dyes to Tencel***

19 The Tencel fabric (10 g) was dyed in a Mathis Labomat dyeing machine with 1%, 5% and
20 10% o.m.f. (on mass of fabric) of the specified dye following commercial application
21 recommendations. Tencel fabrics were introduced into dyebaths containing 1%, 5% and 10%
22 o.m.f. of the C. I. Reactive Blue 19 and C. I. Reactive Black 5, respectively, at 40°C with a
23 liquor to goods ratio of 15:1, and 50, 50 and 80 g/L sodium chloride, respectively, added over

1 15 minutes. 5 g/L sodium carbonate was then added and the dyebath maintained at 40°C for a
2 further 30 minutes. 2 g/L of sodium hydroxide was then added and the dyeing continued for a
3 further 60 minutes at 40°C. The fabric was removed from the dyebath and rinsed thoroughly
4 in deionised water prior to after-soaping, final rinsing and air drying.

5 Tencel fabrics were introduced into the dye bath containing 1%, 5% and 10% o.m.f. of the C.
6 I. Reactive Red 228, at 60°C with a liquor to goods ratio of 15:1, and 50, 70 and 80 g/L
7 sodium chloride, respectively, added over 30 minutes. 15, 20 and 20 g/L sodium carbonate,
8 respectively, were then added and the dye bath temperature maintained to 60°C for a further
9 60 minutes. The dyebath was then dropped and the fabric rinsed thoroughly in deionised
10 water prior to soaping, final rinsing and air-drying.

11 **2.2.2 After-Soaping Treatment [23]**

12 In order to remove any unfixed dye from the dyed Tencel, the dyed fabrics were after-soaped
13 with a 1 g/L aqueous non-ionic detergent solution at 100°C for 15 minutes at a liquor to
14 goods ratio of 50:1. At the end of the wash-off, the dyed samples were rinsed in hot water at
15 80°C, then in cold water and finally air-dried at room temperature.

16 **2.2.3 Application of Reactive Dyes to Cotton**

17 Reactive dyeing of the cotton fabric was performed following the method described above.
18 However, only the 4% o.m.f. dye applications were used with other parameters remaining the
19 same.

20 **2.2.4 Laundering Process ISO 105 C09 Wash Test**

21 The dyed fabrics were washed following the ISO 105 CO9 procedure, either with or without
22 the perborate and TAED (tetraacetylenediamine) incorporated into the treatment

1 solution [15]. The washed fabrics were rinsed in warm water and then air dried prior to
2 further analysis.

3 The wash solution was prepared as recommended with 10 g/L of ECE (phosphate-based)
4 detergent, 12 g/L sodium perborate tetrahydrate and 1.8 g/L TAED being dissolved in 1 L of
5 deionised water. The wash pot containing the fabric and wash solution was rotated in a
6 Washtec-P machine (Roaches) at 40 revolutions per minute, 60°C for 30 minutes. At the end
7 of the wash cycle the fabric sample was washed thoroughly in running cold water and
8 deionised water, respectively, and air-dried prior to colour analysis.

9 **2.2.5 Colour Analysis [23]**

10 The colour strength (K/S) was calculated from reflectance measurements using the single
11 constant Kubelka-Munk equation (Equation 1):

$$12 \quad \left(\frac{K}{S}\right)_\lambda = \frac{(1-R_\lambda)^2}{2R_\lambda} \quad \text{Equation 1}$$

13 Where K is the coefficient of absorption, S is the coefficient of scatter, R is reflectance
14 expressed as a proportional value and λ is the wavelength.

15 The K/S and CIE $L^*a^*b^*$ values were calculated from the mean of four reflectance
16 measurements produced by a Datacolor Spectroflash 600. The CIE $L^*a^*b^*$ values were
17 calculated under illuminant D65 using a 10° standard observer. The K/S values were
18 calculated at the λ_{max} of the dyed fabric. Each fabric sample was folded twice in order to
19 achieve opacity.

20 **2.2.6 Dye Exhaustion and Fixation Analysis [23]**

21 Percentage dye exhaustion ($\%E$) was calculated from Equation 2:

$$1 \quad \%E = \frac{C_0 - C_1}{C_0} \times 100\% = \frac{A_0 - A_1}{A_0} \times 100\% \quad \text{Equation 2}$$

2 Where C_0 and C_1 are the concentrations of the dye before and after dyeing (g/L), respectively,
 3 and A_0 and A_1 are the absorbance values of the dyebath before and after dyeing at the λ_{max} of
 4 each dye, respectively.

5 For each dyeing, the total fixation efficiency (T), which is the percentage of the dye originally
 6 applied to the fabric becoming covalently bonded, was calculated using Equation 3:

$$7 \quad \%T = \frac{C_0 - C_1 - C_1'}{C_0} \times 100\% = \frac{A_0 - A_1 - A_1'}{A_0} \times 100\% \quad \text{Equation 3}$$

8 Where C_0 , C_1 and C_1' are the respective concentrations (g/L) of the dye before (C_0) and after
 9 dyeing (C_1) and in the wash-off solutions (C_1'), respectively; and A_0 , A_1 and A_1' are the
 10 corresponding absorbance values of the liquors.

11 From the dye exhaustion and the total fixation efficiency values, the fixation values of the
 12 dye absorbed (F), sometimes termed the fixation ratio were calculated using Equation 4:

$$13 \quad \%F = \frac{\%T}{\%E} \times 100\% \quad \text{Equation 4}$$

14 **2.2.7 XPS Analysis**

15 XPS spectra were obtained with a Kratos Axis Ultra instrument at a base pressure of 3×10^{-9}
 16 torr. The samples were irradiated with monochromatic Al K_{α} X-rays (1486.6 eV) using a spot
 17 size of $400\mu\text{m} \times 1000\mu\text{m}$ and a power of 150W, from which the surface chemical
 18 compositions were obtained. In addition, high-resolution nitrogen (1s) spectra were recorded
 19 with pass energy of 20eV, from which the nitrogen chemical states were determined. All
 20 binding energy values were calculated relative to the carbon (1s) photoelectron at 285.0eV.
 21 Charge compensation for these electrically insulating materials was achieved using a beam of
 22 low energy electrons from a flood gun. To ensure reproducibility, the samples were analysed

1 in duplicate or triplicate and data analysis was performed using the CASA XPS software
2 [24].

3 **2.2.8 Stripping of Dye from Coloured Cotton Fabric Prior to Lyocell Regeneration**

4 The acid/alkali stripping of reactive dyes from cotton fabrics was performed using a
5 sequential treatment described previously [20, 21]. The dyed fabrics were initially soaked for
6 2 hours in 10 mL/L sulphuric acid at room temperature, liquor: goods ratio of 30:1, before
7 raising the liquor temperature to 60°C and further treating for 1 hour. Treated samples were
8 then divided in two equal portions where one portion was warm rinsed and neutralised in 0.2
9 mL/L NaOH followed by warm rinsing in water and air dried (*Acid Treated Cotton*). The
10 other portion was transferred into a boiling solution of 23% (w/v) NaOH for 10 minutes
11 followed by rinsing in warm water for 10 minutes. The alkali treated sample was then
12 neutralised in 0.2 mL/L acetic acid prior to warm rinsing and air drying (*Acid/Alkali Treated*
13 *Cotton*).

14 The *Acid/Alkali Treated Cotton* was then further treated for 60 minutes at 85°C in a bath
15 containing 1M hydrogen peroxide (35% Vols), 1.2 g/L sodium hydroxide, 1.8 g/L sodium
16 carbonate and 7 g/L sodium silicate, at a liquor to goods ratio of 30:1, followed by water
17 rinsing and air drying (*Acid/Alkali/Peroxide Treated Cotton*).

18

19 **3. RESULTS AND DISCUSSION**

20 **3.1 Effect of ISO 105 C09 Wash Test on Surface Chemistry and Colour of Dyed Lyocell**

21 In this study C. I. Reactive Blue 19, Reactive Black 5 and C. I. Reactive Red 228 were
22 selected as representative mono-functional, bi-functional and tri-functional reactive dyestuffs
23 with both anthraquinonoid and azo chromophores, respectively. In addition Tencel fabric was

1 selected for the preliminary surface colorant study as the base fabric processing history was
2 known and no surface nitrogen contaminants were present. Examination of the XPS spectra
3 of the dyed fabrics indicated the presence of carbon, oxygen and nitrogen and whereas the
4 carbon and oxygen can be primarily attributed to the cellulosic fibre, the nitrogen, at a
5 binding energy of 398-400eV, can solely be attributed to the nitrogen atoms of the dye
6 molecules. Therefore by using this elemental tag it is possible to probe the presence of the
7 dyes at the surface and their durability to “activated” laundering.

8 Table 1 indicates that increasing application levels of the reactive dyes in general results in a
9 progressive rise in the surface nitrogen content of the dyed Lyocell fabric. However it is
10 evident that the observed increased XPS surface nitrogen intensity with increasing dye
11 fixation does not mirror the calculated bulk nitrogen content increase, suggesting that there is
12 probably rapid saturation at the fibre surface with the fixed dye. Nevertheless the inherent
13 higher atomic nitrogen content in the C. I. Reactive Black 5 (9.5% N Atomic Composition)
14 and C. I. Reactive Red 228 (11.7% N Atomic Composition) dye molecules relative to the C.
15 I. Reactive Blue 19 molecule (5.6% N Atomic Composition) are translated into an observed
16 higher XPS N(1s) signal intensity at the Lyocell fibre surface.

17 **INSERT TABLE 1**

18 The effect of increasing the concentration of C. I. Reactive Blue 19 dye applied to the Lyocell
19 fabric was to increase the colour strength K/S and decrease fabric lightness L^* , Table 2.
20 However it is evident that colour saturation occurs between 5-10% o.m.f. of dye application
21 and as expected a relatively small colour strength increase occurs after the 5% o.m.f.
22 application level. The effect of the ISO 105 CO9 laundering on the dyed fabrics was to
23 reduce the colour strength and increase fabric lightness but there was relatively little
24 difference between the treatments with and without perborate. This relatively small difference

1 of colour strength and fabric lightness reflects the durability of the covalent bond and the
2 resistance of the anthraquinone chromophore to the activated perborate/peracetic acid
3 oxidative laundering conditions. Typically with the ISO 105 CO9 test method the 1% dye
4 application level is regarded as providing the critical benchmark of dye sensitivity to
5 oxidative-bleach fading and in this case the C. I. Reactive Blue 19 dyestuff would be
6 regarded as exhibiting an acceptable commercial stability performance.

7 The effect of the ISO 105 CO9 laundering, with and without perborate, was to reduce the
8 surface nitrogen content. This reduction was marginally greater with the perborate/TAED
9 present in the wash formulation. However, at the 1% o.m.f. dye application level the
10 measured/detected XPS surface nitrogen concentrations are low (0.1-0.2% atomic nitrogen)
11 and accordingly it is difficult to be confident about any surface nitrogen content changes,
12 particularly as the colour analysis indicates little visual change.

13 **INSERT TABLE 2**

14 Examination of Table 3 indicates the effect of the ISO 105 CO9 treatment was to reduce the
15 colour strength and fabric lightness of the C. I. Reactive Red 228 dyed fabrics, in particular
16 the 1% o.m.f. application level exhibited a halving of the colour strength K/S value. At the
17 10% o.m.f. dye application level the higher concentration of dye “masks” the sensitivity of
18 the azo chromophore to the activated perborate/peracetic acid environment and the colour
19 change is less obvious. However the loss of surface nitrogen at the fibre/solution interface is
20 clearly greater following exposure to the more “aggressive” perborate/TAED environment
21 than the comparable non-oxidative treatment. Oakes [25] has previously reported that the
22 oxidative degradation of azo dyes leads to destruction of the chromophore and release of
23 gaseous nitrogen and benzene. This chemical modification to the dye would explain the

1 observed relatively greater loss of nitrogen from the fibre surface due to laundering under
2 activated oxidative conditions.

3 **INSERT TABLE 3**

4 Examination of Table 4 indicates the effect of the ISO 105 CO9 treatment, with
5 perborate/TAED, was to reduce the colour strength and increase the fabric lightness of the C.
6 I. Reactive Black 5 dyed fabrics. In particular the 1% o.m.f. application level exhibited a
7 halving of the colour strength K/S value, again confirming the sensitivity of the azo
8 chromophore to perborate/TAED laundering conditions. At the 10% o.m.f. dye application
9 levels the higher dye concentration “masks” the sensitivity of the azo chromophore to the
10 activated perborate/peracetic acid environment and the colour change, as indicated by K/S
11 and L^* was again relatively small, ~ 3 and 1.2, respectively.

12 However, examination of the XPS surface nitrogen content for the 1% o.m.f. C. I. Reactive
13 Black 5 dye application indicates again the activated bleaching conditions reduced the surface
14 nitrogen content of the fabric relative to the control fabric. Therefore it is surprising that with
15 the higher dye application levels, i.e. 5% and 10% o.m.f., comparable levels of surface
16 nitrogen were lost from the dyed fibre on exposure to both the oxidative and non-oxidative
17 washing environments. The reason for this behaviour is uncertain.

18 **INSERT TABLE 4**

19 ***3.2 Effect of Sequential Acid/Alkali/Peroxide Treatments on Dyed Cotton***

20 The initial study assessing the laundering stability of the typical reactive dyes on Lyocell
21 fabric highlighted that the anthraquinone-based dye was more resistant to activated bleaching
22 during domestic laundering of dyed Tencel fabrics relative to azo-based chromophoric dyes.
23 Similarly with the comparable reactive dyed cotton fabrics (4% o.m.f.) the Reactive Blue 19

1 dyed cotton exhibited the smallest change following ISO 105 CO9 laundering, Tables 2, 3
2 and 4. These observations have therefore demonstrated that most reactive dyes bound to
3 cellulosic materials are stable to chemicals used in domestic laundering detergents and that
4 complete removal of the colorants throughout the garment lifetime is unlikely. Although
5 some of the dyes are possibly being removed during the usage period, most dyes will remain
6 linked to the fibres at the end of the garment's usage. This suggests that colorants need to be
7 stripped from waste garments prior to reprocessing of the materials for new fibre
8 regeneration.

9 Previous studies on the removal of a commercial formaldehyde-based easy care finish
10 (Dimethylol Dihydroxyethylene Urea, DMDHEU) from uncoloured cotton indicated the
11 effectiveness of a sequential acid/alkali process and provided the chemical "stripping"
12 framework for this study [20, 21]. However, this study applied a more aggressive sequential
13 acid/alkali/peroxide stripping process in order to completely strip both colourants and any
14 crosslinks present on cellulosic material.

15 It is evident that following the complete sequential acid, alkali and peroxide treatments the
16 colour strength, K/S , of the reactive dyed cotton fabrics decreased dramatically, Figure 2. The
17 acid treatment had the least effect on the reactive dyed cotton fabrics indicating the stability
18 of the dye chromophore and the covalent bonding of the colorant to the cellulose to acidic
19 hydrolysis. However subsequent alkali treatment had a significant effect on the azo-based C.
20 I. Reactive Black 5 and C. I. Reactive Red 228 dyed cotton fabrics resulting in K/S values of
21 0.3 and 0.4, respectively, compared to the original K/S values of 29.7 and 26.0, respectively,
22 which highlights the chemical sensitivity of the azo-chromophore and the instability of the
23 covalently bound azo-based dyes to hot alkaline conditions. Further hydrogen peroxide
24 treatment stripped more dye from the C. I. Reactive Black 5 fabric resulting in a K/S of 0.04,
25 similar to that of the undyed cotton fabric. The treatment also stripped more dye from the C.

1 I. Reactive Red 228 dyed fabric resulting in a K/S of 0.1 which again demonstrates the
2 instability of the C. I. Reactive Red 228 azo dye to oxidative bleaching, despite the dye
3 having three reactive groups which potentially could offer better dye-fibre bonding.

4 **INSERT FIGURE 2**

5 The anthraquinone chromophore of the C. I. Reactive Blue 19 dye has previously been
6 reported to enhance the stability of the dye to acidic hydrolysis [26, 27] but in this study,
7 while only a small decrease in colour strength following acid treatment of the blue dyed
8 fabric was observed, no enhanced stability was observed relative to the azo-based dyes,
9 Figure 2. Nevertheless, while the subsequent alkali treatment substantially decreased the
10 colour strength from 22.9 to 9.7, this loss was not as great as observed for the other two azo-
11 based dyes studied. Further decreases in colour strength were achieved when the previously
12 acid/alkali treated fabrics were treated in the oxidative peroxide bleaching bath resulting in a
13 K/S of 4.2. However the relatively smaller decrease in the colour strength observed for the
14 Blue 19 dyed fabric again confirms the higher stability of the anthraquinone chromophore to
15 the combined acid/alkali hydrolytic reaction and oxidative bleaching conditions used in this
16 study. Furthermore the results confirms the less effectiveness of the acid/alkali/peroxide
17 treatments in stripping the anthraquinone-based reactive dye covalently bound to cotton.

18 Similar to the colour strength behaviour observed for the reactive dyed cotton fabrics
19 following sequential acid/alkali/peroxide treatments the observed lower fabric lightness, L^* ,
20 changes also reflects the greater stability of the anthraquinone chromophore and covalent
21 bonding of the reactive dye to the cotton fibre, Figure 3. These quantitative analyses are also
22 borne out by the visual assessment of the treated fabrics, Figure 4, and highlight that the
23 sequential acid/alkali/peroxide treatments will not be a totally effective commercial treatment
24 for producing a white cellulosic feedstock for Lyocell fibre regeneration. Indeed on the basis

1 of this oxidative stripping study it may well be considered whether anthraquinones are
2 excluded from the dyer's colour palette and alternative colorant systems used if a truly closed
3 loop approach is to be developed for extending the "working" lifetime of cellulosic fibres.

4

5 **INSERT FIGURE 3 AND FIGURE 4**

6 While the decolorisation of the dye chromophore is an important consideration in producing a
7 white feedstock for subsequent fibre regeneration, it is also important to recognise that
8 crosslinking of the cellulosic polymer by coloured reactive dyes and colourless easy care
9 finishes is also a key commercial factor. Crosslinking within the fibre reduces the cellulose
10 solubility in the NMMO processing solvent and accordingly reduces the efficiency and
11 commercial viability of the regeneration process. Therefore any proposed degradative
12 stripping process will have to address both issues and is likely to be most effective after
13 fabric deconstruction when the fibres are in an aqueous pulp form and the fibre surface area
14 and accessibility are maximised. The influence and optimisation of the combined stripping
15 treatments on the fibre colour, cellulose solvent solubility and subsequent fibre regeneration
16 will be the subject of a future publication.

17

18 **4. CONCLUSIONS**

19 XPS analyses of the surface of dyed Lyocell fabric has demonstrated the presence of the
20 reactive dyes within the outer 10 nm of the fibre. The XPS N(1s) photoelectron signal
21 increased in intensity with increasing dye application, but plateaus as the outer surface region
22 becomes saturated with dye at the higher application concentrations.

1 ISO 105 C09 treatment of the C. I. Reactive Blue 19 dyed Lyocell produced relatively little
2 colour change and surface nitrogen loss due to the oxidative stability of the anthraquinone
3 chromophore and the durability of the functional groups binding the dye to the cellulose. In
4 contrast the effect of the oxidative bleaching test on the C. I. Reactive Red 228 dyed fabric
5 was to reduce the colour strength and surface nitrogen at all application levels due to the
6 chemical sensitivity of the azo chromophore to activated bleaching conditions. In contrast the
7 effect of bleaching on the C. I. Reactive Black 5 dyed fabric at 1% o.m.f. application level
8 was to reduce colour strength, increase fabric lightness L^* and decrease the surface nitrogen
9 content. However surprisingly at the 10% o.m.f. dye application level there was relatively
10 little colour change and surface nitrogen content loss following oxidative bleaching, the
11 reason at present being uncertain.

12 This study has demonstrated that reactive dyed Lyocell is relatively stable to oxidative
13 laundering formulations and that dye will still be bound to the fibres at the end of the
14 garment's wear lifetime. A sequential acid/alkali/peroxide treatment was investigated as a
15 route to stripping all reactive dyes from Lyocell in order to obtain a white feedstock for new
16 fibre regeneration. However despite the aggressive nature of the combined treatments the
17 anthraquinone-based C. I. Reactive Blue 19 was still more resistant to chemical stripping than
18 the azo-based Reactive dyes covalently bound to Lyocell. Therefore in any potential of
19 recycling of waste cellulosic garments through fibre regeneration a more effective stripping
20 sequence will be necessary to completely remove all colorants and easy care finishes from
21 first life, waste cellulosic garments.

22

23

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5

6

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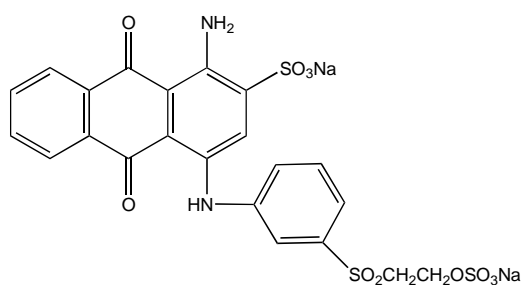
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1 Figure 1 Structures of Reactive Dyes used in Study

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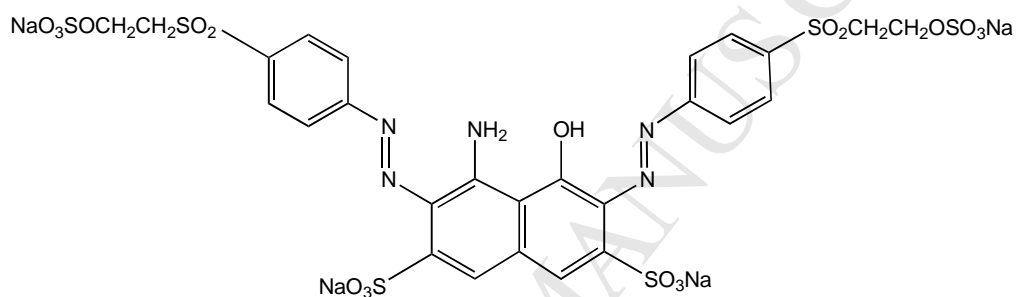


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C. I. Reactive Blue 19

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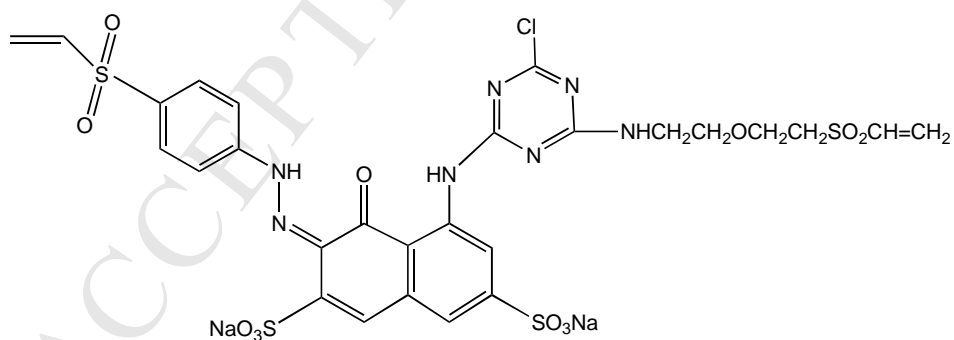
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C. I. Reactive Black 5

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C. I. Reactive Red 228

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1 Table 1. The Exhaustion, Fixation and Nitrogen Content of Reactive Dyes at the Surface and
 2 within the Bulk of Dyed Lyocell Fabrics.

% o.m.f. Reactive Dye Applied to Fabric	Actual % o.m.f. of Dye Bound to Fabric	Calculated Dye Nitrogen on Fibre, % o.m.f.	XPS Surface Atomic Nitrogen Content, %
C.I. Reactive Blue 19 (5.6% N Atomic Composition)			
1	0.6	0.03	0.2
5	2.3	0.13	0.5
10	3.4	0.19	1.2
C.I. Reactive Black 5 (9.5% N Atomic Composition)			
1	0.8	0.08	0.8
5	2.5	0.24	1.5
10	5.7	0.54	2.1
C. I. Reactive Red 228 (11.7% N Atomic Composition)			
1	0.6	0.07	0.9
5	3.0	0.35	1.5
10	4.8	0.56	2.6

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1 Table 2. Effect of ISO 105 CO9 Laundering Conditions, with and without Perborate, on the
 2 Surface XPS Atomic Nitrogen Composition, Colour Strength and Lightness of C. I. Reactive
 3 Blue 19 Dyed Lyocell Fabric.

Sample Treatment	Atomic N(1s) Composition (%)	<i>K/S</i>	<i>L*</i>
1% o.m.f. Dye Applied, (0.6%) [#]	0.2	6.1	45.7
1% o.m.f. Dyed Fabric Control Wash*	0.2	5.4	47.5
1% o.m.f. Dyed Fabric CO9 Wash ⁺	0.1	5.7	46.5
5% o.m.f. Dye Applied, (2.3%) [#]	0.5	19.2	29.4
5% o.m.f. Dyed Fabric Control Wash*	0.6	17.7	30.5
5% o.m.f. Dyed Fabric CO9 Wash ⁺	0.5	16.6	31.3
10% o.m.f. Dye Applied, (3.4%) [#]	1.2	20.4	27.6
10% o.m.f. Dyed Fabric Control Wash*	1.1	19.1	28.1
10% o.m.f. Dyed Fabric CO9 Wash ⁺	0.9	18.0	28.9
4% o.m.f. Reactive Dyed Cotton Fabric			
Dyed Cotton Fabric	-	22.9	27.2
CO9 Control Washed*	-	22.0	27.5
CO9 Washed ⁺	-	22.5	27.4

4

5 [#] Actual amount of reactive dye bound to fabric.

6 * ISO 105 CO9 Washing with ECE Detergent only (without Perborate and TAED).

7 ⁺ ISO 105 CO9 Washing with ECE Detergent, Perborate and TAED.

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1 Table 3. Effect of ISO 105 CO9 Laundering Conditions, with and without Perborate, on the
 2 Surface XPS Atomic Composition and Colour of C. I. Reactive Red 228 Dyed Lyocell
 3 Fabric.

Sample Treatment	Atomic N (1s) Composition (%)	<i>K/S</i>	<i>L*</i>
1% o.m.f. Dye Applied, (0.6%) [#]	0.9	12.4	43.0
1% o.m.f. Dyed Fabric Control Wash*	0.7	10.8	44.4
1% o.m.f. Dyed Fabric CO9 Wash ⁺	0.4	5.8	50.3
5% o.m.f. Dye Applied, (3.0%) [#]	1.5	25.5	32.4
5% o.m.f. Dyed Fabric Control Wash*	1.0	24.9	32.5
5% o.m.f. Dyed Fabric CO9 Wash ⁺	0.8	19.5	35.8
10% o.m.f. Dye Applied, (4.8%) [#]	2.6	26.7	29.7
10% o.m.f. Dyed Fabric Control Wash*	1.9	23.3	30.9
10% o.m.f. Dyed Fabric CO9 Wash ⁺	1.1	22.1	32.5
4% o.m.f. Reactive Dyed Cotton Fabric			
Dyed Cotton Fabric	-	26.0	35.3
CO9 Control Washed*	-	24.7	36.4
CO9 Washed ⁺	-	17.5	39.5

4

5 [#] Actual amount of reactive dye bound to fabric.

6 * ISO 105 CO9 Washing with ECE Detergent only (without Perborate and TAED).

7 ⁺ ISO 105 CO9 Washing with ECE Detergent, Perborate and TAED.

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1 Table 4. Effect of ISO 105 CO9 Laundering Conditions, with and without Perborate, on the
 2 Surface XPS Atomic Nitrogen Composition, Colour Strength and Lightness of C. I. Reactive
 3 Black 5 Dyed Lyocell Fabric.

Sample Treatment	Atomic N (1s) Composition (%)	<i>K/S</i>	<i>L*</i>
1% o.m.f. Dye Applied, (0.8%) [#]	0.8	15.5	27.3
1% o.m.f. Dyed Fabric Control Wash*	0.9	13.0	29.2
1% o.m.f. Dyed Fabric CO9 Wash ⁺	0.5	8.2	33.2
5% o.m.f. Dye Applied, (2.5%) [#]	1.5	27.6	15.7
5% o.m.f. Dyed Fabric Control Wash*	1.3	23.2	17.9
5% o.m.f. Dyed Fabric CO9 Wash ⁺	1.3	21.5	18.4
10% o.m.f. Dye Applied, (5.7%) [#]	2.1	27.9	14.8
10% o.m.f. Dyed Fabric Control Wash*	2.1	24.8	16.0
10% o.m.f. Dyed Fabric CO9 Wash ⁺	2.1	24.5	16.3
4% o.m.f. Reactive Dyed Cotton Fabric			
Dyed Cotton Fabric	-	29.7	15.4
CO9 Control Washed*	-	28.1	15.4
CO9 Washed ⁺	-	27.6	16.3

4

5 [#]Actual amount of reactive dye bound to fabric.

6 * ISO 105 CO9 Washing with ECE Detergent only (without Perborate and TAED).

7 ⁺ ISO 105 CO9 Washing with ECE Detergent, Perborate and TAED.

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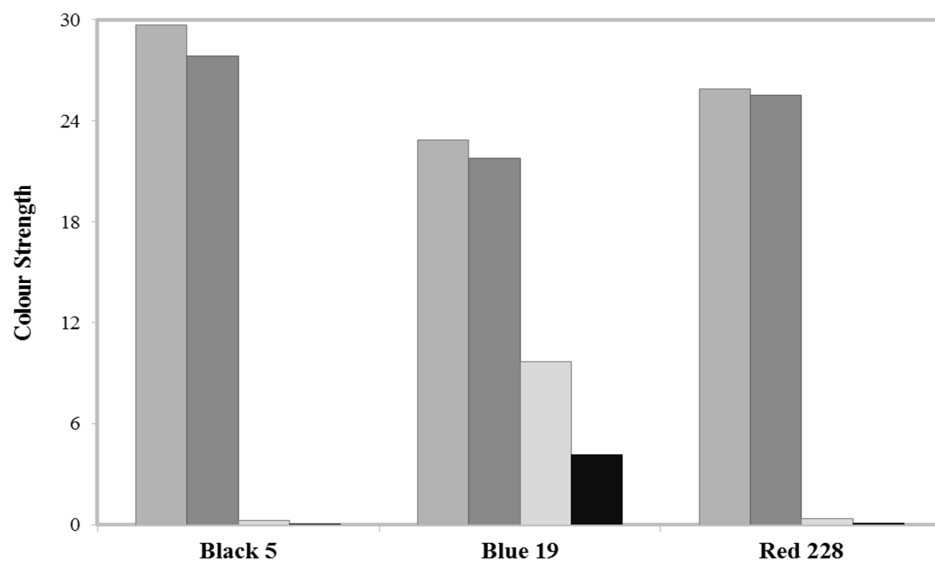
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1 Figure 2. Colour Strength, *K/S*, of Reactive Dyed (4% o.m.f.) Cotton Fabric Treated with
2 Sequential Acid/Alkali/Peroxide Solutions. □ Original dyed fabric; ■ Acid treated fabric;
3 □ Acid/Alkali treated fabric; ■ Acid/Alkali/Peroxide treated fabric.

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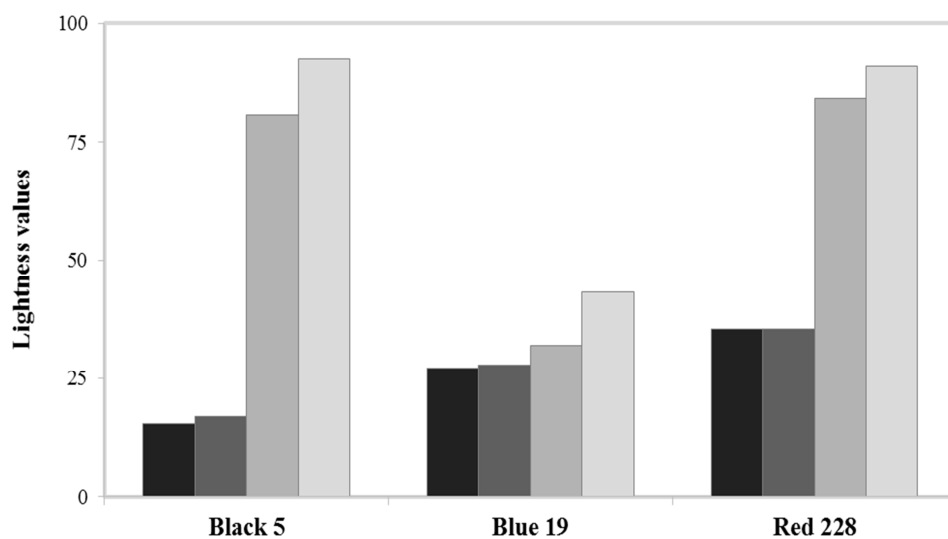
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1 Figure 3. Lightness, L^* , of Reactive Dyed (4% o.m.f.) Cotton Fabric Treated with Sequential
2 Acid/Alkali/Peroxide Solutions. ■ Original dyed fabric; ■ Acid treated fabric; □ Acid/Alkali
3 treated fabric; □ Acid/Alkali/Peroxide treated fabric.

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1 Figure 4. Colour of Reactively Dyed Cotton Fabrics Following Stripping with Sequential
2 Acid/Alkali/Peroxide Solutions.

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Colorant	Dyed fabric	Acid treated	Acid/Alkali treated	Acid/Alkali/Peroxide	Undyed fabric
Reactive Black 5					
Reactive Blue 19					
Reactive Red 228					

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- Effect of oxidative bleaching on reactive dyed cellulosic surfaces and colour was evaluated.
- The anthraquinone dye chromophore was more stable to chemical degradation than the azo dye chromophore.
- Reactive dyes will typically be present on cellulosic fibres at the end of a garments “first lifetime” usage.
- Combined acid, alkali and peroxide treatment decolourised azo-based reactive dyed cellulosic fibres but anthraquinone-based dyes were more resistant.
- The impact of reactive dyes on the potential recycling of “white” waste cellulosic feedstock and new fibre regeneration was explored.