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Surface chemical analysis of Tencel treated with a cationic fixing agent

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The nature and wash durability of the cationic fixing agent Matexil FC-ER applied to Tencel fabric, at pH 6 and 11, respectively, was investigated by X-ray Photoelectron Spectroscopy (XPS). The N(1s) XPS spectrum of the Matexil FC-ER film indicated that the concentration of uncharged and quaternary nitrogen species was in the ratio of 5:1. For both pH 6 and pH 11 applications, the surface concentration of the cationic fixative appeared to be independent of pH and the relative proportion of cationic nitrogen relative to the original film, increased at the fibre surface. The ISO 105 CO6/C2S wash test removes the uncharged nitrogen from the fibre surface leaving only the cationic nitrogen species. The surface Matexil FC-ER was durable to washing, while in contrast a direct dye applied to the Tencel fibre was not. Combination with the cationic fixing agent increased the fastness of the dye at the Tencel fibre surface. © *2003 Kluwer Academic Publishers*

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1. Introduction

Direct dyes applied to cellulosic fibres, in general, have poor wash fastness due to the dye being bound to the fibre by physico-chemical forces such as van der Waals forces, dispersion forces, ionic interaction, hydrogen bonding and hydrophobic interactions which are relatively weak and reversible [1, 2]. As a result of this comparatively poor wash fastness, a variety of processes have been developed to improve the wash fastness of direct dyes on cellulosic substrates [3]. Traditionally the fixing agents have been based on formaldehyde but more recently chemical manufacturers have been promoting formaldehyde-free cationic polymers to improve the wet fastness ratings. The cationic fixing agents contain quaternary ammonium species that complex with the dye anion inside the fibre reducing its aqueous solubility and thereby improving the wash fastness rating [3]. While the non-reactive cationic fixing agents do improve the initial wash fastness, their long-term durability/performance is less clear, with a previous study [4] suggesting that the effect can be lost after one or two domestic washings.

In this study the fibre surface/interface is examined in order to monitor the deposition and interaction of the fixing agent and any subsequent loss due to laundering. Since the fibre surface is most sensitive to any 'aggressive' environment it can provide a valuable insight into the washing process.

The X-ray Photoelectron Spectroscopy (XPS) technique has been used to characterise the nature of the surface species, in particular the outer 3–5 nm, present on Tencel fibres treated with the cationic fixing agent, Matexil FC-ER. The technique involves measuring the kinetic energy of the photoelectrons that are emitted from the outermost layers of the fibres during exposure to an X-ray source [5]. The characteristic binding energies (BE) of the photoelectrons allows identification of the emitting atoms, their chemical environment and oxidation state. In addition, measurement of the spectral peak areas leads to quantitative information about the surface composition of the fibres.

2. Experimental

2.1. Fabric

Tencel fabric was kindly donated by Acordis Holdings, UK. The Tencel fabric was further washed twice in deionised water at 90°C for 20 min and then extracted in acetone, rinsed in deionised water and air-dried.

2.2. Dye

The direct dye Sirius Blue S-BRR (C.I Direct Blue 71) was kindly supplied by Dystar, UK, and used without any purification.

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2.3. Detergent

The ECE (phosphate-based) reference detergent and multifibre test fabric used in the ISO 105 CO6/C2S test protocol was purchased from the Society of Dyers and Colourists, Bradford, UK.

2.4. Cationic fixing agent

Matexil FC-ER was kindly donated by Uniqema, UK.

2.5. Sample preparation

A reference film of Matexil FC-ER was produced by partly immersing a clean, scalpel blade in the Matexil FC-ER solution and placing a few drops onto aluminium foil. Using the blade, the drop was spread into a thin film and left to air dry for about one hour.

2.6. XPS technique and instrumentation

XPS measurements were performed with a Surface Science Instruments (SSI) M-Probe Spectrometer operating at a base pressure of 3×10^{-9} torr. The samples were irradiated with monochromatic Al K_α X-rays (1486.6 eV) using an elliptical X-ray spot size of $1000\ \mu m \times 400\ \mu m$ and $\sim$180 W power. The survey spectra were recorded with a pass energy of 150 eV, from which the surface chemical compositions were determined. In addition, high resolution carbon and nitrogen spectra were recorded with a pass energy of 25 eV, from which the chemical states of those elements were determined.

Where nitrogen levels were close to the detection limits, extended acquisition time narrow scan spectra were recorded with a pass energy of 150 eV (lowest resolution, highest sensitivity). Charge compensation for electrically insulating specimens was achieved using a beam of $\sim$4 to 9 eV electrons at a flood gun current of $\sim$0.1 mA with an electrically grounded 90% transmission nickel mesh screen positioned $\sim$1.0 mm above the sample surfaces. The standard electron take off angle used for analysis was 35° giving a maximum analysis depth in the range of 3–5 nm.

2.7. Application of direct dye and Matexil FC-ER

The Tencel fabric was introduced into the dyebath containing 2% on mass of fabric (o.m.f.) Sirius Blue S-BRR (CI Direct Blue 71) and 5 g/l Glauber's salt, at 25°C and a fabric to liquor ratio of 1:20. The temperature was raised to 80°C at 2°C/min and the remaining electrolyte added over a period of 15 min. The dyebath was then raised to 100°C and dyeing continued for a further 30 min. The dyed sample was then rinsed under running tap water for 15 min, washed with deionised water and air-dried.

Matexil FC-ER was subsequently applied to dyed and control undyed Tencel fabric at pH 6 and pH 11, the treatment bath pH being adjusted to 6 and 11 by using potassium dihydrogen phosphate and sodium carbonate solutions, respectively. The application bath was set at 40°C and the dyed and undyed Tencel was treated for 30 min with a fabric to liquor ratio of 1:10. The fabric was then cold-rinsed under tap water for 10 min and air-dried.

2.8. ISO 105 CO6/C2S test

The fabric samples, 10 cm × 4 cm, were sewn to a similar-sized multifibre test fabric which consisted of secondary cellulose acetate, cotton, nylon 6.6, polyester, acrylic and wool.

The detergent solution was prepared as recommended with 4.0 g of ECE (phosphate-based) reference detergent being dissolved in 1000 ml of de-ionised water. Prior to use, 1.0 g of sodium perborate tetrahydrate was added to the detergent solution and the pH adjusted to 10.5, if necessary, by adding solid sodium carbonate.

50 ml of the detergent solution was transferred to a stainless steel pot along with 25 steel balls and the fabric swatch. The pot was rotated in a Washtec-P machine (Roaches) at 40 revolutions per minute, 60°C, for 30 min. At the end of the wash cycle, the spent detergent liquor was discarded and the fabric swatch washed thoroughly in running cold water and de-ionised water, respectively, and air-dried prior to ranking.

3. Results and discussion

The regenerated cellulosic fibre, Tencel, was used as a substrate for dyeing and for XPS analyses as it is free of natural impurities such as nitrogen-based proteins, pectins and waxes usually associated with cotton. Matexil FC-ER is a non-reactive cationic fixative manufactured by the cyclo-polymerisation of diallyl dimethyl ammonium chloride via free radical initiation, Fig. 1. Electron spin resonance spectroscopy and C^{13} NMR spectroscopy have confirmed that the polymer consists of a 5:1 ratio of five-membered pyrrolidone rings to six-membered piperidine rings [6].

In the N(1s) XPS spectrum, nitrogen bound to carbon in primary, secondary or tertiary amines or amides, typically occur at B.E values of 399–400 eV whereas cationic quaternary ammonium nitrogen species are shifted to a higher B.E value of 401.5–402.5 eV [5]. The N(1s) XPS spectrum of a Matexil FC-ER film indicates

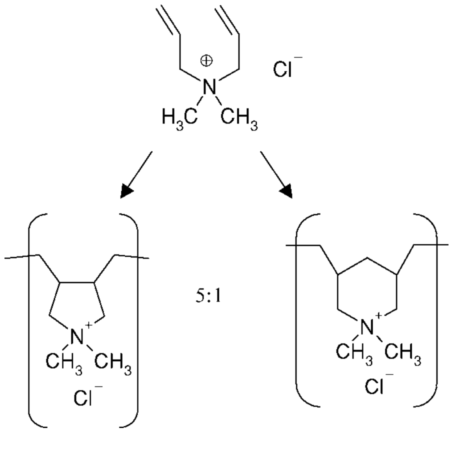

Figure 1 Proposed structural components of Matexil FC-ER.

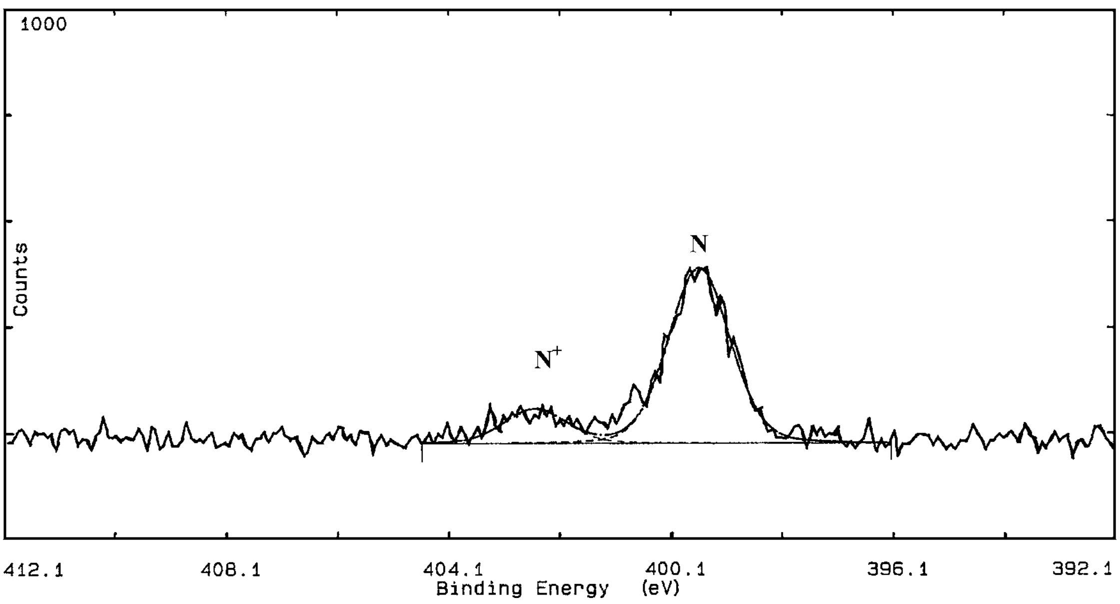

Figure 2 N (1s) XPS spectrum of Matexil FC-ER film.

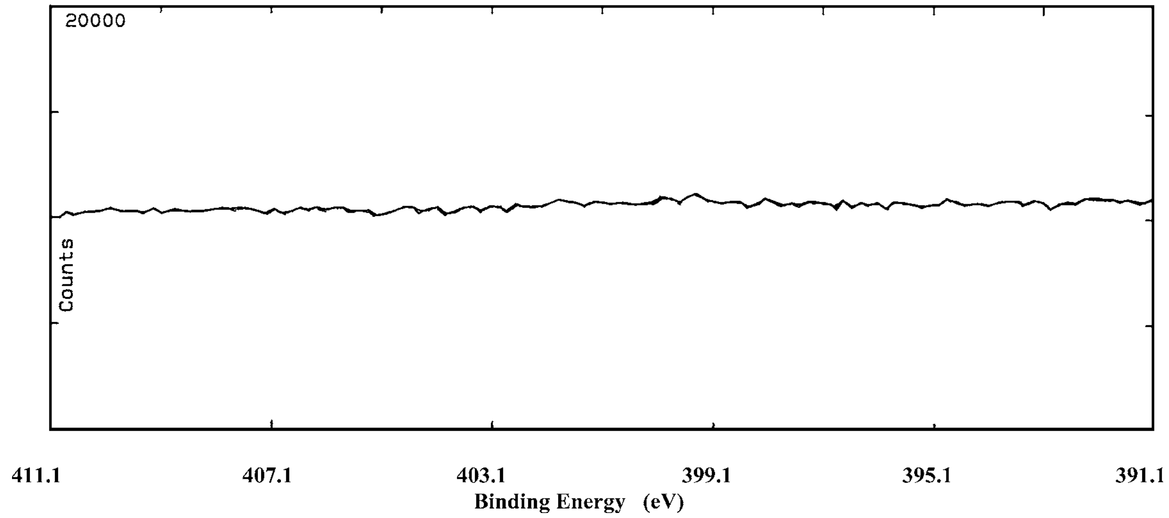

Figure 3 N (1s) XPS spectrum of Tencel fabric.

the presence of both "uncharged" and "charged" quaternary nitrogen species, their relative concentrations being approximately 83 and 17%, respectively, Fig. 2. The commercial product has a surprisingly high content of uncharged nitrogen species either due to contamination or possibly due to undesired free-radical side-reactions occurring during the cyclo-polymerisation. These uncharged nitrogen species may be part of the polymer backbone itself or distinct uncharged moieties. The N(1s) XPS spectrum of the acetone-extracted and water washed Tencel revealed that nitrogen signals were absent from the fibre surface, Fig. 3.

In the initial preliminary experiments the concentration of Matexil FC-ER applied was the commercially recommended 4% o.m.f. level at pH 6. However, the XPS analysis of the N(1s) region detected only very weak nitrogen signals, (detection limit is estimated to be ∼0.1 atomic %). To improve the nitrogen detection and spectral quality the application level was raised to 10% and 20% o.m.f. at pH 6. At the 10% o.m.f. application level the surface nitrogen content was 0.7 atomic %, and for the 20% o.m.f. application level, Fig. 4, the surface nitrogen content was also 0.7 atomic %. With all three application levels the relative concentrations of uncharged nitrogen, at a BE of 400 eV, to cationic nitrogen, BE of 402.5 eV, was approximately 45%:55%. This relative increase in the cationic component will be related to the charged species having greater substantivity for the fibre.

A previous study has reported the application of Matexil FC-ER at pH 11 improved the wash fastness of the dyed material probably due to the increased exhaustion/substantivity of the cationic polymer onto the more ionised cellulosic substrate and greater dye/fixative interactions [3]. However, in this study little increase in the nitrogen surface content was observed for the application levels at pH 11 or in the relative proportion of charged and uncharged nitrogen.

Renfrew [7] has reported that the quantity of bound cationic fixative was almost independent of parameters such as time, temperature and pH, with the surface concentration limited mostly by agent-agent repulsion. In

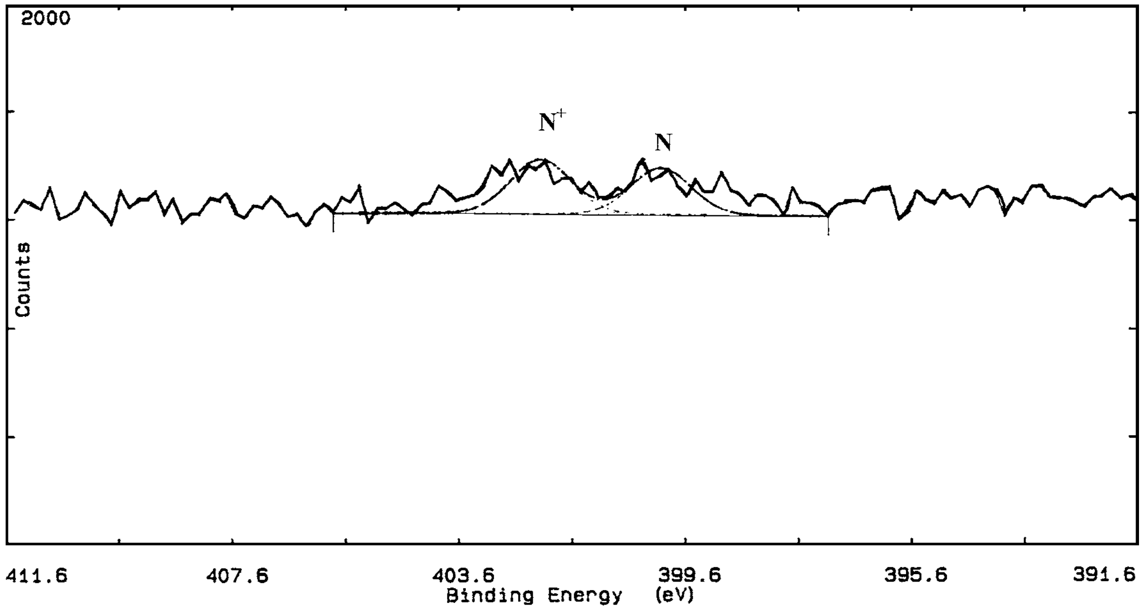

Figure 4 N (1s) XPS spectrum of Matexil FC-ER treated (20%) o.m.f. pH 6) undyed Tencel.

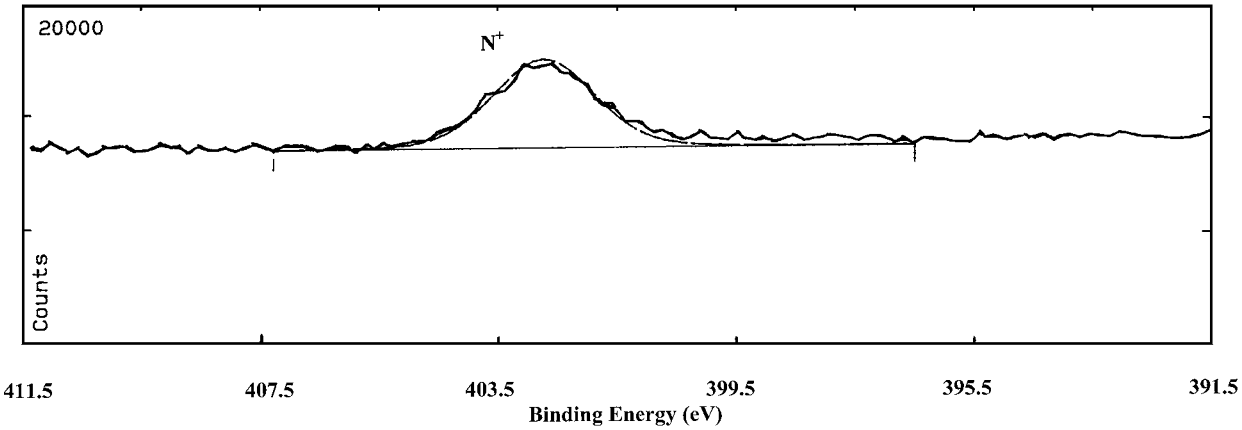

Figure 5 N (1s) XPS spectrum of Matexil FC-ER treated (20% o.m.f. pH 6) undyed Tencel, washed ×3.

addition, at pH 11, there is a potential risk of shade changes for some cellulosic dyes when after-treated in alkaline media as a result of nucleophilic attack on the dye-fibre system. Therefore, the slight improvement in wash fastness rating may be assigned to removal of surface dye rather than greater interaction between dye and fixative [8].

With any non-covalently bound textile fibre dye fixative its durability to washing is always debatable, particularly at the fibre surface. The effect of washing after both one cycle and three cycles was to remove the uncharged nitrogen containing species and leave only the charged nitrogen containing polymeric species at the fibre surface, Fig. 5. It is also possible the alkaline cleaning conditions and the oxidative nature of the detergent formulation produces further degradation of the cationic polymer leading to loss of polymer after conversion to a less substantive uncharged polymeric form. Nevertheless, it is evident that after the washing action the polymeric surface nitrogen species is more obvious and has increased in surface concentration, 1.4 atomic %, possibly due to surface fibrillation revealing the polymer in the fibre sub-surface. Further washing to three cycles reduces the surface nitrogen content to 1.0 atomic % nitrogen. Comparable washing experiments for pH 11 Matexil FC-ER treated Tencel again showed an initial increase in surface nitrogen to 1.5 atomic %, followed by a decrease to 1.0 atomic % after three wash cycles.

Previously Sugdon [9] has similarly reported potential degradation of Matexil FC-ER and conversion of the cationic nitrogen into an uncharged nitrogen during alkaline laundering, Fig. 6.

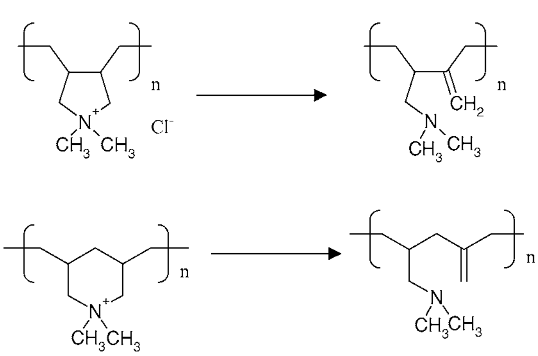

Figure 6 Possible charged and uncharged species in "Degraded" Matexil FC-ER polymer.

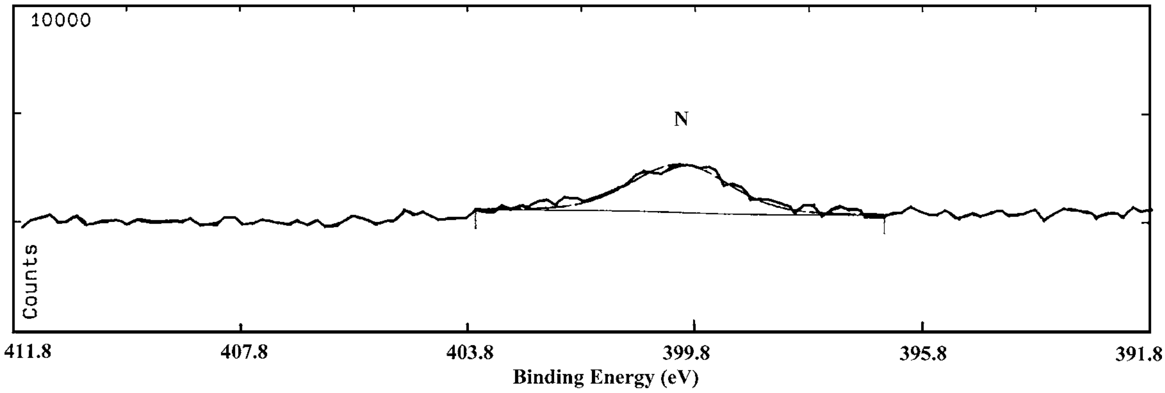

Figure 7 N (1s) XPS spectrum of dyed Tencel (2% o.m.f. Sirius Blue S-BRR).

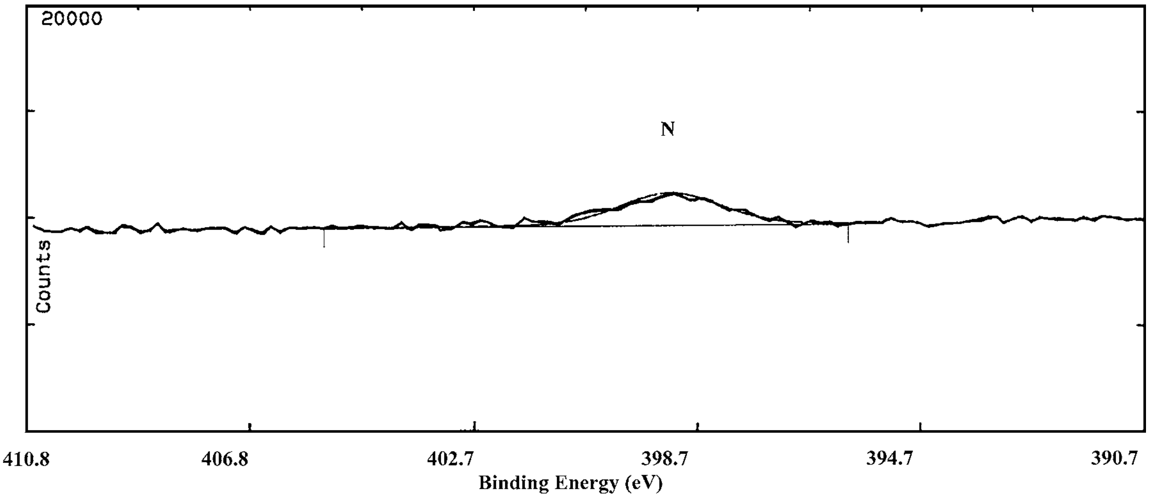

Figure 8 N (1s) XPS spectrum of dyed Tencel (2% o.m.f. Sirius Blue S-BRR), washed ×1.

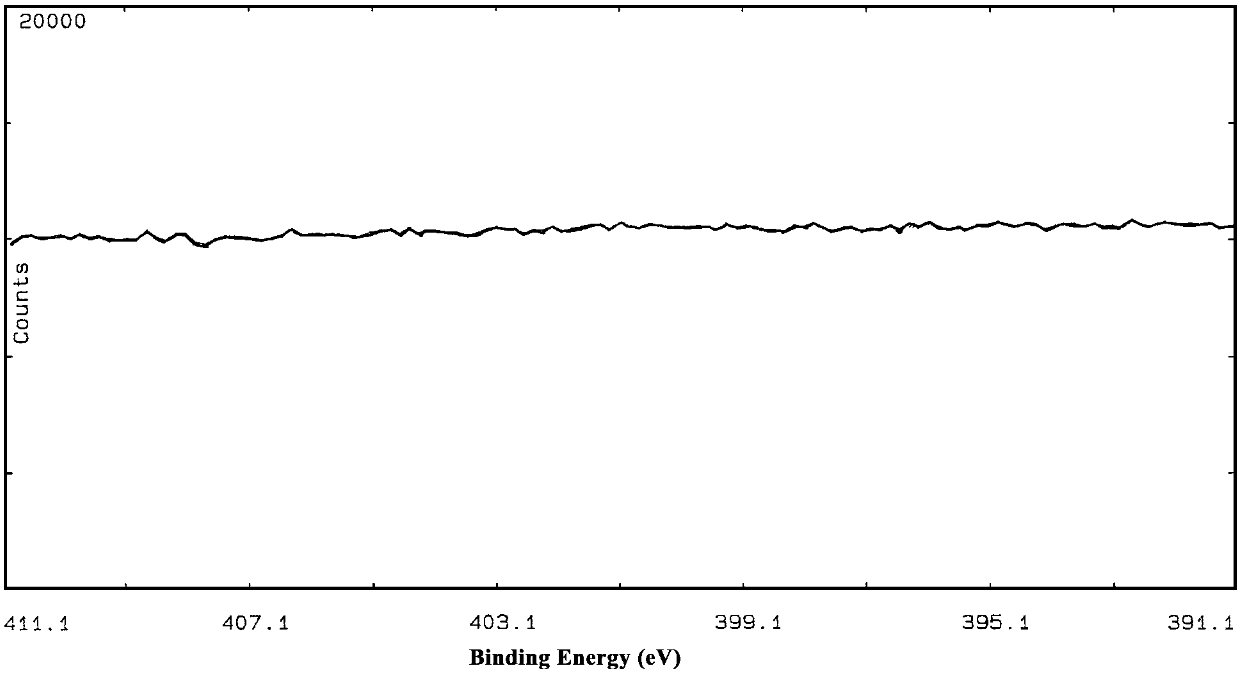

Figure 9 N (1s) XPS spectrum of dyed Tencel (2% o.m.f. Sirius Blue S-BRR), washed ×3.

The effect of dyeing with a direct dye was to impart an obvious colouration to the Tencel, but in addition also produced an increase in intensity at a BE of 400 eV in the N(1s) XPS spectrum, 0.5 atomic %, of the 2% o.m.f. Sirius Blue S-BRR dyed fabric, Fig. 7. The uncharged nitrogen signal can be assigned to the dye molecule. The effect of repeated laundering was to progressively reduce the surface nitrogen from the dye due to the relatively poor affinity of the direct dye, Figs 8 and 9. Moreover, since XPS is primarily a surface analysis

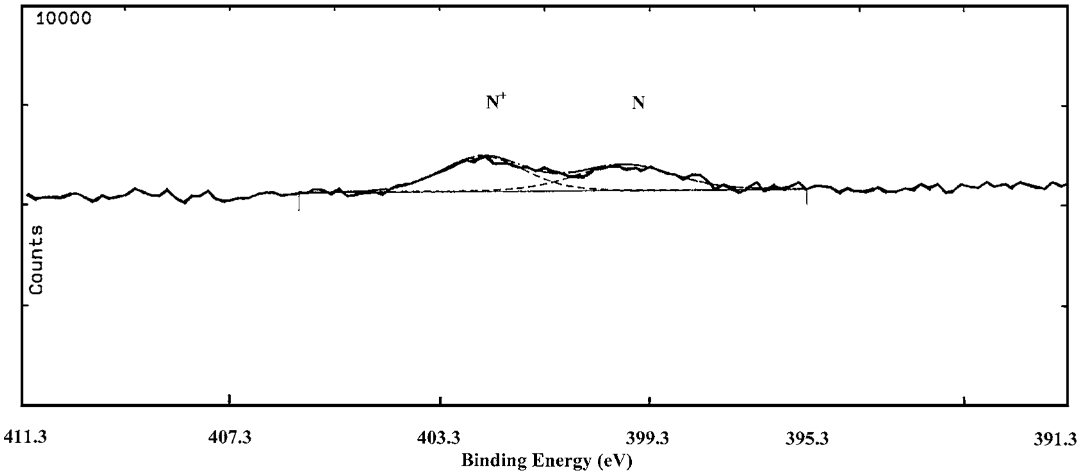

Figure 10 N (1s) XPS spectrum of dyed Tencel (2% o.m.f. Sirius Blue S-BRR) and 20% o.m.f. Matexil FC-ER (pH 6).

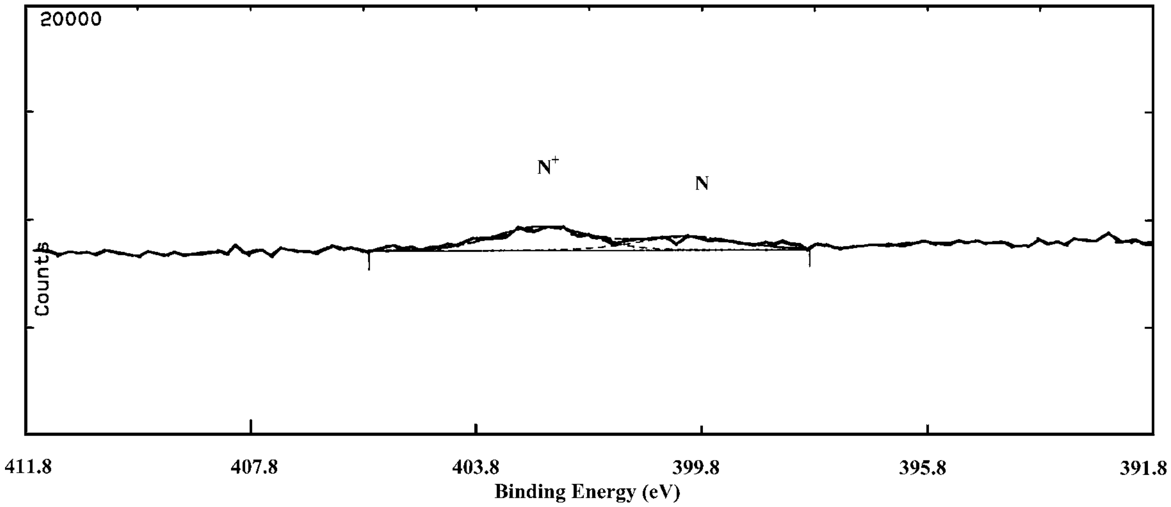

Figure 11 N (1s) spectrum of dyed Tencel, aftertreated with 20% o.m.f. Matexil FC-ER, washed ×3.

technique probing the outer 3–5 nm of the fibre, it may be that the fibrillation of the Tencel accelerated the surface dye loss due to increased accessibility. Ultimately no surface nitrogen signal was detected although the sample still remained visually coloured. The propensity of Tencel to wet fibrillate under mechanical action has been widely reported in the literature, together with the associated colour loss during the laundering process [10].

The purpose of the cationic fixing agent was to reduce the colour loss during washing and hence extend the lifetime of the garment. Examination of the N(1s) XPS spectrum of the direct dyed and cationic aftertreated Tencel indicates surface nitrogen intensity, 0.6 atomic %, which can be assigned to the uncharged, dye nitrogen, at a BE of 400 eV, and the cationic Matexil FC-ER, at a BE of 402.5 eV, Fig. 10. The effect of repeated laundering was to reduce the surface nitrogen intensity, but even after three wash cycles the dye nitrogen and the Matexil FC-ER nitrogen can still be clearly demonstrated, Fig. 11. In addition to the electrostatic attraction between the dye sulphonate functionalities and polymer cationic charges, other forces such as van der Waals and hydrophobic bonding may increase dye insolubilisation leading to the observed improvements in dye wash fastness.

4. Conclusions

X-ray Photoelectron Spectroscopy has successfully investigated the nature and wash durability of the cationic dye fixative Matexil FC-ER. Surprisingly, the commercial product has a relatively low content of charged nitrogen species with the major uncharged nitrogen species either being part of the overall positively charged polymer or distinct moieties. Only the strongly cationic segments of the polymer proved to be durable to repeated washings on undyed Tencel while the uncharged nitrogen was lost due to a probable combination of poor affinity for the fibre and possible alkaline degradation. Initially washing produced an increase in surface nitrogen due to the wet fibrillation of the Tencel fibre surface revealing sub-surface nitrogen, but after three washes the surface nitrogen decreased.

The XPS technique successfully monitored the loss of dye nitrogen from the fibre surface. The cationic fixing agent, despite some nitrogen losses, retained dye at the fibre surface as both charged nitrogen from the fixative and uncharged dye nitrogen species were clearly detected even after three ISO 105 CO6/C2S washes. Dye complexation at the surface therefore led to the observed improved wash fastness of the dye.

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