Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Dyes and Pigments 72 (2007) 80–87

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

Effect of cationisation on reactive printing of leather and wool

A.A. Haroun [a,*], H.F. Mansour [b]

[a] National Research Center, Department of Chemistry of Tanning and Leather Technology, Cairo, Egypt
[b] Textile Printing, Dyeing & Finishing Department, Faculty of Applied Arts, Helwan University, Cairo, Egypt

Received 19 January 2005; received in revised form 11 March 2005; accepted 22 July 2005
Available online 13 October 2005

Abstract

The resurgent interest in clothes made of leather and wool substrates has led to developments of brilliant colours with different shades on leather and wool that hold promise for reopening this market for the two substrates. It is necessary to use more than one class of dyestuff under variety of conditions and to modify the two components before printing. Fiber reactive dyes with three different reactive groups, mono-chloro triazine (Cibacron Yellow P6GS), dichloro-triazine (Procion Red MX-5B) and vinyl sulphone (Remazol Brilliant Orange FR), were used to print both unmodified and modified, i.e. cationised leather and wool substrates using Tenofix Extra ECO and Solfix E cationic reagents. Pre-cationisation of leather and wool brings an improvement in the depth of the obtained prints as well as washing and light fastness properties.

Keywords: Cationisation; Chrome tanned leather; Wool; Reactive dyes

---

1. Introduction

Approximately 25% of the total print production in the world is performed by reactive printing [1]. The reactive dyes are one of the most commonly used dyes for textile printing because of their high wet fastness, brilliant colours and variety of hue [2,3]. In general, the reactive dyes used in printing often have a degree of fixation of only 60%, whereas in dyeing a degree of fixation of over 90% can be achieved [4]. The following aspects may be of great importance in dyestuff substantively: first, the number and position of the negatively charged sulphonic acid groups (dye-SO3) and the attraction to positively charged cationised leather and wool substrates. Secondly, the amino groups of the untreated leather and wool or the unblocked portion in the cationised ones which is capable of entering into hydrogen bond formation with groups such as −OH, −CO, −N=N− and Cl in the dyestuff molecule. Also, hydrogen atom in the dye molecule may bind with oxygen in the leather hydroxyl groups. Thirdly, reactive dyestuffs that posses high planarity have abundant opportunities for hydrogen bonding and van der Waals forces to take place between leather or wool and dyestuff. The chemical modification of leather and wool in order to improve its colouration with reactive dyes has received considerable attention in recent years [5,6]. Localized application of *N*-(3-chloro-2-hydroxypropyl)-trimethyl ammonium chloride (CHTAC) in printing might produce unique fashion design effects on textile products by providing latent patterns of cationic ammonium ($NH3^+$) sites [7].

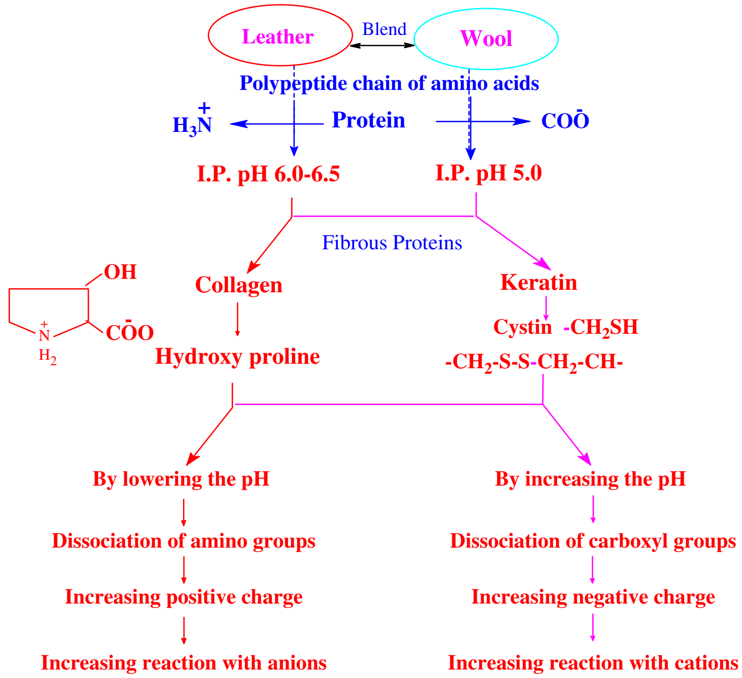
All of the pretreatments introduced cationic groups in the form of quaternary, tertiary or secondary

---

* Corresponding author. Fax: +20 2 33 70931.
E-mail address: haroun68_2000@yahoo.com (A.A. Haroun).

0143-7208/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2005.07.019

amino residues. Unlike dyeing, up to date research work published on the printing of cationised wool and leather, rarely did. Lewis and Lei [8] have considered a number of different fiber pretreatments that allow reactive dyeing to be performed under neutral to slightly acidic conditions in the absence of electrolyte. Cationic auxiliaries which have positive charges like basic dyes, can be used by affecting the isoelectric point of the dyed leather to reach leveling and penetrating leather dyeing [9]. Both leather and wool substrates consist of fibrous protein which contains polypeptide chains of amino acids [10], as shown in the following scheme:



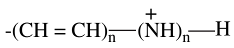
Leather contains tanning agents bound at one or many points, which may possibly react with dyestuffs, like mineral complexes of chromium or other metals, as well as other substances such as fats, surfactants, proteins. There exist numerous analogies in behaviour of collagen and other proteins like wool or silk. Among the specific features of leather colouration as contrasted with textile fiber colouration are the necessity to dye textile fibers in bulk, impossibility to use hot process for leather (boiling) and own colour of tanned leather, which makes leather different from raw fiber which is usually white [11]. This work examined the pre-cationisation treatment of leather and wool substrates by exhaust method and its effect on their printability with the different classes of reactive dyes.

2. Experimental

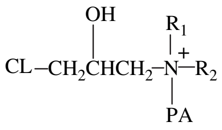
2.1. Materials

(1) Chrome tanned leather was obtained from local tannery in Cairo, with thickness range 1.2–1.9 mm, %Cr2O3 3.4–3.9, neutralized by 1.5% sodium bicarbonate and sodium formate.
(2) Hundred percent mill scoured and bleached wool, supplied by El Mahalla Com., El Mahalla El Kobra, Egypt.
(3) Cationic agents were supplied by Ciba as commercial samples as follows:

- Tenofix Extra ECO with a functional group polyethylene polyamine, its optimum condition are 50 °C, pH 5, Sp. Gr. 1.3 (20 °C), of 40% solid content.
- Solfix E based on polyaminochlorohydrin quaternary ammonium compound with epoxide reactivity structure.

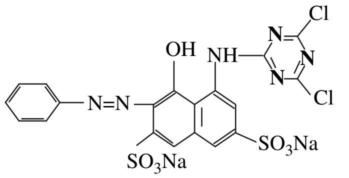

$-(CH = CH)_n\!-\!\overset{+}{(NH)}_n\!-\!H$

Tenofix Extra ECO

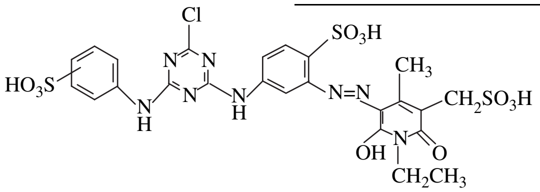


(R_1, R_2 = alkyle, PA = Polyamino)
Solfix E

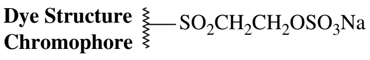
(4) Three different commercial reactive dyestuffs, represented their different classes and were obtained from Dystar chemicals L.P. as follows:



Procion Red MX-5B
C.I Reactive Red 2



(-SO_3H group in 3 and 4 position)
Cibacron Yellow P-6GS
C.I Reactive Yellow 095



Remazol Brilliant Orange FR
C.I. Vinyl sulphone Reactive Dye

(5) British gum thickener, supplied by Egypt company, for starch and glucose, Cairo, Egypt.

(6) Casein (binder), sodium lauryl sulphate, sodium carbonate, acetic acid were all of laboratory grade materials.

2.2. Methods

2.2.1. Cationisation treatment [12,13]

Leather and wool samples were treated with each Solfix E, and Tenofix ECO separately. The treatment was carried out according to the exhaust method. Solfix E was activated by reacting it with sodium hydroxide at 1:1 molar ratio and pH 8.0, this converts the chlorohydroxypropyl group in Solfix to an epoxy form to react with wool. The optimum condition of the treatment was studied when applying different concentrations of the cationic reagents (1, 3, 5, 7 and 9 %owf) at different temperatures (25, 40, 55 and 75 °C). The treatment process took place for 30 min.

2.2.2. Printing

The printing paste was applied on the cationised leather and wool samples and the untreated ones according to the conventional flat screen-printing method [14].

The printing paste was formulated according to the following recipe [15]:

British gum (stock thickening)	600 g
Dye	40 g
Casein (binder)	100 g
Sodium lauryl sulphate	40 g
Water	*X* g
Total	1000 g

The effect of dye concentration on the untreated and cationised leather and wool samples was examined between 40, 80, 120 and 160 g/kg, at pH values 3, 5 and 7.

2.2.3. Steaming

The steaming process was carried out on the untreated and the cationised leather and wool samples, at different time intervals 5, 10, 15, 20 and 25 min. For the wool samples the steaming temperatures were examined as 105 and 110 °C, while in case of leather, the temperature was adjusted to 105 °C for 5 min to avoid the shrinking effect on the fiber at high temperature.

2.2.4. Washing procedure [16]

After the steaming process, the printed samples were soaped in an aqueous solution containing 2 g/l of Hostapal CV-ET and enough ammonia solution to adjust pH to 8.0, for 30 min at liquor-to-goods ratio of 50:1, at 60 °C, after that the samples were rinsed and air dried.

2.2.5. Testing and measurements

- The colour strength of the untreated and cationised prints was measured as K/S values using Ultra Scan XE apparatus [17,18].
- Colour fastness to washing, rubbing and artificial light for wool was tested according to AATCC technical manual [19]. While in case of leather, the washing fastness was tested according to Heidemann et al. [20] and the fastness to rubbing and artificial light was tested according to European standards [21] and DIN [22] (German standards), respectively.
- Determination of nitrogen percentage [23]:
  The percentage of the nitrogen content in the leather and wool samples was determined according to the modification of semi-micro Kjeldahl method.

Table 1
Effect of the cationisation treatment on the nitrogen content of both the substrates

Substrates	Nitrogen content (%)
Untreated leather	8.5
Cationised leather	12.0
Untreated wool	6.0
Cationised wool	13.0

3. Results and discussion

3.1. Cationisation effect

As shown in Table 1, it is clear that the nitrogen content of the cationised leather and wool samples increased relative to the untreated ones.

Fig. 1 shows that the colour strength (K/S) values of the cationised leather and wool samples increased relative to the untreated ones. This follows the expected trend because the cationic treatment leads to an increase in the dye uptake, which results in an increase in the depth of shade. Tenofix ECO improves the leather printability when compared with Solfix E, which was more preferable in case of wool, this depends on the additional positive charges on the surface due to cationisation treatment. Schemes 1 and 2 represent the reaction mechanisms of Solfix E and Tenofix ECO on leather and wool substrates, respectively, the reaction of Solfix E is similar to that of reactive dyes as shown in Scheme 1.

Fig. 2 shows the effect of cationic reagents' concentration on the colour strength of printed leather and wool samples with Procion Red MX-5B. The results show that the maximum colour strength (K/S) value of the cationised leather was achieved at 9% Tenofix ECO concentration. This may be because the adsorption rate of the cationic reagent at the negatively charged leather surface gradually increased until it reached a maximum, which leads to all the negative charges at the cationised leather surface being neutralized to form cationic leather, as shown in Scheme 2. During chrome tanning of collagen, the carboxyl groups participated in the chromium ion complex, while the other collagen groups, mainly ε-amino groups of lysine and imidazole histidine groups remained unbounded [24]. So, in case of the cationised leather with Tenofix ECO, the ability of the reactive dyes to interact with chrome crosslinked leather increased, consequently, the colour strength improved.

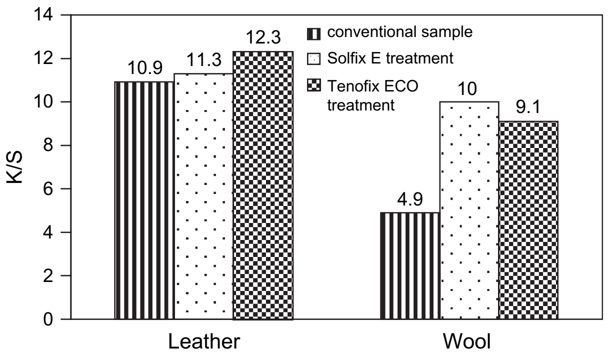
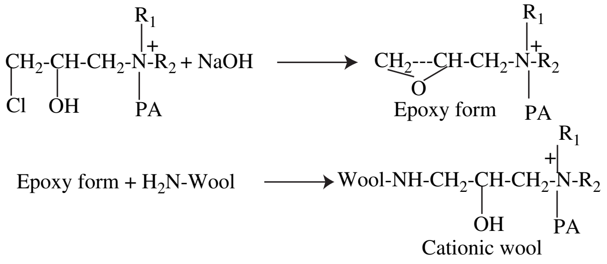
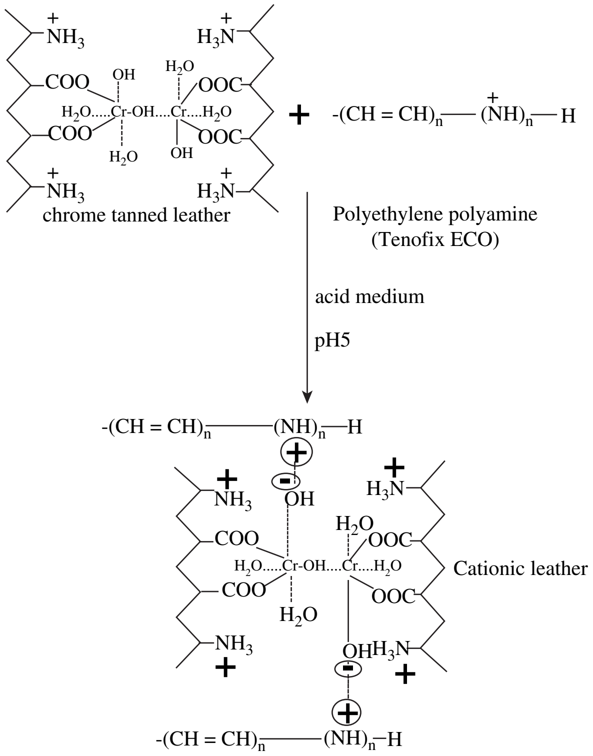


Fig. 1. Effect of cationic reagents on the colour strength of the printed leather and wool samples using Procion Red MX-5B.



Scheme 1.

On the other side, the colour strength (K/S) values of the printed wool samples decreased with increasing Solfix E concentration, this may be due to the competing hydrolytic side reaction of the chlorine atom to form epoxy followed by converting it to hydroxy derivative due to the presence of high temperature in the aqueous solution at high Solfix concentration, as shown in Scheme 3.



Scheme 2.

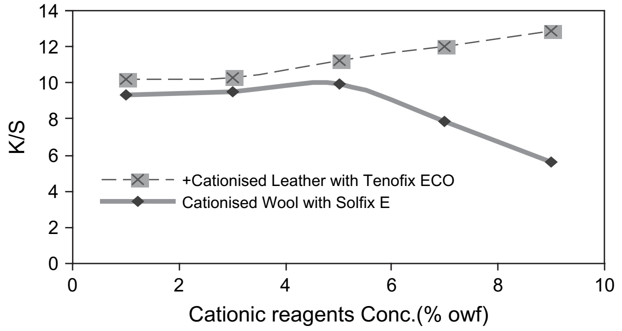


Fig. 2. Effect of cationic reagent concentration on the colour strength of the printed leather and wool samples using Procion Red MX-5.

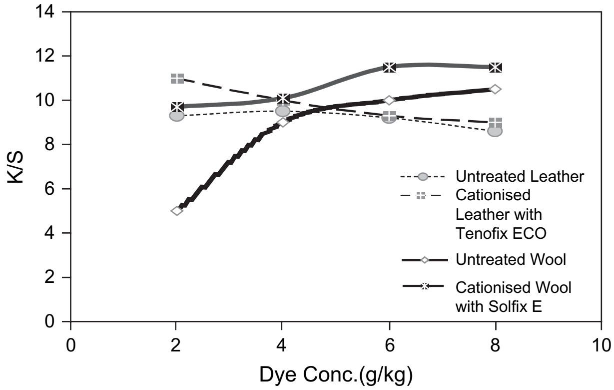


Fig. 3. Effect of Cibacron Yellow P6GS concentration on the colour strength of the printed leather and wool samples.

3.2. *Effect of the dye concentration*

The influence of the overall dye molecule structure is quite important. This effect is illustrated by the significant differences in colour yield which increases among the three categories of the studied dyes. The *K*/*S* values clearly demonstrated that the cationisation enhanced the colour yield of reactive prints because pretreatment with cationic reagents would introduce cationic groups into leather and wool samples, thus improving both substantivity and reactivity. At the same time, the printed cationic samples appeared much darker than the untreated ones when compared visually.

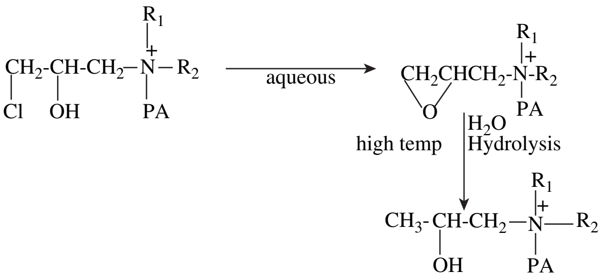
Fig. 3 shows the effect of Cibacron Yellow P6GS concentration on the *K*/*S* of the printed leather and wool samples. The curves illustrated that the maximum *K*/*S* value of the untreated leather was achieved at dye concentration 4 g/kg, while in case of cationised leather, the *K*/*S* values decreased by increasing the dye concentration. On the other side, the maximum colour strength value of the untreated wool was achieved at dye concentration 8 g/kg, while in case of the cationised wool, the maximum *K*/*S* value was achieved at 6 g/kg. This may be due to the increase in the cationised samples' reactivity, consequently, the dye concentration needed decreased.

Fig. 4 shows the effect of Procion Red MX-5B concentration on the *K*/*S* of printed leather and wool samples. The curves illustrated that the maximum *K*/*S* value of the cationised leather was achieved at dye concentration 4 g/kg, while the *K*/*S* values of the untreated leather gradually increased by increasing the dye concentration, this may be due to the greater affinity of the cationised leather towards Procion Red MX-5B compared with the untreated one. On the other side, the maximum *K*/*S* value of the cationised wool was achieved at dye concentration 4 g/kg, while in case of the untreated one, the maximum *K*/*S* value was achieved at 6 g/kg.

Fig. 5 shows the effect of Remazol Brilliant Orange FR concentration on the *K*/*S* of the printed leather and wool samples. The curves illustrated that the maximum colour strength of the cationised leather and wool samples was achieved at dye concentration 6 g/kg, while in case of the untreated ones, the colour strength gradually increased with increasing dye concentration.

It can be concluded that for the cationised leather and wool prints, low dye concentration was recommended relative to the untreated ones.

Fig. 6 shows the effect of the printing paste pH on the *K*/*S* of the printed leather and wool samples with Cibacron Yellow P6GS. The curves illustrated that the maximum *K*/*S* of the cationised leather was achieved at pH 3–5, while in case of the neutral medium, it



Scheme 3.

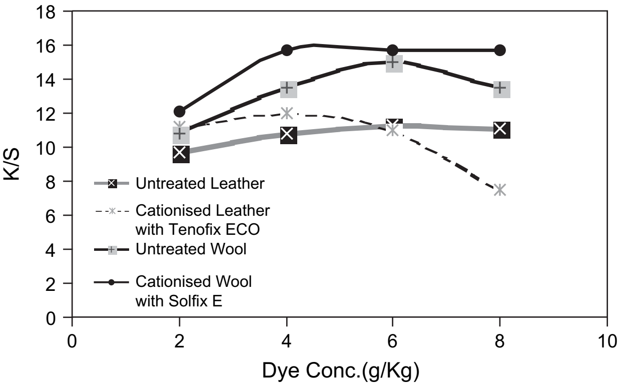


Fig. 4. Effect of Procion Red MX-5B concentration on the colour strength of the printed leather and wool samples.

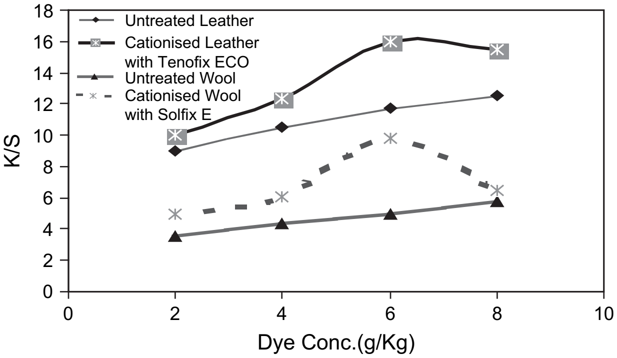


Fig. 5. Effect of Remazol Brilliant Orange FR concentration on the colour strength of the printed leather and wool samples.

decreased relative to the untreated one. This may be due to, in the acidic medium, the reactive dye acts as anionic dye, so, the negative charges at all the anionic groups of the used dye were attracted by the positive charges of the cationised leather. On the other side, the *K*/*S* of the cationised wool was maximum at neutral medium, while the optimum pH of the untreated wool was in the acidic medium (pH 3.0). Cationisation of wool gives additional sites to the fabric, so, the isoelectric point was changed and the printability of the cationised wool was increased in the neutral medium, while in case of the untreated wool, the printability was increased in the acidic medium.

Figs. 7 and 8 show the effect of the printing paste pH on the *K*/*S* of the printed leather and wool samples with Procion Red MX-5B and Remazol Brilliant Orange FR. The curves illustrated that the optimum pH in case of the cationised leather is 5.0, while in case of the untreated one is 3.0. On the other side, the optimum pH in case of the cationised wool is 7.0, while in case of the untreated one is 3.0.

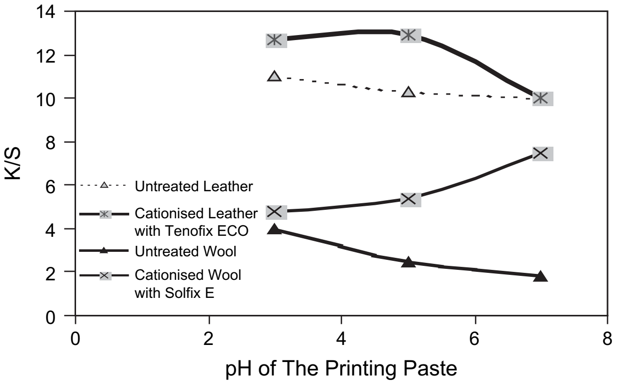


Fig. 6. Effect of pH on the colour strength of the printed leather and wool samples using Cibacron Yellow P6GS.

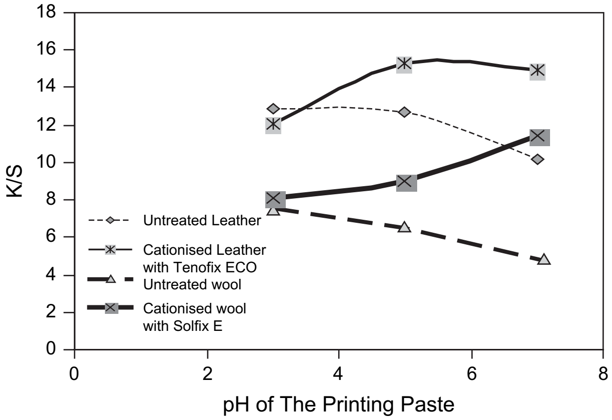


Fig. 7. Effect of pH on the colour strength of the printed leather and wool samples using Procion Red MX-5B.

3.3. Steaming

When the leather and wool samples entered the steamer, steam condensed on them, releasing their latent heat of condensation and heat of absorption, increasing the temperature of both substrates, and the steam moisture around them. For the untreated wool the optimum steaming condition was at 105 °C, for 20 min, while the cationisation treatment reduces the steaming time to only 5 min. Furthermore, there is a clear decrease in the steaming time needed to reach maximum colour strength. Also, the high steaming temperature for prolonged time causes gradual hydrolytic destruction of the cystine side linkages of wool leading to the formation of sulphydryl compound and sulphenic acid as follows [25]:

$$\underbrace{R-CH_2-S-S-CH_2-R_1}_{\text{cystine linkage}} + H_2O \xrightarrow[\text{at hight temp}]{\text{hydrolysis}}$$
$$R-CH_2-SOH + R_1-CH_2-SH$$

On the other side, in case of the untreated and cationised leather, the steaming temperature and time were adjusted to minimum printed dye fixation requirements

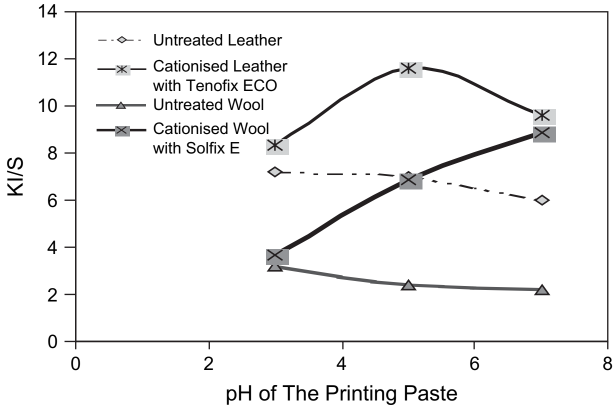


Fig. 8. Effect of pH on the colour strength of the printed leather and wool samples using Remazol Brilliant Orange FR.

Table 2
Effect of pre-cationisation on the fastness properties of the printed leather and wool samples

Substrate	Used dye	Modification	K/S	Fastness properties				
				Washing		Rubbing		Light
				Cotton[a]	Wool[a]	Dry	Wet	
Leather	A	Untreated	8.0	4–5	4	4–5	3–4	4
		Cationised	11.0	5	5	5	4	5–6
	B	Untreated	9.0	3	3	3–4	2–3	5
		Cationised	12.0	4	4	3–4	2–3	7
	C	Untreated	10.0	4	3–4	4	3	5–6
		Cationised	13.0	4–5	5	4	3	6
Wool	A	Untreated	4.2	4	4	4–5	3–4	5–6
		Cationised	5.0	4–5	4–5	5	4	6
	B	Untreated	3.5	3	2–3	3–4	2–3	5–6
		Cationised	6.2	3–4	3–4	3–4	2–3	6–7
	C	Untreated	2.5	3	3–4	4	3	6–7
		Cationised	7.0	3–4	4	4	3	7

A: Cibacron Yellow P6GS, B: Procion Red MX-5B, C: Remazol Brilliant Orange FR.

[a] Staining on the fabric.

(105 °C for 5 min) in order to avoid the direct exposure of the leather fiber to heat which causes fiber shrinking.

3.4. Fastness properties

As shown in Table 2, most of the fastness properties were improved by cationisation due to the formation of ionic bonds between the cationised leather and wool samples and the used dyestuffs. Due to presence of both the binder (casein) and the thickener which contribute to the negative/positive charges of the print paste according to pH, it would be expected that, the ionic interaction between the paste and the cationised leather and wool samples will enhance the washfastness. However, when the cationic reagent concentration was increased the degree of staining decreased because less dye was transported to the washing bath, this means that, if the cationisation level or cationic reagent concentration is appropriate for the dye concentration, 100% fixation of the printed dye can be achieved. The washfastness results with cationised leather were better for colour change and staining compared with the cationised wool. These results show that the staining problem can be solved for industrial applications by avoiding excess dye usage and by optimizing the washing off process. The solubility of any high molecular weight hydrolysed dye molecules that remain after fixation to cationic leather or wool is expected to be low, therefore, less dye desorption is expected during washing, consequently, the fastness ratings are improved. The high molecular weight binder and cationic reagents, which are well distributed at the treated leather and wool surfaces, prevent the aggregation of the dye molecules, this means that, the effect of the light fading decreased accompanied by an improvement in the light fastness. This improvement in light fastness of the cationised leather with the three reactive dyes follows the order:

Procion > Remazol > Cibacron

But in case of the cationised wool the following is the order:

Remazol > Procion > Cibacron

The rubbing fastness was slightly altered, in other words, no significant difference in the rubbing fastness of the cationised leather and wool samples compared with the untreated ones.

4. Conclusion

Choosing an appropriate pretreatment system for printing leather and wool substrates involves the careful selection based on experimentation of the appropriate set of conditions and dye to achieve brilliant shades with high colour strength and colour fastness. The colour strength depends on the structure of the reactive dyestuff as well as the type of substrate and the extent of modification.

The effect of the dye concentration on the colour strength of cationised leather and wool prints investigated showed that low dye concentration was recommended compared with the untreated ones. This means that using pre-cationisation treatment in reactive printing on both the substrates leads to a decrease in the dye concentration of around 30%, in addition to the cationisation pretreatment that accelerates the fixation rate of the printed dye.

References

[1] Krigel R. Melliand International 1998;2:133.

[2] Miles LWC. Textile printing. 2nd ed. Bradford: Society of Dyers and Colorist; 1994.

[3] Iyer ND. Colourage 2000;12:69.

[4] Kanik M, Hauser PJ. Coloration Technology 2002;118:300.

[5] Hauser PJ, Tabba AH. Coloration Technology 2001;117:282.

[6] Hauser PJ. American Association of Textile Chemists and Colorists 2000;32(6):22.

[7] Chaudhary AN, Smith B. American Association of Textile Chemists and Colorists January 2003;27.

[8] Lewis DM, Lei XP. Journal of the Society of Dyers and Colorist 1991;107:102.

[9] Otto G. Das Faerben des leders Teil (I). Darmstadt, Germany: Eduard Roether Verlage; 1962. p. 96.

[10] Pocket book for the leather technologists. 2nd ed. Germany: BASF Aktiengesellschaft; 1986.

[11] Bienkiewicz K. Physical chemistry of leather making. Florida, USA: Robert E. Krieger Pub.; 1983. p. 445 [chapter 18].

[12] Cardamone JM, Turner JD. American Association of Textile Chemists and Colorists 2000;32(6):49.

[13] El-Shishtawy RM, Nassar SH. Coloration Technology 2002; 118:115.

[14] Miles LWC. Textile printing. 2nd ed. Bradford: Society of Dyers and Colorist; 1994. p. 185 [chapter 5].

[15] Tiwan SK, Prajapati KG, Charia MM. Colourage September 2001;17.

[16] Hauser J, Kanik M. American Association of Textile Chemists and Colorists 2003;3:27.

[17] Kubelka P, Munk FZ. Techniques and Physics 1931;12:593.

[18] Goreczky LHL, Ungarn RH. Das Leder 1987;18:111.

[19] AATCC technical manual. North Carolina: AATCC; 2002.

[20] Heidemann E, Harenberg O, Bresler H. Das Leder 1969;20:273.

[21] Euro-Standard NMP551 Nr.09–97D: leather tests for colour fastness – colour fastness to rubbing; 1997.

[22] DIN54004: determination of colour fastness to light of dyeing; 1983.

[23] Official analytical methods. 15th ed. Arlington, USA: Association of analytical chemists; 1990.

[24] Bienkiewicz K. Physical chemistry of leather making. Florida, USA: Robert E. Krieger Pub.; 1983. p. 413–6 [chapter 17].

[25] Sadov F, Korchagin M, Matetsky A. Chemical technology of fibrous materials. Moscow: MIR Publishers; 1973. p. 82–6 [chapter 7].