

## Effect of pretreatment of wool fabric with keratin on its dyeability with acid and reactive dyes

A Kantouch, O Allam, L El-Gabry & H El-Sayed<sup>a</sup>

Textile Research Division, National Research Centre, Dokki, Cairo, Egypt

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Keratin has been extracted from wool using ammonium thioglycolate under nitrogen atmosphere and then used for treating wool fabric in the presence of epichlorohydrin as a cross-linking agent. The treated fabrics are then dyed with acid and reactive dyes at various temperatures. Complete exhaustion of these dyes on the treated fibres takes place at room temperature within 20 min. Higher dyeing temperatures result in complete exhaustion of the dyebath within a short time. The dyeing kinetics of the treated fibres are also evaluated. The half dyeing time of the treated samples decreases to <12 s against the 300 s for the untreated ones. The wash and rub fastness of the dyed fabrics have also been assessed. It is found that urea-bisulphite solubility values assure that epichlorohydrin is able to form permanent crosslinks between keratin and wool. Scanning electron micrographs of the treated fabrics disclose formation of very thin keratin layer onto wool surface.

**Keywords:** Acid dye, Dyeing, Keratin, Reactive dye, Wool

### 1 Introduction

Keratin is a tough, insoluble protein found in the outer layer of the skin of human beings and many other animals. Keratins are a family of structural proteins found abundantly in wool, hair, feather, hooves, and fingernails. These keratinous materials are often referred to as “hard” keratins (as opposed to soft keratins that are found in epithelial tissues).

Although there are tremendous amounts of keratin wastes<sup>1</sup>, keratins also show some uses in the global market. Feather meals, for instance, are used for animals.<sup>2</sup> Keratin-based cosmetics are used for treatment of human hair and skin<sup>3, 4</sup>. Keratin materials have found their roles among many other fields, viz. concrete<sup>5</sup>, ceramic<sup>6</sup>, fertilizers<sup>7</sup>, fire fighting compositions<sup>8</sup>, wound healing<sup>9</sup>, leather tanning<sup>10</sup>, production of biohydrogen<sup>11</sup>, and shrink-proofing of wool<sup>12</sup>.

Many hydrolytic and non-hydrolytic methods are used to extract keratin from natural resources. Most of these methods utilize oxidizing or reducing agents in presence of auxiliaries such as sodium dodecyl sulphate, urea, and EDTA<sup>13-15</sup>.

In the present work, keratin was extracted from cheap coarse Egyptian wool fibres using a simple method. Being a natural proteinic biopolymer, the extracted keratin can be crosslinked to wool fabric

aiming to enhance its dyeability with acid and reactive dyes.

### 2 Materials and Methods

#### 2.1 Materials

Marino light-weight wool fabrics were purchased from Misr Company for Spinning and Weaving, El-Mehalla El-Kobra, Egypt. Egyptian wool fleece (Barki) was purchased from the local market, from which keratin was extracted.

Two acid dyes and two reactive dyes were used in this investigation (Table 1). They are commercial grades and used as provided. Thioglycolic acid was supplied from El-Nasr for Medical and Chemical Company Cairo, Egypt. Ammonium hydroxide and epichlorohydrin were purchased from Fluka, Steinheim, Germany. Egyptol<sup>®</sup> PLM, a nonionic detergent based on nonanoly phenol ethoxylate, was supplied from Starch and Detergent Company, Alexandria, Egypt.

#### 2.2 Methods

##### 2.2.1 Scouring

The raw greasy wool was scoured to remove suint, dirt, and soluble impurities. Scouring was carried out in the laboratory using 1 g/L Egyptol<sup>®</sup> PLM in presence of 1 g/L sodium carbonate as a builder to facilitate removal of contaminants. Scouring of wool was carried out at 50 °C for 30 min with occasional

<sup>a</sup>To whom all the correspondence should be addressed.  
E-mail: hosam@trdegypt.com

Table 1 – Acid and reactive dyes used in dyeing of wool fabrics

Dye	Functional class	C.I. Name	Supplier
Supranol Brilliant Blue BLW	Monosulphonic	Acid Blue 203	Egypt Colors, Egypt
Acid Fast Red EG	Disulphonic	Acid Red 1	POL, Poland
Remazol Red G	Vinyl sulphone	Reactive Red 180	Dystar, Germany
Lanasol Blue 3G	$\alpha$ -bromo acrylamide	Reactive Blue 69	Ciba-Geigy, Switzerland

shaking; material-to-liquor ratio (MLR) was 1:50 (owf). Wool fibres were then thoroughly washed with hot and cold water and finally dried at 105 °C for 1h.

### 2.2.2 Extraction of Keratin from Wool

Pure Egyptian wool fleece (5 g) was treated at 50 °C for 4 h, under nitrogen gas atmosphere in 100 mL solution containing ammonium hydroxide/water (1:1) in presence of 1.5 mL thioglycolic acid. The obtained hydrolysate was centrifuged at 4000 G for 10 min, and the supernatant liquid containing the more soluble keratin fraction was collected<sup>16</sup>.

### 2.2.3 Treatment of Wool with Keratin

Wool fabrics were immersed in 4 % aqueous keratin solution in presence of 1% epichlorohydrin. The pre-soaked fabric was passed through a padding mangle applying a pressure of 10 kg cm<sup>-2</sup>, to have a pick up of 100 %. The sample was finally dried and baked at 140 °C for 5 min.

### 2.2.4 Dyeing of Wool

Untreated as well as treated wool fabrics were dyed with C.I. Acid Blue 203, C.I. Acid Red 1, C.I. Reactive Blue 69, and C.I. Reactive Red 180, each separately, using 4 % dye (owf), 5 pH and 0 – 120 min time. The MLR was 1:100 at different dyeing temperatures (25° - 85 °C). The colour strength (K/S) of the dyed fabrics was measured using HunterLab Universal Software Ultrascan (USA), using the following Kubelka-Munk equation<sup>17</sup>:

$$K/S = \left[ \frac{(1-R)^2}{2R} \right]$$

where  $K$ ,  $S$  and  $R$  are the absorption coefficient, scattering coefficient, and reflectance respectively.

### 2.3 Dyeing Kinetics

Treated and untreated wool fabrics were dyed with 2 % and 4 % (owf) of C.I. Acid Blue 203 at 85 °C and pH 5 using a liquor ratio 1:100, for various periods of time. Aliquots of the dyeing bath were taken for the determination of extent of dye exhaustion after

different periods. After dyeing, the wool fabric was rinsed thoroughly with running water and air dried. The per cent of dye exhaustion was estimated by a spectrophotometric method.

#### 2.3.1 Dye Exhaustion

Measurement of the residual dye in the dyeing bath was determined using JENWAY- 6405 U/V spectrophotometer<sup>18</sup>.

#### 2.3.2 Time of Half Dyeing

Dyeing of the fibres was performed on a 5 g sample using 4 % dye (owf) at different temperatures (40° – 85°C). Each set included dyeing for intervals of time between 5 min and 180 min. Samples were removed from the dyebath immediately after the prescribed dyeing time and the amount of the dye remaining in the dye bath was determined spectrophotometrically<sup>19</sup>. For each dyeing temperature, the per cent exhaustion versus dyeing time was plotted. Time of half dyeing ( $t_{1/2}$  min) was determined from these plots.

#### 2.3.3 Specific Dye Rate Constant

The specific dye rate constant ( $K^{\circ}$ ) could be further estimated using the following equation<sup>20</sup>:

$$K^{\circ} = 0.5 C_{\infty} (d \cdot t_{1/2})^{1/2}$$

where  $d$  is the fibre diameter (cm); and  $C_{\infty}$  the amount of dye taken up by the fibre at equilibrium conditions.

#### 2.3.4 Apparent Diffusion Coefficient

Samples of the examined fibres (5 g) were dyed in dye solution (500 mL) for 3 h. The amount of dye taken up by the fibres ( $C_{\infty}$ ) was determined spectrophotometrically.

Another dyeing test was performed for a short period (10 min) and  $C_t$  was similarly determined. The values of  $C_t/C_{\infty}$  were calculated and the apparent diffusion coefficient ( $D$ ) could then be calculated using the following Hill's equation<sup>19</sup>:

$$D(\text{cm}^2\text{s}^{-1}) = \frac{C_t}{C} \times \frac{d^2}{T} \times 100$$

where  $d$  is the diameter of the fibre in  $\mu\text{m}$ .

### 2.4 Fastness Properties

The colour fastness of the dyed wool fabrics to washing was determined according to the AATCC test method 61–1075 using a laboratory laundrometer<sup>21</sup>.

### 2.5 Urea-bisulphite Solubility

Urea-bisulphite solubility of untreated as well as keratin/ECH treated fibres was determined according to the IWTO-11-65 (E) test method.

## 2.6 Scanning Electron Microscopy

The untreated as well as keratin/ECH treated fibres were mounted on aluminium stubs, and sputter coated with gold in an S150A sputter (coated Edward, UK), and examined by JEOL (JXA-840A) Electron Probe Microanalyzer (Japan).

## 3 Results and Discussion

Wool fabrics were treated with keratin/ECH mixture to enhance their dyeability with acid and reactive dyes, and hence decrease the amount of dye in the effluent. The effect of different dyeing conditions on the dyeability of the treated as well as untreated wool fabrics was studied.

### 3.1 Effect of Dyeing Temperature

Untreated as well as treated wool fabrics were dyed with C.I. Acid Blue 203, C.I. Acid Red 1, C.I. Reactive Blue 69, and C.I. Reactive Red 180 using 4 % shade, 5 pH, 60 min treatment time, 1:100 MLR and different dyeing temperatures (25° - 85 °C).

The results (Fig. 1) show that in case of untreated as well as treated fabrics, as the dyeing temperature increases, the extent of dyeing (*K/S*) increases, irrespective of the dye used. At room temperature (30 °C), only limited improvement in the *K/S* value of the treated fabrics as compared to untreated wool is observed; however the shades of these samples are still too light and reached *K/S* of 5 – 10. The highest *K/S* value is only achieved at 85 °C for 60 min in dyeing with reactive dyes for both treated and untreated wool.

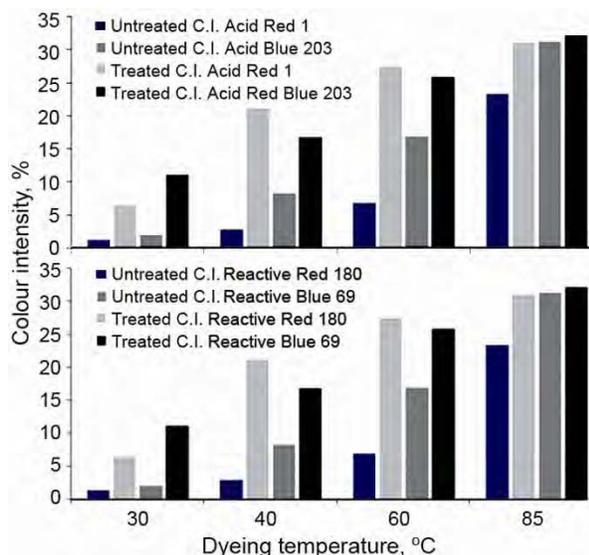


Fig. 1 – Effect of treatment of wool fabrics with keratin/ECH on its dyeability with both acid and reactive dyes (4 % owf, pH 5, MLR 1:100, 60 min)

### 3.2 Effect of Wool Treatment on Dyeability

Being proteinic in nature, keratin macromolecules are supposed to bind chemically to wool. To ensure permanent crosslinking of keratin onto wool, epichlorohydrin is added as a crosslinker.

The effect of treatment of wool fabric with keratin/ECH on its dyeability with the acid dye Supranol Blue BLW (C.I. Acid Blue 203) at different temperatures (40° - 85°C) was studied and the results are shown in Figs 2 and 3. It is found that the dye bath used in dyeing of pretreated wool fabric samples using Acid Blue 203 is almost completely exhausted within 5–30 min, depending on the dyeing temperature. This time is much shorter than the time needed for complete exhaustion of the dyebath in case of dyeing the untreated wool fabric using the same dye. Pretreatment of wool fabric results in complete exhaustion of the dyebath

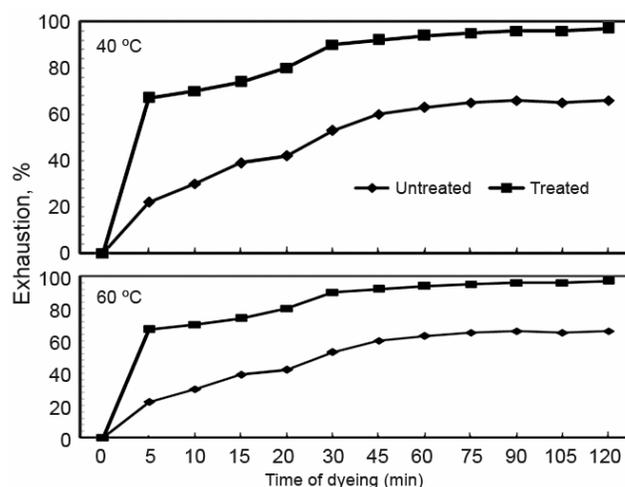


Fig. 2 – Effect of treatment of wool with keratin/ECH (4 % w/w) on its dyeability with C.I. Acid Blue 203 (4% o.w.f, MLR 1:100, pH 5 at 40°C and 60 °C)

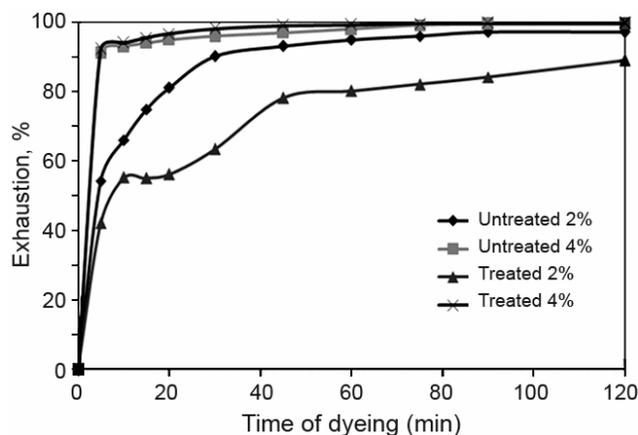
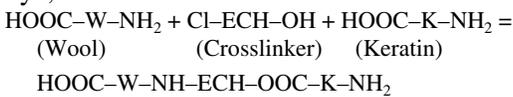


Fig. 3 – Effect of treatment of wool with keratin/ECH (4 % w/w) on its dyeability with C.I. Acid Blue 203 (2 & 4% owf, MLR 1:100, pH 5 at 85° C)

within 30 min upon dyeing at room temperature, or within 5 min upon dyeing at 60 °C.

These results can be explained in terms of measuring the ability of keratin to form permanent crosslinks with wool polypeptide chains. The modified wool has greater number of cationic groups which results in enhanced absorbability of the anionic acid dye. Being protein containing a lot of amino and amide groups, in acid medium, keratin has sufficient cationized basic nitrogen-containing groups able to bind with the anionic sulphonic groups in the acid dye, as shown below:



### 3.3 Dyeing Kinetics

Table 2 shows the values of half-dyeing time ( $t_{1/2}$ ), specific dyeing rate constant ( $K'$ ) and the apparent diffusion coefficient ( $D$ ) calculated for the untreated as well as keratin-treated wool fabrics dyed with C.I. Acid Blue 203. Data of this table reveal that, irrespective of the dyeing temperature and the dye yield, the half-dyeing time of the keratin-treated wool fabrics decreases sharply compared to the untreated one. Again, the enhanced rate of dyeing might be attributed to the extra cationized amino and amide groups created along the polypeptide chains of wool as a result of its chemical bonding with keratin. It is also observed that the specific dyeing rate constant ( $K'$ ) of wool fabrics increases remarkably upon treatment with keratin/ECH. The diffusion coefficient ( $D$ ) of the dyed wool samples increases in the case of keratin treated fabrics compared with the untreated one.

### 3.4 Fastness Properties

The washing and crocking fastness of untreated as well as keratin-treated wool fabrics dyed with C.I.

Table 2—Time of half dyeing ( $t_{1/2}$ ), specific dyeing rate constant ( $K'$ ) and diffusion coefficient ( $D$ ) of wool fibres dyed with the acid dye C.I. Acid Blue 1 (4% owf) at pH 5, and MLR 1:100

Sample	Dyeing temperature, °C	$t_{1/2}$ , s	$K' \times 10^{-3}$ cm/s	$D \times 10^{-11}$ cm <sup>2</sup> .s <sup>-1</sup>
Untreated	40	300	8.2847	3.601
Keratin-treated	40	25	49.777	4.449
Untreated	60	360	10.245	3.444
Keratin-treated	60	55	34.176	5.447
Untreated	85	600	9.425	3.502
Keratin-treated	85	36	42.285	5.502
Untreated <sup>a</sup>	85	295	14.09	4.139
Keratin-treated <sup>a</sup>	85	12	73.24	5.441

<sup>a</sup>Dyed with 2% owf C.I. Acid Blue 1.

Acid blue 203 are summarized in Table 3. It is observed that the fastness properties of wool fabrics against washing and crocking are not affected after treatment with keratin/ECH. This indicates that keratin is bound to the wool fabrics by permanent cross-links which are fast to washing and rubbing conditions.

### 3.5 Scanning Electron Microscopy

In order to monitor any change in the morphological structure of wool fibre after being treated with keratin/ECH, scanning electron microscopic study was conducted for both untreated and keratin-treated wool fabrics.

Figure 4 shows the normal surface morphology of the untreated wool fibres. This figure also clarifies that treatment of wool fabric with keratin/ECH results in formation of a very thin layer of cross-linked keratin on the surface of wool fibres. Nevertheless, part of the added keratin, cross-linked with the fibre

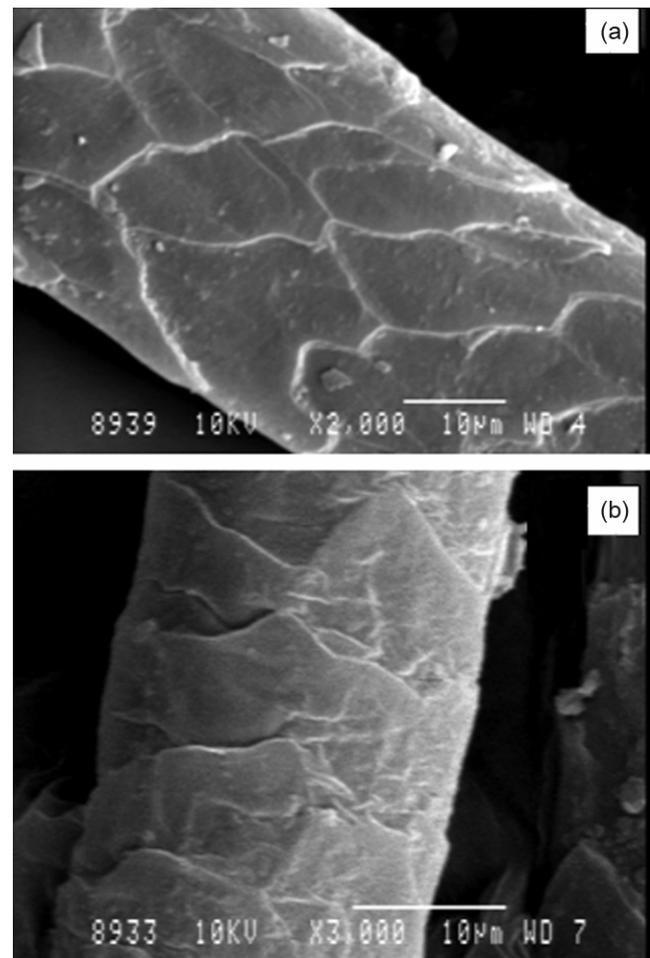


Fig. 4 – Scanning electron micrograph of (a) untreated and (b) treated merino wool fabrics

Table 3 – Fastness properties of the dyed wool fabrics to washing and crocking  
[Dyeing with C.I. Acid Blue 203 (4% owf), pH 5, and MLR 1:100]

Sample	Dyeing temp., °C	Washing			Crocking	
		Alt	St <sub>w</sub>	St <sub>n</sub>	Dry	Wet
Untreated	30	3	4-5	4-5	4	3
Keratin-treated	30	3-4	4-5	5	4	3
Untreated	40	4	4-5	4-5	4	3
Keratin-treated	40	4-5	4	5	4	3
Untreated	60	4	4-5	4-5	4	3
Keratin-treated	60	4-5	4-5	5	4	3
Untreated	85	4-5	4-5	5	4	3
Keratin-treated	85	5	4-5	5	4	3

Alt.– Alteration, St<sub>w</sub>– Staining on wool fabric, and St<sub>n</sub>– Staining on nylon fabrics.

interior, results in durable dyed wool. This criterion is confirmed by measuring the solubility of untreated as well as treated wool fibres in urea-bisulphite solution. The urea-bisulphite solubility of the keratin/ECH-treated wool fabric is found to be 4.6 %, compared to 39.4% for the keratin-treated, and 44 % for the untreated one. This is a strong clue that keratin, in presence of epichlorohydrine, forms crosslinks not only with the fibre surface, but also with the different changes of the bulk of the fibre. This hypothesis is in harmony with the results of the fastness properties of the dyed wool fabrics (Table 3).

#### 4 Conclusion

The biopolymer keratin can be permanently cross-linked to wool when using epichlorohydrine. The treated wool shows enhanced dyeability with acid (mono-sulphonic and disulphonic) and reactive (vinyl sulphone and  $\alpha$ -bromo acrylamid) dyes. Being a natural biodegradable protein, keratin would be an acceptable eco-friendly substitute for other unacceptable chemicals used traditionally in wet processing of wool. Further studies are going on to apply keratin to some synthetic fibres to impart certain desired dyeing properties.

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