The effect of corona treatments on the hygral expansion of wool worsted fabrics

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The effect of dry corona and aqueous treatments on the hygral expansion of wool gabardine has been investigated. Increasing the severity of the corona treatment produced a concomitant reduction in the hygral expansion of the fabric. X-ray photoelectron spectroscopy has been used to study the chemical modification of the wool fibre surface.

INTRODUCTION

Absorption of moisture by wool fabrics generally produces an increase in dimensions due to fibre and yarn swelling. This behaviour has been termed 'hygral expansion' and is an inherent property of woven wool fabrics [1]. Hygral expansion is influenced by fibre length and diameter [2,3], cover factor [4], yarn crimp [1] and the degree of set introduced during finishing [5]. Although low levels of hygral expansion can be beneficial, values above 5–6% can lead to difficulties during tailoring [6,7].

The degree of hygral expansion induced in a wool fabric during dyeing is a result of the fabric being set in a new configuration dictated by the dyeing condition [8]. The setting mechanism is catalysed by free thiols present in the wool and proceeds via a nucleophilic substitution reaction known as thiol–disulphide interchange [7] (Scheme 1).

$$—S_1—S_2— + —S_3^- \longrightarrow —S_1^- + —S_2—S_3—$$

Scheme 1

A variety of methods to control high levels of hygral expansion resulting from piece dyeing have been proposed [5,8,9]:

(a) Incorporate oxidising agents or thiol blocking agents in the dyebath to interrupt the thiol/disulphide setting process
(b) Apply a polymer treatment
(c) Reset after stretching the fabric
(d) Mill the fabric
(e) Treat with a surfactant
(f) Dye at low pH.

In this study the effect of surface-specific corona treatments on the hygral expansion of dyed wool fabric has been investigated. The corona treatment consisted of passing the fabric between electrodes and bombarding the substrate surface with electrons. The collision of the electrons with air also generated ozone and nitrogen oxides, which further reacted with the wool surface. Amino acid analysis of the cuticle of corona-treated wool has indicated that this oxidising environment results in the formation of cysteic acid [10]. Corona treatment can also confer improved shrink-resistance, spinnability and cardability for wool and mohair [11–13].

X-ray photoelectron spectroscopy allows the chemical species present at the wool surface to be identified up to a depth of 3 nm, and does not require the removal of the outer epicuticle prior to surface analysis [14]. The kinetic energy E_k of the emitted photoelectrons has been measured by this technique, and from this the electron binding energy E_b can be calculated using the following relationship (Eqn 1):

$$E_b = h\nu - E_k \quad (1)$$

where $h\nu$ is the known photon energy. Measurement of E_b enables the emitting atom to be identified and its oxidation state determined. Furthermore, measurements of the peak intensity allows quantitative analysis to be performed.

EXPERIMENTAL

Materials

Dyed 100% wool gabardine fabrics, 270 g/m^2, were supplied by Jaeger Tailoring, Burgess Hill, UK and Parkland, Bradford, UK. The fabrics had been piece dyed and subsequently pressure decatised. Undyed, scoured polyester fabric was given an identical corona treatment to that of the dyed wool gabardine. Undyed wool gabardine, 230 g/m^2, was supplied by Parkland.

Corona treatment

The corona treatments were kindly performed by Softal electronic GmbH, Hamburg, Germany. The fabric samples were treated with a discharge intensity ranging from 160 to 3200 W min/m^2. The fabric was treated on both sides to ensure uniformity.

Surface analysis

X-ray photoelectron spectra were obtained using an ESCA-3 spectrometer (Vacuum Generators). The samples were attached to the spectrometer probe with double-sided adhesive tape and analysed with MgK_α radiation (1253.6 eV). The spectrometer pressure was 5.33 μPa (4×10^{-8} torr). All binding energy values were calculated relative to the carbon (1s) photoelectron peak at 285.0 eV. The peak areas used to obtain the surface composition were corrected using Wagner's sensitivity factors [15].

Hygral expansion and set measurements

The percentage hygral expansion H of fabric was measured by the reported method [6], and is given by Eqn 2:

$$H = \frac{\text{Length (wet)} - \text{Length (dry)}}{\text{Length (dry)}} \times 100 \qquad (2)$$

The level of set was determined using Eqn 3 [5]:

$$\text{Set (\%)} = \frac{180 - \theta}{180} \times 100 \qquad (3)$$

where θ is the yarn angle.

Colour measurement

The colour of the fabric was measured on an ICS-Texicon Spectraflash.

Dyeing procedure

Undyed wool gabardine and undyed corona-treated wool gabardine were dyed under the following conditions. The dyebath was set at 40°C (liquor ratio 10:1) and held for 20 min, after which time the temperature was raised to 100°C over 30 min. Boiling was continued for 15, 30, 60 or 120 min.

All dyebaths contained 5% o.w.f. sodium sulphate, 1% o.w.f. Lyogen MF(S) and were buffered to pH 5 with 2% o.w.f. sodium acetate/acetic acid. The effect of incorporating 2% o.w.f. of the reductive bleaching agent Erioclarite B (CGY) on hygral expansion was also examined. The corona-treated dyed fabrics were subsequently either treated at 40°C in a solution containing 2 g/l cationic softener or 2 g/l silicone softener.

RESULTS AND DISCUSSION

The use of the lightweight wool fabrics in men's and women's suiting has increased the need for finishers to control the dimensional stability of fabric. Fabric dyeing imparts a high degree of set to the wool, but this increase can be reduced or even eliminated by the incorporation of set-inhibiting reagents into the dyebath. Dyed fabric can either be stretched and reset or lightly milled to correct problems introduced by high hygral expansion. Both these treatments increase interactions between yarns, hence reducing yarn decrimping under high swelling conditions. Recently corona treatment of wool to impart shrink-resistance and improve printability has been reported and the commercial implications of the process examined [16].

Increasing the level of corona treatment produces a reduction in the hygral expansion of the dyed wool fabrics (Table 1). Thorsen found that corona treatment of wool increases the frictional properties, and the observed reduction in hygral expansion in this study was probably due to increased interfibre friction [17]. Subsequent application of a cationic softener to the corona-treated wool increased the hygral expansion of the wool fabric, probably because of a decrease in interfibre friction (Table 1).

Corona treatments are regarded as 'surface specific', and for porous fabrics the treatment not only modifies fibre surfaces at the fabric exterior, but is also able to penetrate into the bulk of the fabric structure. While the reduction in hygral expansion appears to be related to surface frictional properties, it may not be the only factor, since the swelling of the fibres which leads to hygral expansion, is a bulk phenomenon.

Goto *et al.* recently reported that plasma treatments of wool in oxygen, argon, methane, trifluoromethane and tetrafluoromethane atmospheres decreases hygral expansion, though it is difficult to ascertain the effectiveness of the treatments from results presented [18]. Measurement of the colour difference between treated and untreated fabric in the present work indicated that, although the differences are small, there is a discernible change after corona treatment (Table 2).

The industrial benefits of using corona pretreatments on wool to improve shrink-resistance, dyeing and printing have been documented by Byrne *et al.* [16]. In the present work corona pretreatment reduced the increase in the hygral expansion during subsequent dyeing (Table 3). However, the application of softener after dyeing once again reduced the benefits considerably. Increasing dyeing time gave an increase fabric set, which as expected was unaffected by the corona pretreatment.

To understand the physico-chemical changes occurring

Table 1 Hygral expansion of corona-treated wool gabardine

Corona treatment (W min/m²)	Hygral expansion,warp (%)		
	Fabric 1[a]	Fabric 2[b]	Fabric 1[a,c]
Untreated	9.0	4.9	9.0
160	8.8		
320	7.2		
640	7.2		8.9
1280	7.7	3.1	
1920	6.8		8.5
2560	6.7		8.4
3200	6.3	3.0	

a Supplied by Jaeger
b Supplied by Parkland
c Treated with cationic softener, 2 g/l

Table 2 Effect of corona treatment on fabric colour

Corona treatment (W min/m²)	ΔE^a
160	0.36
320	0.69
1280	0.83
1920	0.86
3200	0.85

a Measured relative to untreated fabric, CMC(2:1) system, illuminant D_{65}, 10° observer on wool gabardine (Jaeger) dyed black.

Table 3 Hygral expansion *H* and set of corona-treated dyed wool gabardine

	No corona treatment		Treatment at 640 W min/m²		Treatment at 3200 W min/m²	
Dyeing time (min)	*H* (%)	Set (%)	*H* (%)	Set (%)	*H* (%)	Set (%)
0	3.0		2.7		2.5	
15	5.9	47	4.4	46	3.2	47
30	5.9	54	6.1	54	3.6	52
60	6.3	66	6.3	61	4.1	62
120	7.3	73	6.6	70	4.2	76
Bleaching[a]						
15	8.5 (88)	64	6.3 (9.1)	61	6.0 (8.9)	69
30	8.7 (10.8)	68	6.9 (9.7)	74	5.9 (9.0)	67
60	9.1 (10.6)	69	6.7 (10.0)	72	6.6 (9.7)	70
120	9.2 (9.7)	74	8.1 (10.8)	72	7.5 (11.2)	79

a Erioclarite B (2% o.w.f.) reductive bleaching agent incorporated in dyebath; figures in parentheses indicate results of aftertreatment with silicone softener

at the wool fibre surface as a result of the corona treatment, X-ray photoelectron spectroscopy was used to probe the wool epicuticle (the outer 3–5 nm of the fibre). The epicuticle is reported to consist of protein and lipid material, which in turn are composed of carbon, hydrogen, oxygen, nitrogen and sulphur [19,20]. The carbon (1s), nitrogen (1s) and oxygen (1s) peaks in the spectrum of wool occurred at binding energy values of 285.0, 399.6 and 531.6 eV respectively. The main sulphur (2p) peak of untreated wool occurred at a binding energy of 164 eV (Figure 1). This peak has been assigned to the disulphide bond (S^{2+}) of cystine residues [21].

Corona treatment of wool caused a marked changes in the sulphur (2p) photoelectron spectrum. The oxidative corona treatment produced an increase in peak intensity at 168 eV (S^{6+}) due to the formation of cysteic acid (Figure 1). Interestingly, even under the most severe treatment condition of 3200 W min/m², only 47% of the surface sulphur was oxidised to the S^{6+} form. This is in contrast to the commercial Kroy chlorination, where all the surface was shown by X-ray photoelectron spectroscopy to be converted to the oxidised S^{6+} form [14].

Like the sulphur (2p) signal, the carbon (1s) signal in the wool photoelectron spectrum was broad, indicating the presence of more than one species. Corona treatment of wool produced an increase in intensity of the higher binding energy component of the carbon (1s) spectrum, evidence for oxidation of the wool surface, although again the level of oxidation was surprisingly low. It is probable that hydroxy, aldehyde/ketone and carboxylic acid species were formed by the corona treatment.

Yasuda has reported fixation of nitrogen onto the surface of polyester fibres as a result of plasma treatment. In this study corona-treated (640 W min/m²) polyester fabric under the same conditions as the wool gabardine also showed the presence of a small nitrogen signal in the X-ray photoelectron spectrum [22]. Whether similar fixation of nitrogen at the surface of the wool fibre occurs during the corona treatment is at present uncertain. However, an increase in the surface nitrogen concentration was noted (Table 4). The oxidative nature of the reaction was confirmed by the large increase in surface oxygen concentration.

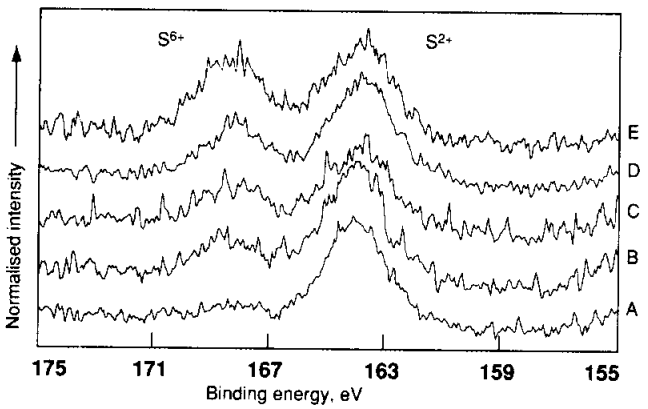

Figure 1 X-ray photoelectron spectrum of the main sulphur (2p) peak of untreated wool (for key see Table 4)

Table 4 Elemental composition of surface of corona-treated wool[a]

Sample	Corona treatment (W min/m²)	Composition (%) Carbon	Nitrogen	Oxygen	Sulphur
A	Untreated	77.9	6.9	12.2	2.9
B	320	68.2	6.9	22.2	2.7
C	640	68.1	6.7	22.4	2.8
D	1280	65.4	9.8	21.4	3.4
E	3200	65.7	8.6	22.1	3.6

a Hydrogen cannot be measured

CONCLUSIONS

The hygral expansion of dyed wool fabrics can be reduced by corona treatment. The oxidative treatment increases interfibre friction, thus restricting yarn movement/decrimping. Subsequent application of softeners to the treated fabric increases the level of hygral expansion in corona-treated fabrics. Corona treatments produce a visible change in colour of dyed fabrics.

X-ray photoelectron spectroscopy indicates that the corona treatment oxidises the wool fibre surface. Even at the severest treatment conditions only 47% of the surface disulphide bonds (S^{2+}) are oxidised to cysteic acid (S^{6+}).

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