Available online at www.sciencedirect.com
ScienceDirect
Dyes and Pigments 74 (2007) 258–261
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Aftertreatment of direct dyes on wool and nylon 6 with syntans and a syntan/cationic system

M. Feiz [a,*], S. Mallakpour [b], M.A. Azizollahi [a]

[a] *Textile Department, Isfahan University of Technology, Isfahan 84156-83111, Iran*
[b] *College of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Iran*

Received 23 November 2005; received in revised form 7 January 2006; accepted 6 February 2006
Available online 9 May 2006

Abstract

Three different syntans were synthesized by condensation of (1) *p*-cresol, formaldehyde and 4-hydroxy benzene sulfonic acid, (2) *p*-cresol, formaldehyde and 6-hydroxy-2-naphthalene sulfonic acid, (3) *p*-cresol, formaldehyde and phenol, followed by sulfonation; the structures of these syntans were characterized using ^{1}H NMR and FTIR. The effect of aftertreatment with the synthesized syntans, a commercial syntan and a syntan/cation system on the wash fastness of dyed nylon 6 and wool fabrics was determined. Aftertreatment of the dyeings using above syntans improved the wash fastness; further improvement was achieved by the sequential application of a cationic compound to the fabrics.

Keywords: Syntans; Wash fastness; Aftertreatment; Wool; Nylon 6

1. Introduction

At present, one method which can be used for improving the wash fastness of anionic dyes on nylon is an aftertreatment with a synthetic tanning agent (syntan). As the name implies, syntans were developed as alternatives to natural tannins in the tanning of leather, subsequent development leads to products that were specifically intended for use in aftertreatment of dyed nylon [1–4]. Syntans for nylons are, typically, water-soluble anionic formaldehyde polycondensates of dihydroxy diarylsulfones (typically dihydroxy diphenyl sulfone) [5,6]. These syntans can be prepared by three basic routes [7].

(a) Condensation of the phenol with formaldehyde followed by sulfonation;
(b) Sulfonation of the phenol followed by condensation with formaldehyde [8];
(c) Condensation of the phenol with formaldehyde followed by sulfonation and then further condensation with formaldehyde.

Current theories regarding the mechanism of wash fastness improvement of anionic dyes on nylon by aftertreatment with these agents propose that the desired molecular mass of such polycondensates is below 1000 g/mol as larger molar mass compounds tend to be insoluble in water [9,10]; preferred compounds exhibit a minimum branching and cross-linking [11]. Although syntans are commonly marketed as sodium sulfonates other metal cations have also been used [12].

Some syntans contain additional polar groups such as carbamid, sulfamid or ureido [13,14]. It is considered that condensation products in which each repeat unit contains only one sulfonate group are more effective than corresponding products in which each repeat unit contains two or more sulfonate groups. Also syntan becomes more effective as the ratio of repeating units containing sulfonates groups that are devoid of sulfonate groups increases [12].

Selected direct dyes which exhibit good affinity for nylon and wool are economically more attractive than acid dyes

* Corresponding author.
E-mail address: m_feiz@cc.iut.ac.ir (M. Feiz).

0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.02.015

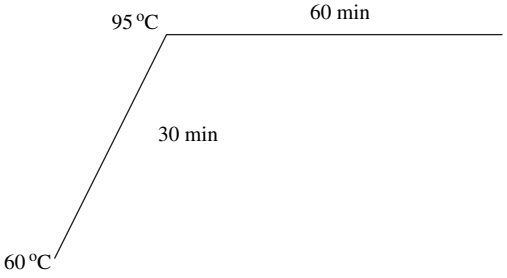


Fig. 1. Dyeing method.

for certain colours and so can be used to produce dark colours. The purpose of this investigation is to study the aftertreatment of direct dyes on wool and nylon with syntans and cationic system.

2. Experimental

2.1. Materials

2.1.1. Fabrics

Knitted nylon 6 fabric (69 g^{-2}) and serge twill, semi-worsted wool (314 g^{-2}) were used. Nylon and wool were scoured before use by treating in a solution of 2 g l^{-1} of Epicol ESB70 (a non-ionic surfactant) at 40 °C for 15 min, the scoured fabric was rinsed thoroughly in tap water and allowed to dry in the open air.

2.1.2. Dyes

The following commercial direct dyes were used. *Chrysophenine GX* (C.I. Direct Yellow 12, from Kaseihin Kogyo Kyokai), *Direct Orange SE* (C.I. Direct Orange 26, from Multicrom), and *Direct Green 6* (C.I. Direct Green 6, from Pigmentos Y Oxidos).

Commercial sample of *Cetafix AFA* (Avocet Dye & Chemical Co. Ltd) as a synthetic tanning agent and *Fixogen CD* (an aminoplast cationic resin, from Francolor, Paris) as cationic agent were used. Other chemicals were purchased from Merck Chemical Co.

FTIR spectra were recorded on a Bomem-MB 100 and ^1H NMR spectra were obtained using a Bruker-TM 500 MHz instrument.

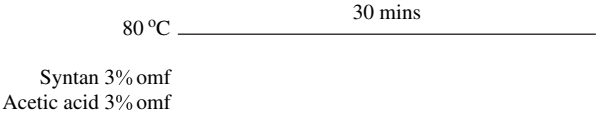
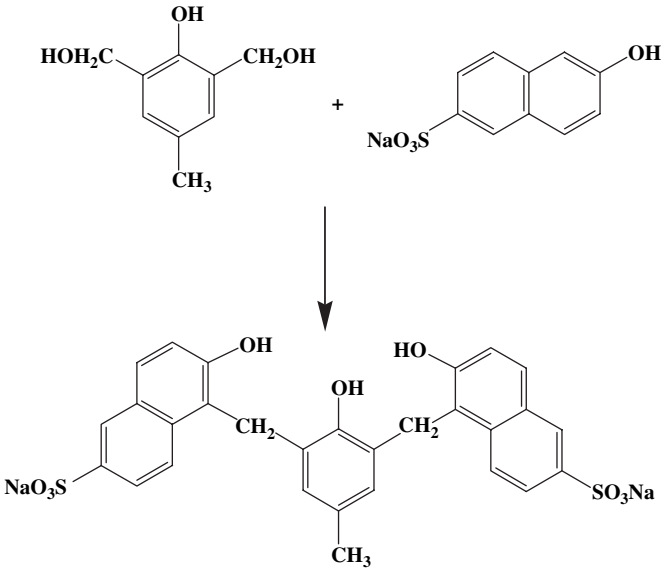


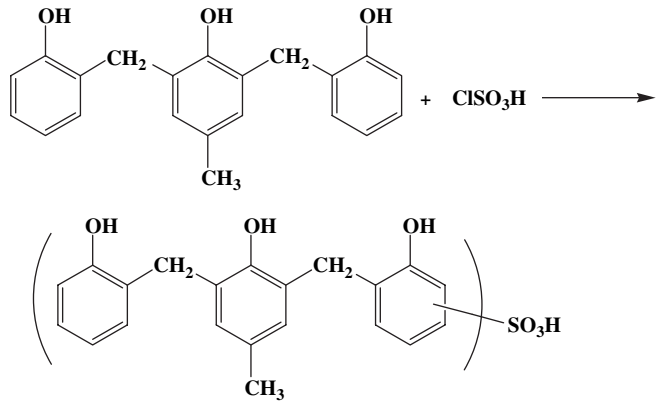
Fig. 2. Syntan aftertreatment.



Scheme 1.

2.2. Synthesis of syntan A

Syntan A was prepared in three steps. In the first step, 2-naphthol was reacted with sulfuric acid according to the procedure described earlier [15], which gave 6-hydroxy-2-naphthalene sulfonic acid. In the second step, to a mixture of *p*-cresol (10.8 g, 0.1 mol), 8 ml water and 40% aqueous formaldehyde (17 g, 0.22 mol) was added 5 ml of 30% aqueous sodium hydroxide. The solution was heated to 58 °C and maintained at this temperature for 90 min. After this time the reaction mixture was allowed to cool and then acidified with 40% aqueous sulfuric acid. Crushed ice was added and the dimethylol derivative of *p*-cresol separated as an oil, and then solidified upon standing at room temperature. The aqueous layer was removed and the solid compound was washed with water until free of sodium sulfate. In the third step, a mixture of 6-hydroxy-2-naphthalene sulfonic acid (44.8 g, 0.2 mol) was dissolved in a minimum amount of water and conc. hydrochloric acid (0.4 ml), and stirred at 40 °C in a three-neck round-bottomed flask. To this mixture was added



Scheme 2.

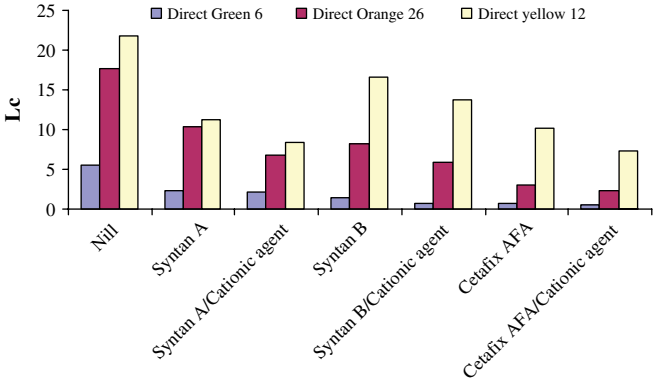


Fig. 3. Effect of aftertreatment on dyed nylon 6.

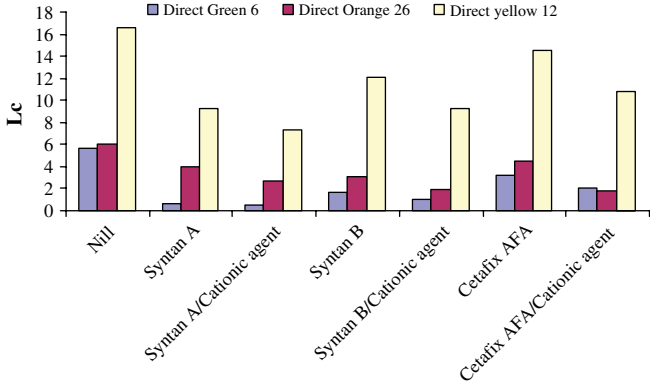


Fig. 4. Effect of aftertreatment on wool.

the above dimethylol compound and the temperature was increased to 95 °C and maintained at 94–98 °C for 2 h; the solution was then cooled to 25 °C and left for 48 h. The resulting compound was obtained as brown crystals (46.40 g, 80%) that were soluble in water.

2.3. Synthesis of syntan B

Phenol (95 g, 1.02 mol) and conc. hydrochloric acid (2 ml) were stirred at 40 °C. To this mixture the dimethylol of *p*-cresol (84 g, 0.5 mol) (as described in the synthesis of syntan A) was added and the temperature was then increased to 95 °C and maintained at this temperature for 2 h. After this time steam was injected into the reaction mixture to remove unreacted phenol. Upon cooling, the solid compound was obtained. To the above finely ground resin (20 g, 0.07 mol) were added 20 ml of carbon tetrachloride and chlorosulfonic acid (23 g, 0.17 mol). The mixture was stirred at 40 °C and maintained at this temperature for 2 h. After this time 25 ml of water was added and the resulting solution neutralized with 30% aqueous sodium hydroxide. A yellow-brownish, water-soluble solid compound was obtained.

2.4. Synthesis of syntan C

Phenol was reacted with sulfuric acid according to the method published earlier [16]; 4-hydroxy benzene sulfonic acid was obtained. The reactions between *p*-cresol, formaldehyde, 4-hydroxy benzene sulfonic acid were identical to those described for the synthesis of syntan A, except that 4-hydroxy benzene sulfonic acid was replaced with 6-hydroxy-2-naphthalene sulfonic acid. This compound due to insufficient solubility in water was not a suitable syntan for improvement of wash fastness of direct dyes. Thus, was not used in this work.

2.5. Dyeing

All dyeings were carried out using fabric (1.5 g) which had been wetted out in cold tap water, sealed in stainless steel dye pots of 150 ml capacity housed in a Ahiba-Polymat Laboratory scale dyeing machine using a liquor ratio of 30:1. The dyeing method used is shown in Fig. 1, according to the recommended method [17].

2.6. Syntan aftertreatment

Samples of dyed nylon 6 and wool were aftertreated in sealed, stainless steel dye pots of 150 ml capacity housed in a Ahiba-Polymat Laboratory dyeing machine according to a recommended method [3] using a liquor ratio of 30:1. The aftertreatment method is shown in Fig. 2. At the end of aftertreatment the samples were removed, rinsed thoroughly in tap water and dried in air.

2.7. Cationic agent aftertreatment

Samples of dyed, syntanned nylon 6 and wool fabric were aftertreated with Fixogen CD in sealed, stainless steel dye pots in a Ahiba-Polymat Laboratory-scale dyeing machine. At the end of aftertreatment with syntan (2% omf), the syntanned dyed material was rinsed thoroughly with tap water and treated with the cationic agent (2% omf) using a liquor ratio of 50:1 at pH 5 (adjusted using acetic acid) for 20 min at 50 °C. The treated dyeing was then rinsed thoroughly with tap water and allowed to dry in air.

Table 1
Lc data obtained from aftertreatment on nylon 6

C.I.	Cetafix AFA /cationic agent	Cetafix AFA	Syntan B /cationic agent	Syntan B	Syntan A /cationic agent	Syntan A	Nill
Direct Green 6	0.53	0.67	0.78	1.51	2.23	2.35	5.54
Direct Orange 26	2.28	3.04	5.93	8.3	6.74	10.27	17.6
Direct Yellow 12	7.38	10.14	13.7	16.61	8.32	11.31	21.87

Table 2
Lc data obtained from aftertreatment on wool

C.I.	Cetafix AFA /cationic agent	Cetafix AFA	Syntan B /cationic agent	Syntan B	Syntan A /cationic agent	Syntan A	Nill
Direct Green 6	2.11	3.26	0.98	1.63	0.57	0.61	5.69
Direct Orange 26	1.85	4.52	1.93	3.04	2.67	4.03	6.08
Direct Yellow 12	10.84	14.5	9.27	12.12	7.35	9.26	16.61

2.8. Fastness determination

The wash fastness of the dyed and aftertreated samples was determined according to the ISO CO6/E1 for nylon 6 and ISO CO6/B1 for wool at two different washing temperatures (70 °C, 95 °C for nylon 6 and 50 °C, 70 °C for wool). At the end of the fastness tests the absorbance of the residual wash solution was measured using a Varian Cary 300 spectrophotometer, and the absorbance (A) was converted to concentration (C) using Beer's–Lambert law. The percent of dye loss that occurred during the wash test was calculated using Eq. (1), where M_w is the amount of dye lost during washing, M_0 and M_d are the amounts of dye at time 0 and at the end of dyeing process.

$$\mathrm{Lc} = (M_w/(M_0 - M_d)) \times 100 \quad (1)$$

3. Results and discussion

Scheme 1 shows the synthesis of syntan A.

The IR spectrum of syntan A showed characteristic sulfonate salt absorption peaks at 1185 and 1115 cm^{-1}, aromatic hydroxyl group at 3420 cm^{-1} and methylene group at 2917, 2859, and 1479 cm^{-1}. The ^{1}H NMR spectrum of syntan A assigned characteristic bands of the aromatic ring proton between 7 and 8 ppm, and the methylene proton around 4.04 ppm; a peak due to the methyl group appeared at 2.26 ppm. Also, characteristic band of the hydroxyl proton appeared at 6.19 ppm.

Scheme 2 shows the synthesis route for the syntan B.

The IR spectrum of syntan B showed characteristic sulfonate salt absorption peaks at 1169, 1035, and 614 cm^{-1}, aromatic hydroxyl group at 3449 cm^{-1} and methylene group at 2921 cm^{-1}. The ^{1}H NMR spectrum of syntan B assigned characteristic bands of the aromatic ring proton between 7.00 and 8.00 ppm, and the methylene proton around 2.29 ppm. A peak due to the methyl group appeared at 3.76 ppm and the characteristic band of the hydroxyl proton appeared at 6.56 ppm.

Fig. 3 and Table 1 show the effect of the aftertreatment of dyed nylon 6 with syntans, from which it is evident that a marked improvement in wash fastness of the three direct dyes occurred. However, the use of the syntans in conjunction with the cationic agent was more effective in reducing the extent of dye removed during washing. This can be explained in terms of the greater interaction between cationic agent and the anionic syntan, which produces a complex molecule during aftertreatment that is less soluble in aqueous solution.

Fig. 4 and Table 2 show the effect of the aftertreatment of dyed wool with the syntans. An improvement in wash fastness was clearly obtained and further improvement was achieved using the syntans in conjunction with the cationic agent.

4. Conclusions

Two syntans were synthesized and the structures of these syntans were determined by ^{1}H NMR and FTIR techniques. The aftertreatment of the direct dyes on wool and nylon 6 with these synthesized syntans as well as a commercial syntan improved wash fastness. The sequential application of a cationic compound to the syntanned dyeing caused a further improvement in wash fastness. Furthermore it is interesting to mention that synthesized syntans A and B are more effective than commercial syntan (Cetafix AFA) in wash fastness improvement, this could be due to more active ingredient content of the synthesized syntans.

References

[1] Burkinshaw SM. The application of dyes. In: Waring DR, Hallas C, editors. The chemistry and application of dyes. New York: Plenum Publishing; 1990. p. 237–380 [chapter 7].
[2] Burkinshow SM, Maseka KD. Dyes Pigments 1996;30:21.
[3] Blackburn RS, Burkinshaw SM. J Soc Dyers Colour 2000;116:3.
[4] Burkinshow SM, Bahojb-Allafan B. Dyes Pigments 2003;58:205.
[5] Tomita M, Tokitaka M. J Soc Dyers Colour 1980;96:297.
[6] Cook CC. Rev Prog Color 1982;12:73.
[7] Chen PS. Syntans and newer method of tanning. The chemical elements. Massachusetts; 1950.
[8] Kelson JS, Holt LA. J Soc Dyers Colour 1992;108:327.
[9] USP 4,619,853; 1986.
[10] USP 4,680,212; 1987.
[11] Cook TF. Stain blockers for nylon carpets. New Jersey: Text Res Inst; 1991.
[12] Burkinshaw SM. Chemical principles of synthetic fiber dyeing. London: Blackie; 1995.
[13] Speakman JB, Saville AK. J Text Inst 1946;37:271.
[14] Hill R. Fiber from synthetic polymers. Amsterdam: Elsevier; 1946. 1953.
[15] Gilbert E. Sulphonation and related reaction. New York: John Wiley &Sons, Inc.; 1965.
[16] Othmer K. Encyclopedia of chemical technology. New York: John Wiley &Sons, Inc.; 1967.
[17] Giles CH. A laboratory course in dyeing. Bradford, UK: The Society of Dyers and Colorists; 1971.