

# Surface chemical analysis of 1,2,3,4-butanetetracarboxylic acid modified cotton

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Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and X-ray Photoelectron Spectroscopy (XPS) have been used to characterise butanetetracarboxylic acid (BTCA) powder and BTCA modified cotton fibre surface. The wash durability of crease resist BTCA finish at the cotton surface has been demonstrated and enhanced binding of sodium cations to the carboxyl rich fibre surface observed. Similarly increased affinity of copper ions to the polycarboxylic acid treated cotton was observed. Domestic laundering of the copper impregnated BTCA fabric in a perborate containing detergent produced increased strength loss relative to comparably laundered unmodified cotton and DMDHEU treated cotton fabric. © 2003 Kluwer Academic Publishers

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## 1. Introduction

The consumer has increasingly demanded garments manufactured to high specifications and performance. Associated with this quality performance has been the development of the “easy care” label for garments with their wrinkle free appearance, dimensional stability and ease of cleaning. For cellulosic-based materials, however, an inherent problem is their ease of creasing and poor crease shedding. To overcome this technical deficiency and introduce “memory” into the fibre/fabric structure, formaldehyde-based durable press (DP) reagents have been developed which introduce covalent crosslinks between the adjacent cellulosic chains [1–4]. These crosslinks introduce crease resistance and crease recovery into the fabric so that when the fibres, yarns and overall fabrics are distorted in use or during laundering, the fabric will return to its original flat or creased (creases or pleats) configuration when the crosslinks were originally introduced. Most commonly the DP finish is applied by a simple pad, dry, heat cure (160°–200°C) process to white or coloured fabric or garments, with the major formaldehyde-based DP reagent being 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU). However, while formaldehyde is relatively cheap and an effective crosslinking agent for cellulose and proteins, it is

also an irritant, mutagenic in certain bacterial and animal species and is classified as a probable human carcinogen [2, 5, 6]. Therefore exposure limits have been established in many countries and a concerted effort has been undertaken to develop formaldehyde-free DP finishing agents [4, 7]. One alternative development to emerge has been based on polycarboxylic and (PCA) systems where ester crosslinks rather than the ether-type crosslinks of DMDHEU are introduced to impart easy-care properties, Fig. 1. The best performing PCA system is 1,2,3,4-butanetetracarboxylic acid (BTCA), although citric, maleic, itaconic and polymaleic acid derivatives have all been evaluated in terms of performance, discolouration and cost [4].

In this study the effect of BTCA modification to the surface chemical behaviour of cotton, its subsequent laundering and metal ion interactions are investigated. To comprehensively probe these modifications Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and X-ray Photoelectron Spectroscopy (XPS) were utilised to study the fibre surface interface where the interaction with any “aggressive” media is greatest [8, 9]. The depth of analysis of these instrumental systems typically ranges from 1–10 nm and provides the necessary analytical flexibility to fully characterise the fibre surface.

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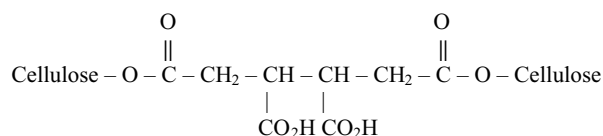


Figure 1 Typical crosslink introduced into cotton cellulose by esterification with BTCA.

The surface sensitive XPS technique allows the chemical species present at a fibre surface to be identified up to a depth of 3–10 nm. In XPS the diagnostic parameter is the electron binding energy (BE), which is determined (Equation 1) by measuring the kinetic energy (KE) of photoelectrons emitted by x-rays photons, of energy  $h\nu$ , impinging on the sample surface:

$$\text{KE} = h\nu - \text{BE} \quad (1)$$

The value of the binding energy is not only characteristic of the emitting atom (i.e. enables elemental identification) but also has a precise value, which is dependent on the chemical environment of that atom. In addition to providing qualitative information, by measuring the photoelectron peak intensity the surface composition can also be quantified.

ToF-SIMS is also a surface sensitive technique able to probe the outer 1–2 nm of materials. It involves bombarding the materials surface with a primary particle beam and analysing the emitted secondary ions. In addition to providing elemental information the technique is able to detect larger molecular species. Thus in combination with XPS comprehensive characterisation of fibre surfaces can be achieved.

## 2. Experimental

### 2.1. Materials

A plain woven, bleached, mercerised, 100% cotton fabric was used throughout this study and was supplied by Phoenix Calico Ltd., UK.

BTCA, sodium hypophosphite hydrate (SHP), copper sulphate pentahydrate and magnesium chloride hexahydrate were supplied by Aldrich Chemicals Ltd. The sodium hypophosphite and magnesium chloride were incorporated into the respective crease resist formulations as recommended catalysts to optimise fibre modification. Fixapret CPN was kindly donated by BASF and is a DMDHEU-based solution.

#### 2.1.1. Chemical treatment

The cotton fabric was padded at 90% wet pick up (w.p.u.) with a solution containing 8.0% BTCA and 4.1% SHP, dried at 85°C for 5 min, cured at 180°C for 90 sec, rinsed in running water and tumble dried. After further drying at 105°C for 1.5 h the fabric weight gain was determined to be 5.7% o.w.f.

The cotton fabric was padded at 80% w.p.u. with a solution containing 6.0% Fixapret CPN and 1.2%  $\text{MgCl}_2$ , dried at 100°C for 5 min and cured at 160°C for 4 min, rinsed in running water and tumble dried. After further drying at 105°C for 1.5 h the fabric weight gain was determined to be 2.7% o.w.f.

The treated fabrics were washed in a domestic washing machine using a standard cotton cycle at 60°C with an overall 1.5 kg load of cotton fabric. The detergent used was the standard ECE detergent with the recommended dosage of sodium perborate.

The untreated, Fixapret CPN and BTCA modified cotton fabrics were gently agitated in a 50 ppm  $\text{Cu}^{2+}$  solution, pH 7, at 30°C, for 20 min with a liquor:goods ratio of 30:1. The fabrics were then rinsed in excess water and air dried.

### 2.2. Instrumental analysis

The spectral reflectance of the cotton fabrics were measured using a Spectraflash spectrophotometer, with a 10° standard observer and D65 illuminant, and were the average of four measurements.

ToF-SIMS spectra were obtained under *static* conditions using a PHI 7000 instrument equipped with a reflectron analyser, a  $\text{Cs}^+$  ion source (8 eV, pulse length 1.25 ns) and a pulsed electron flood source (50–70 eV) for charge compensation. The operating pressure was less than 5.33  $\mu\text{Pa}$  ( $4 \times 10^{-8}$  torr), primary ion dose less than  $1 \times 10^{12}$  ions  $\text{cm}^{-2}$ , and an analysis area of 300  $\mu\text{m} \times 300 \mu\text{m}$  in the mass range  $m/z = 0$ –1000.

XPS spectra were obtained using an SSI M-Probe instrument. The samples were analysed with an  $\text{AlK}\alpha$  radiation source (1486.6 eV) with an operating pressure of better than  $3 \times 10^{-8}$  torr and the binding energy (BE) values calculated relative to the C (1s) photoelectron peak at 285.0 eV. The C (1s) spectral peaks were curve-fitted using the standard Gaussian-based software in order to determine carbon species functionality and concentration.

The surface analyses were typically performed in duplicate or triplicate to ensure reproducible sample surface modification over the treated textile.

### 2.3. Strength measurement

The cotton fabrics were conditioned for 24 h at 20°C and 65% RH prior to testing on an Instron Series IX testing system. The tensile strength losses of the unwashed and washed fabrics were determined as a percentage of the original unwashed fabrics and were an average of five measurements in the warp direction.

### 2.4. Crease recovery angle measurement

The crease recovery performances for the untreated fabric, BTCA modified fabric and DMDHEU modified fabric were determined according BS 3086 (1972) under standard atmospheric conditions of 65% R.H. and 20°C. The samples were conditioned for 24 h prior to testing. Ten samples were measured in the warp direction and ten in the weft direction. The value presented is the sum of the warp and weft values.

## 3. Results and discussion

### 3.1. ToF-SIMS analysis of BTCA powder

The parent molecule is observed in the ToF-SIMS negative ion spectrum together with the anhydride form and a range of sodiated and potassiated derivatives,

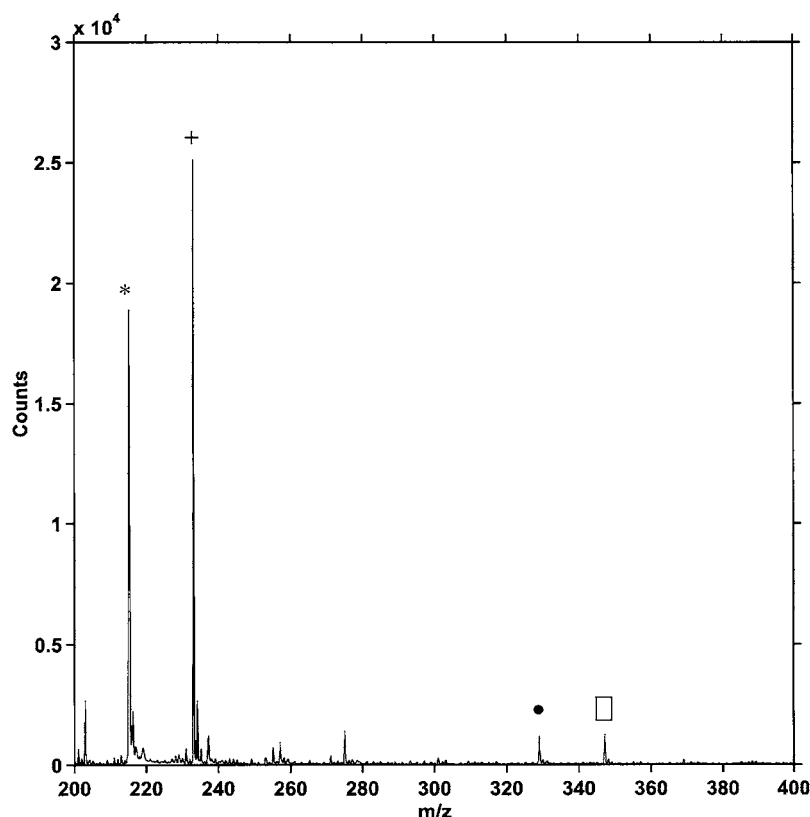


Figure 2 Negative ion ToF-SIMS spectrum of 1,2,3,4-Butanetetracarboxylic acid (BTCA).

Figs 2 and 3. During the reaction of BTCA with cotton cellulose it has been proposed that an acid anhydride intermediate is formed, by acid dehydration at elevated temperature, which then reacts with the cellulose hydroxyls to introduce the crosslinking necessary for durable press finishing [10, 11]. Therefore the detection of a strong anhydride species is probably a result

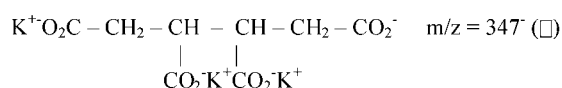
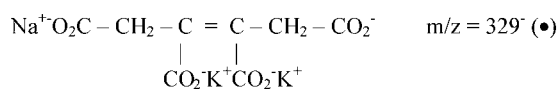
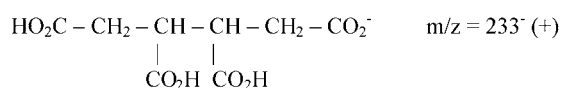
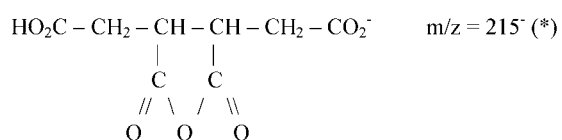


Figure 3 Negative ion assignments in the ToF-SIMS spectrum of BTCA powder.

of the low pressure analytical conditions favouring loss of water.

The positive ion ToF-SIMS spectrum of the BTCA powder shows strong signals for sodium and potassium at  $m/z = 23^+$  and  $39^+$ , respectively, in the lower mass range. In addition in the higher mass range the parent molecular ion and the acid anhydride ion were observed, Figs 4 and 5, together with a series of sodiated and potassiated species at  $m/z = 257^+$ ,  $273^+$ ,  $279^+$ ,  $295^+$ ,  $301^+$ ,  $311^+$ ,  $317^+$ ,  $323^+$ ,  $333^+$ ,  $339^+$  and  $349^+$ .

### 3.2. Modification of cotton with BTCA

The reaction of the polycarboxylic acid with cellulosic polymers occurs through esterification of the hydroxyl, Fig. 1, although not all the carboxylic acids will be able to react with the cellulosic substrate. Examination of the ToF-SIMS spectrum of BTCA modified cotton fabric indicates little change in the  $m/z = 100\text{--}400^{+/-}$  region suggesting the covalently bound BTCA preferentially fragments into smaller moieties during the primary ion sputtering. Similarly in the  $m/z = 0\text{--}100^{+/-}$  range although no “new” ion species could be detected, clear changes in the spectral intensities were observed, in particular the  $m/z = 45^-$  ion, assigned to a  $\text{HCO}_2^-$  ion showed an obvious increase. Quantification of ToF-SIMS data can present difficulties due to the relatively high proportion of neutral secondary particles produced in comparison to positive and negative secondary ions. However, previous ToF-SIMS studies have successfully monitored the relative surface changes on a number of organic systems using the formula  $I_A/(I_A + I_B)$ , where  $I_A$  and  $I_B$  are measured intensities of ions  $A$  and  $B$ , respectively [12–14]. For the calculations  $I_A$  corresponds

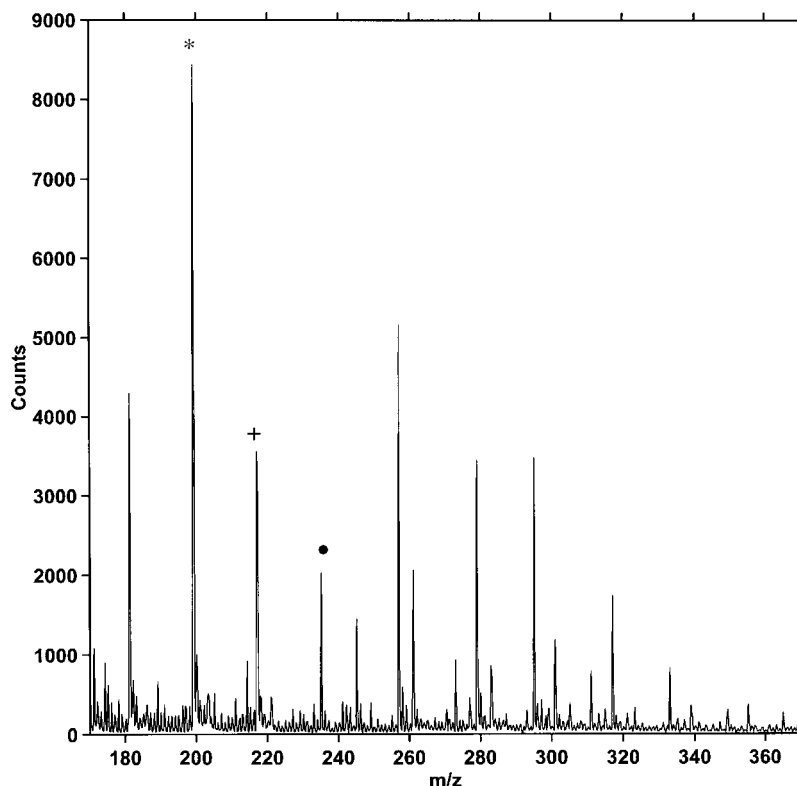


Figure 4 Positive ion ToF-SIMS spectrum of 1,2,3,4-Butanetetracarboxylic acid (BTCA).

to the peak intensity of the  $m/z = 45^-$  ion and  $I_B$  to the peak intensity of the signal at  $m/z = 25^-$  ( $\text{HC}_2^-$ ), a non-specific ion characteristic of organic surfaces, Table I. An alternative method of monitoring the surface carboxylic concentration involves determining the ratio of  $I_A$ / Total Ion Intensity. Again the overall relationship is that by incorporating BTCA into the cotton fibre the surface carboxylate intensity increases, Table I.

Although the ToF-SIMS spectrum of BTCA modified cotton exhibits no distinct characteristic large molecular ions attributable to BTCA, the XPS spectrum does however show an increase in the C (1s) spectrum at BE 289.0 eV, due to the incorporation of carboxyl species, Figs 6 and 7. Both the untreated and BTCA modified cotton show intensity at 286.6 eV which is attributable to the cellulosic C—O species. In addition spectral intensity at 285.0 eV and 288.0 eV can be observed and is assigned to hydrocarbon-based material, and either the expected O—C—O species or carbonyl species, respectively. The intensity ratio of the C—O species, at BE 286.6 eV, to the O—C—O species, at BE 288.0 eV, is approximately 5:1, which is the

same as the theoretical stoichiometric ratio of the cellulose polymer. However, there is an unexpectedly large C—C/C—H component intensity, at BE 285.0 eV, which has not been removed by wet processing and its nature will be discussed in further detail elsewhere [15].

### 3.3. Laundering of BTCA modified cotton

Under alkaline conditions aliphatic esters are susceptible to hydrolysis and therefore in general are of limited use in textiles. However, with the BTCA crosslinking of cotton not all the carboxylic acids are reacted and hence under alkaline conditions deprotonate to the negatively charged carboxylic anion. These are able to provide the necessary electrostatic repulsion of hydroxide ions in the vicinity of the labile ester groups and hence the crease resistant cotton has the necessary hydrolytic stability and durability to domestic alkaline laundering conditions.

Washing the untreated and BTCA modified cotton fabrics under domestic laundering conditions showed an obvious difference in the  $m/z = 0-100^+$  range, where the anionically charged BTCA modified sample has far greater sodium ion signal than the comparable untreated, washed cotton, Figs 8 and 9. This behaviour was observed after both 1 and 5 domestic

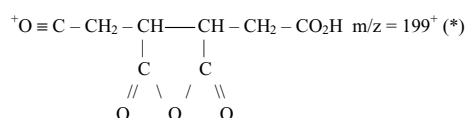


Figure 5 Positive ion assignments in the ToF-SIMS spectrum of BTCA powder.

TABLE I Relative carboxyl content at the surface of cotton materials (calculated from ToF-SIMS peak area data)

Sample	$\frac{I_A}{I_A+I_B} \times 100$	$\frac{I_A}{I_{\text{Total}}} \times 1000$
Untreated cotton	4.6	1.1
BTCA modified cotton	18.2	4.5

$I_A$ ,  $m/z = 45^-$ ,  $\text{HCO}_2^-$ .  
 $I_B$ ,  $m/z = 25^-$ ,  $\text{HC}_2^-$ .

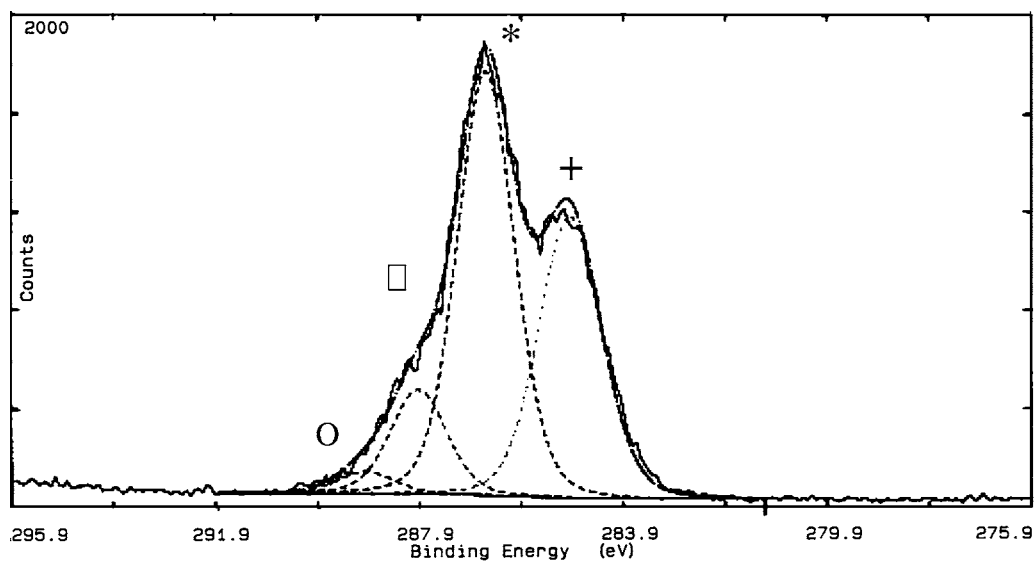


Figure 6 C(1s) XPS spectrum of untreated cotton fabric. (--- represents spectral curve fits with assigned peaks located at 285.0 eV (+), 286.6 eV (\*), 288.0 eV (□) and 289.0 eV (o), respectively).

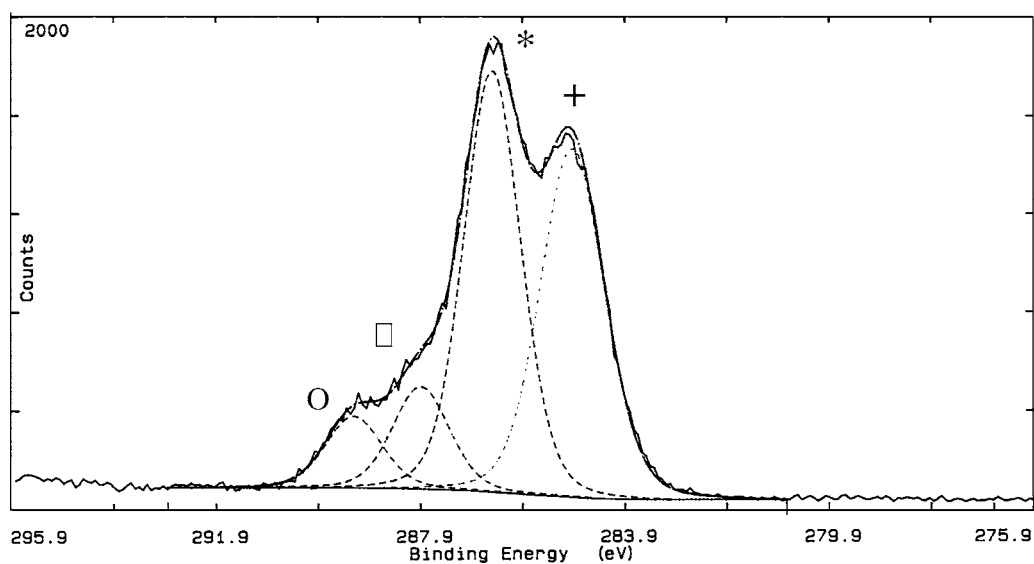


Figure 7 C(1s) XPS spectrum of BTCA modified cotton fabric (--- represents spectral curve fits with assigned peaks located at 285.0 eV (+), 286.6 eV (\*), 288.0 eV (□) and 289.0 eV (o), respectively).

wash cycles. Examination of the higher mass range of the ToF-SIMS positive and negative ion spectra of laundered cotton samples indicates other surface adsorbates are also present, however, their nature and behaviour will be discussed in greater detail elsewhere [16].

While the increased binding of the sodium ions to the BTCA modified cotton can be used as an indicator of increased surface carboxyl content, the XPS C(1s) spectrum of washed BTCA modified cotton indicates some loss in the carboxyl signal contribution to the total carbon 1s signal intensity. In the unmodified cotton the carboxyl signal contribution to the overall C(1s) intensity is 2.5% while for the BTCA modified cotton and washed ( $\times 5$  cycles) BTCA modified cotton, the carboxyl contribution to the C(1s) peak are 7.2% and 3.8%, respectively. This apparent partial loss may be due to the presence of overlying surface adsorbates and/or actual loss of BTCA due to the “exposed” nature of the BTCA ester linkages at the fibre/ liquid interface.

A standard test to evaluate the “easy care” performance of cotton-based fabrics involves measuring the crease recovery angle of a folded fabric swatch, 5 min after removing the deforming load, and its return to a flat, crease-free form. The application of the BTCA finish to the original cotton fabric raised the crease recovery angle (combined warp and weft values) from  $162^\circ$  to  $254^\circ$ . After the five wash cycles the crease recovery angle of the BTCA-treated fabric was only reduced to  $223^\circ$ , which probably reflects that this parameter is more influenced by bulk properties rather than by surface modification.

#### 3.4. Interaction of copper ions with BTCA modified cotton

The introduction of ionic charge into cotton offers many process possibilities, in particular, the dyeing of the anionically charged, crease resist modified cotton with cationic dyes [17, 18]. However, after the obvious

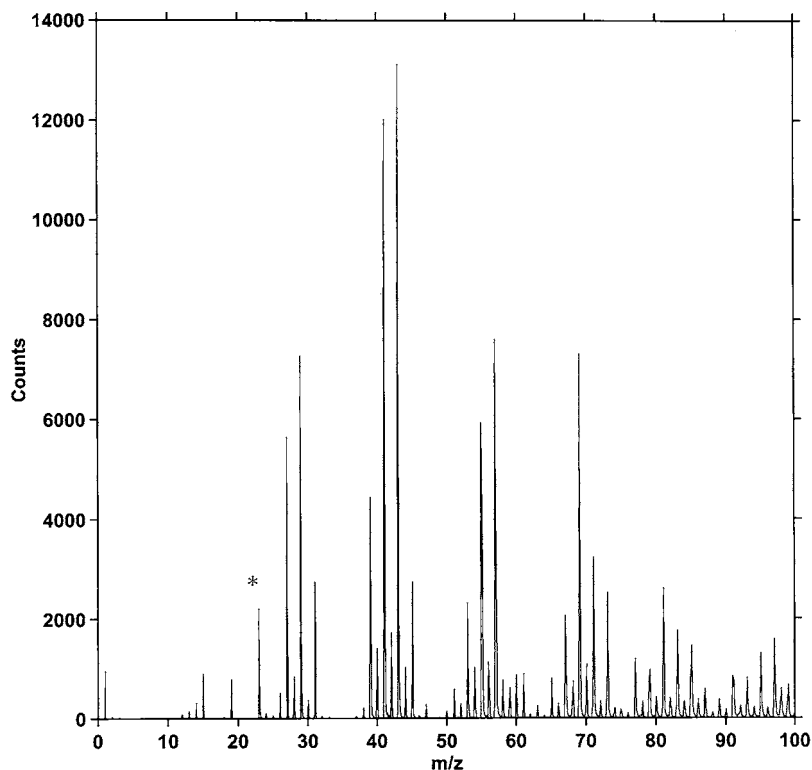


Figure 8 Positive ion ToF-SIMS spectrum of untreated cotton fabric domestically laundered for five wash cycles (\* Na<sup>+</sup> ion, m/z = 23<sup>+</sup>).

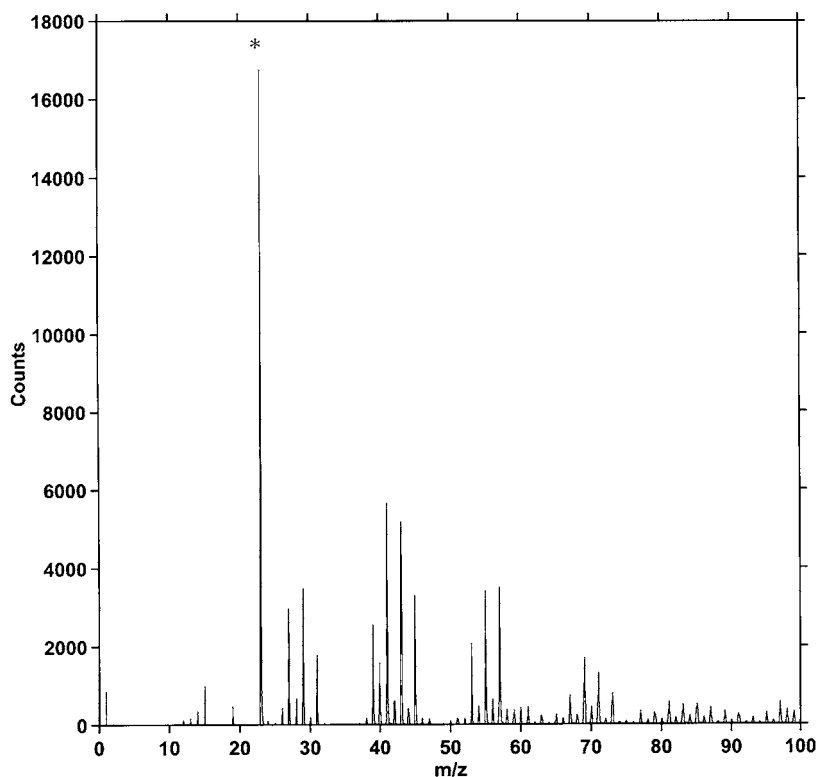


Figure 9 Positive ion ToF-SIMS spectrum of BTCA modified cotton fabric domestically laundered for five wash cycles (\* Na<sup>+</sup> ion, m/z = 23<sup>+</sup>).

binding of the sodium ions to the negatively charged cotton the potential for binding other metal ions, in particular copper ions, was investigated. Examination of the BTCA modified cotton fabric soaked in 50 ppm Cu<sup>2+</sup> solution reveals it is obviously discoloured and to a far greater degree than the comparable untreated and the conventionally DMDHEU crease resist treated cotton, Fig. 10. The binding of the copper ions was

fast to thorough rinsing in water thus demonstrating its substantivity. The related citric acid finish for cotton, similarly containing unreacted carboxyl groups, has also been demonstrated to bind effectively heavy metal cations such as copper, silver and tin to impart rot resistance [19].

While this observation is perhaps unsurprising in the light of polycarboxylic acids functioning in water

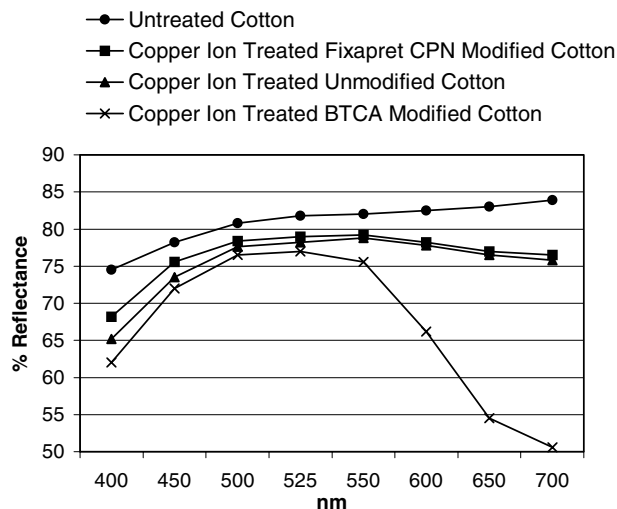


Figure 10 Reflectance spectra of copper ion impregnated cotton fabrics.

purification systems by metal complexation, it may present a potential processing and end-use problem. Therefore the effect of domestically laundering the copper pretreated cotton fabrics in a perborate-based detergent was evaluated. A relatively higher tensile strength loss of 53% was observed for the copper doped BTCA modified cotton after five domestic launderings relative to the comparable copper doped, untreated and Fixapret CPN samples, 24% and 32% strength losses, respectively. Again in the light of the well known heavy metal catalysed decomposition of hydrogen peroxide it is perhaps not unexpected the concomitant increase in strength loss with increasing copper concentration.

#### 4. Conclusions

The nature of BTCA powder and the surface of BTCA modified cotton have been characterised by XPS and ToF-SIMS and an increase in fibre surface carboxyl content observed. The increased carboxyl concentration significantly increases the adsorption of sodium ions during domestic laundering. Similarly the relative adsorption of copper ions from aqueous solution is increased by the BTCA modification leading to obvious discolouration. Washing of the copper doped, BTCA modified cotton in a perborate-based detergent

formulation produces a greater strength loss than comparably treated unmodified and DMDHEU treated cotton, due to the relatively higher levels of bound copper ions.

#### Acknowledgements

The authors wish to thank the Ministry of Culture and Higher Education of Iran for the award of a research scholarship to S. Shekarriz.

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Received 17 April 2002  
and accepted 3 April 2003