Iranian Polymer Journal
15 (5), 2006, 359-365

Available online at: http://journal.ippi.ac.ir

The Aftertreatment of Direct Dyes on Wool and Nylon 6 with Synthetic Tanning Agents and Full Backtan

Mahmood Feiz[1*], Shadpour Mallakpour[2], and
Mohammad Ali Azizollahi[1]

(1) Textile Department; (2) College of Chemistry,
Isfahan University of Technology, Isfahan-84156/83111, Iran

Received 20 July 2005; accepted 9 April 2006

ABSTRACT

Wool and nylon 6 knitted fabrics were dyed using three commercial direct dyes which are suitable for nylon and wool fabrics. The dyed samples were aftertreated, using two different syntans and full backtan. When all dyeings were subjected to two consecutive ISO CO6 wash tests, it was found that all aftertreatments provided an improvement on wash fastness. However aftertreatment of the dyeing using full backtan, improved wash fastness to the greater extent than commercial and synthesized syntans. This improvement for C.I. Direct Yellow 12 is higher, since this dye belongs to class A, which has low wash fastness property; thus, the full backtan in this case is more effective. Although the full backtan is effective in improving the wash fastness of direct dyes on nylon 6 and wool, but, the aftertreatment is rarely used owing to the toxicity of potassium antimony tartarate because it can impair the handle and the light fastness of dyeing as well as impart a shade change in dyeing. An aftertreatment with a syntan has mostly replaced the full backtan as a means of improving the wash fastness of direct dyes on nylon 6 and wool. Syntans offer the advantage of being applied in single stage process and do not suffer from the disadvantage displayed by their natural counterpart, however it is generally accepted that an aftertreatment with a syntan is not as effective as an aftertreatment with the full backtan.

Key Words:
syntan;
full backtan;
wash fastness;
aftertreatment.

(∗) To whom correspondence to be addressed.
E-mail: m_feiz@cc.iut.ac.ir

INTRODUCTION

The advantages of dyeing of nylon and wool with anionic dyes, besides that of cost, have variety of bright colours which can be produced over average of depths and simple application of this dye. In practice, however problems can arise with anionic dyes on nylon and wool since some of them show poor fastness properties [1]. Aftertreatments are thus frequently used to improve the wash fastness by either back tanning with natural tannins and tartar emetic or a syntan [1-3]. Recently the effect of aftertreatment of acid dyes and disulphonated 1:2 pre-metallized acid dyes on nylon 6 by tannic acid and synthetic tanning agents have been reported [4,5].

Synthetic tanning agents (syntans) can be divided into numerous types, however they are mainly prepared from condensation reaction of formaldehyde with phenol sulphonic or naphthol sulphonic acids. Some contain polar groups such as carbamide, sulphonamide and ureides [1]. The main types are as follows:

- Phenolic Type: Aromatic compounds containing phenolic-OH groups, e.g phenol, cresol, naphthol, and bisphenol, which are used as starting materials, though compounds of this type enhance fixation, they tend to give reddish stains on treated fabric. Increasing the number of sulphonic acid groups in that molecule tends to increase its affinity on nylon and wool [1].

- Thiophenolic Type: Syntans of this type can be produced by the reaction of phenolic compounds with molten sulphur. Hydrophilic groups, such as sulphonic acid, methanesulphonic acid or the sodium salt, are introduced into the compound in order to obtain the solubility in water [1].

- Dihydroxy diphenyl sulphone (DOS) Type: Syntans from DOS have been prepared commercially in recent years. DOS Syntans resemble the condensates of phenolic type in that they contain -OH and $-SO_3H$ groups but $-SO_2$ group is para to the phenolic-OH, although preventing discolouration by formation of *p*-quinone, lower light fastness is obtained. An improvement in fixation efficiency can be achieved by forming a complex between the -OH groups and metal ions [1].

It is considered that syntans and full backtan adsorbed at the periphery of the dyed fibre and their ability to provide improvement on the wash fastness, is due to this peripheral layer of syntan or full backtan molecules, reducing the propensity of the dye to diffuse out of the fibres, during the washing periods [6,7].

In this paper a commercial syntan, two different synthetic syntans (which were synthesized) and a full backtan were applied on wool and nylon 6 fabrics. The effectiveness of full backtan, commercial and synthesized syntans for improving the wash fastness of direct dyes on these fabrics were examined.

EXPERIMENTAL

Materials

Fabrics

Knitted nylon 6 fabric (69 $g.m^{-2}$) and one type of scoured serge twill semi-worsted wool (314 $g.m^{-2}$) were used.

Dyes

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

Auxiliaries

Two types of syntans which were synthesized by the reaction of 2,6-bis-hydroxylmethyl-4-methyl phenol with 2-hydroxy naphthalene-6-sulphonic acid (syntan A) and reaction of 2,6-bis-hydroxylmethyl-4-methyl phenol with 4-hydroxy benzene sulphonic acid similar to Cibatex PA [8] and a commercial syntan were used. The commercial syntan with name Cetafix AFA was purchased from Avocet Dye & Chemical Co.

Procedures

Dyeing

All dyeings were carried out using fabrics (1.5 g) which were wetted out in cold tap water, in sealed, stainless steel dye pots of 150 mL capacity housed in

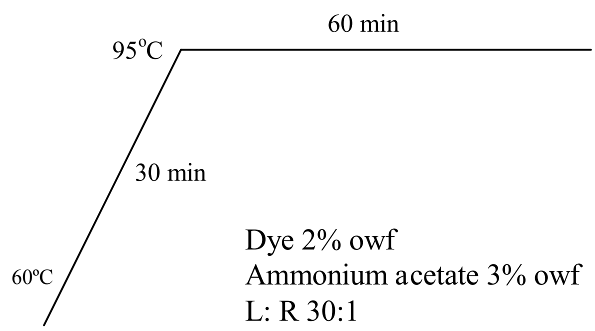

Figure 1. Dyeing method for nylon 6.

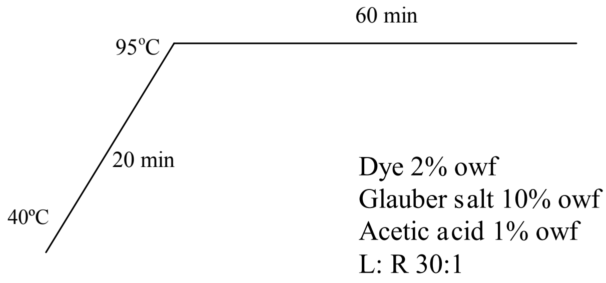

Figure 2. Dyeing method for Direct Orange 26 and Direct Yellow 12 on wool.

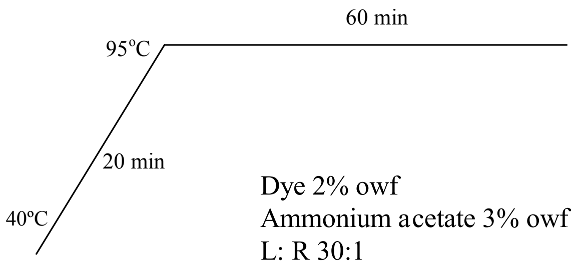

Figure 3. Dyeing method for Direct Green 6 on wool.

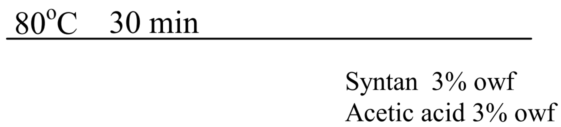

Figure 4. Syntan aftertreatment.

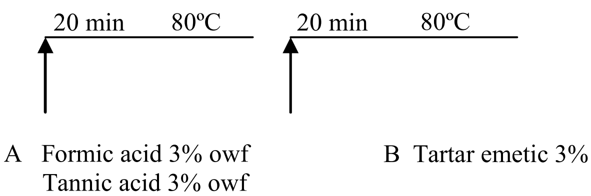

Figure 5. Full backtan aftertreatment.

an Ahiba-Polymat Laboratory scale dyeing machine using a liquor ratio of 30:1. The dyeing method used for nylon is shown in Figure 1, according to the recommended method [9]. The method used for Direct Orange 26, Direct Yellow 12 and Direct Green 6 on wool is shown in Figures 2 and 3.

Syntan Aftertreatment

Samples of dyed nylon 6 and wool were aftertreated in sealed stainless steel dye pots of 150 mL capacity housed in an Ahiba-Polymat Laboratory scale dyeing machine according to a recommended method [10], using a liquor ratio of 30:1. The aftertreatment method is shown in Figure 4. At the end of aftertreatment the samples were removed, rinsed thoroughly in tap water and dried in the open air.

Full Backtan Aftertreatment

The aftertreatment method is shown in Figure 5. The aftertreated samples were removed, rinsed thoroughly in tap water and allowed to dry in air.

Fastness Determination

The wash fastness of the dyed and aftertreated samples was determined using ISO CO6/D1, ISO CO6/E1 for nylon 6 and ISO CO6/D1, ISO CO6/B1 for wool in two washing temperatures. At the end of fastness tests the absorbance of the residual wash solution was measured using a Varian Cary 300 spectrophotometer. The dye stability toward the washing test was calculated using eqn (1), where A_0 and A_d are the absorbance of dye at time 0 and end of dyeing multiply on the number of dilution, A_w is the absorbance of dye in washing liquor at the end of washing multiply by number of dilution and DS is the dye stability in the fibre (wash fastness properties).

$$DS = (1-(A_w/A_0-A_d)) \times 100 \qquad (1)$$

RESULTS AND DISCUSSION

In this work three direct dyes which are suitable for nylon and wool were selected. These dyes belong to class A and C. Because direct dyes have good affinity for nylon and wool and have good wash fastness, therefore the washing temperatures were selected higher than normal, the selected temperatures were 70°C and 95°C for nylon 6, 50°C and 70°C for wool, respectively. In the context of the wash fastness change which the dyeings underwent different aftertreatments and when they were subjected to two consecutive fastness tests at two different washing temperatures, wash fastness was determined by dye

Table 1. Dye stability data obtained for C.I. Direct Yellow 12 on nylon 6 washed at 95°C.

Aftertreatment	A_0	A_d	A_w	DS
Full backtan	14.69	0.1	1.89	86.98
SyntanA	14.69	0.1	2.43	83.34
SyntanB	14.69	0.1	2.97	79.64
CetafixAFA	14.69	0.1	2.97	79.64
Nil	14.69	0.1	3.86	73.54

A_0, A_d, A_w: absorbance×number of dilution.

Table 2. Dye stability data obtained for C.I. Direct Orange 26 on nylon 6 washed at 95°C.

Aftertreatment	A_0	A_d	A_w	DS
Full backtan	12.17	0	0.63	94.82
SyntanA	12.17	0	1.12	90.80
SyntanB	12.17	0	0.79	93.76
CetafixAFA	12.17	0	0.72	94.08
Nil	12.17	0	1.51	87.59

A_0, A_d, A_w: absorbance×number of dilution.

Table 3. Dye stability data obtained for C.I. Direct Green 6 on nylon 6 washed at 95°C.

Aftertreatment	A_0	A_d	A_w	DS
Full backtan	6.34	0.38	0.25	95.81
SyntanA	6.34	0.38	0.29	95.13
SyntanB	6.34	0.38	0.38	93.62
CetafixAFA	6.34	0.38	031	94.80
Nil	6.34	0.38	0.51	91.44

A_0, A_d, A_w: absorbance×number of dilution.

Table 4. Dye stability data obtained for C.I. Direct Yellow 12 on nylon 6 washed at 70°C.

Aftertreatment	A_0	A_d	A_w	DS
Full backtan	14.69	0.1	1.33	90.88
SyntanA	14.69	0.1	1.65	88.69
SyntanB	14.69	0.1	2.35	83.39
CetafixAFA	14.69	0.1	1.48	89.86
Nil	14.69	0.1	3.19	78.13

A_0, A_d, A_w: absorbance×number of dilution.

Table 5. Dye stability data obtained for C.I. Direct Orange 26 on nylon 6 washed at 70°C.

Aftertreatment	A_0	A_d	A_w	DS
Full backtan	12.17	0	0.93	92.36
SyntanA	12.17	0	1.25	89.73
SyntanB	12.17	0	1.01	91.7
CetafixAFA	12.17	0	0.37	96.96
Nil	12.17	0	1.41	82.43

A_0, A_d, A_w: absorbance×number of dilution.

Table 6. Dye stability data obtained for C.I. Direct Green6 on nylon 6 washed at 70°C.

Aftertreatment	A_0	A_d	A_w	DS
Full backtan	6.34	0.38	0.17	97.14
SyntanA	6.34	0.38	0.14	97.65
SyntanB	6.34	0.38	0.09	98.49
CetafixAFA	6.34	0.38	0.04	99.33
Nil	6.34	0.38	0.33	94.46

A_0, A_d, A_w: absorbance×number of dilution.

Table 7. Dye stability data obtained for C.I. Direct Yellow 12 on wool washed at 70°C.

Aftertreatment	A_0	A_d	A_w	DS
Full backtan	14.69	0	2.84	80.57
SyntanA	14.69	0	4.8	67.32
SyntanB	14.69	0	3.33	77.33
CetafixAFA	14.69	0	4.15	71.75
Nil	14.69	0	5.73	60.99

A_0, A_d, A_w: absorbance×number of dilution.

Table 8. Dye stability data obtained for C.I. Direct Orange 26 on wool washed at 70°C.

Aftertreatment	A_0	A_d	A_w	DS
Full backtan	12.17	0	2.1	82.74
SyntanA	12.17	0	2.7	77.81
SyntanB	12.17	0	3.5	71.24
CetafixAFA	12.17	0	2.3	81.10
Nil	12.17	0	4.5	63.02

A_0, A_d, A_w: absorbance×number of dilution.

stability (DS) equation. Advantage of this approach for determination of wash fastness is that even low degree of variation in wash fastness change could be measured. Data values for dye stability are in the range of 0-100, that the higher DS shows higher wash fastness and lower alteration. Tables 1 to 12 and Figures 6 to 9 show the DS data obtained for the three direct dyes.

Traditional Full Backtan on Nylon 6

Aftertreatment of three dyes with the traditional full backtan, markedly improved the wash fastness of each of the dyes at two wash fastness tests. Figures 6 and 7 show the extent to which the full backtan increases dye stability at higher degree, that means the reduction in dye loose during of washing period, therefore provides an improvement in wash fastness.

Table 9. Dye stability data obtained for C.I. Direct Green 6 on wool washed at 70°C.

Aftertreatment	A_0	A_d	A_w	DS
Full backtan	6.34	1.42	0.76	84.55
SyntanA	6.34	1.42	0.78	84.15
SyntanB	6.34	1.42	0.83	83.13
CetafixAFA	6.34	1.42	0.98	80.08
Nil	6.34	1.42	1.36	72.36

A_0, A_d, A_w: absorbance×number of dilution.

Table 10. Dye stability data obtained for C.I. Direct Yellow 12 on wool washed at 50°C.

Aftertreatment	A_0	A_d	A_w	DS
Full backtan	14.69	0	1.25	84.17
SyntanA	14.69	0	1.07	73.21
SyntanB	14.69	0	1.19	81.34
CetafixAFA	14.69	0	1.13	77.28
Nil	14.69	0	0.96	65.31

A_0, A_d, A_w: absorbance×number of dilution.

Table 11. Dye stability data obtained for C.I. Direct Orange 26 on wool washed at 50°C.

Aftertreatment	A_0	A_d	A_w	DS
Full backtan	12.17	0	1.07	87.71
SyntanA	12.17	0	0.97	79.67
SyntanB	12.17	0	1.14	83.90
CetafixAFA	12.17	0	0.98	81.24
Nil	12.17	0	0.85	70.28

A_0, A_d, A_w: absorbance×number of dilution.

Table 12. Dye stability data obtained for C.I. Direct Green 6 on wool washed at 50°C.

Aftertreatment	A_0	A_d	A_w	DS
Full backtan	6.34	1.42	0.45	92.45
SyntanA	6.34	1.42	0.41	85.13
SyntanB	6.34	1.42	0.44	89.18
CetafixAFA	6.34	1.42	0.43	87.68
Nil	6.34	1.42	0.37	75.91

A_0, A_d, A_w: absorbance×number of dilution.

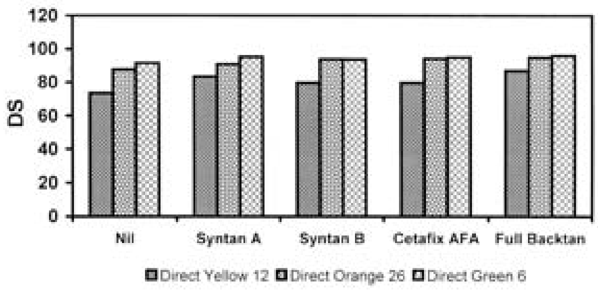

Figure 6. Effect of aftertreatments on nylon 6 washed at 95°C.

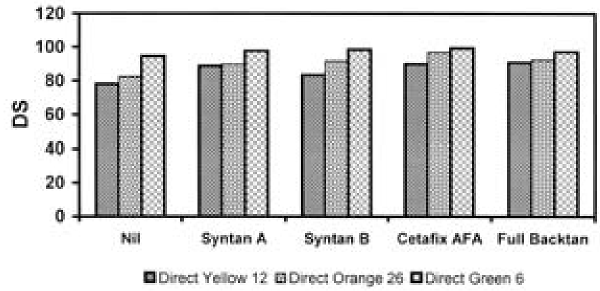

Figure 7. Effect of aftertreatments on nylon 6 at 70°C.

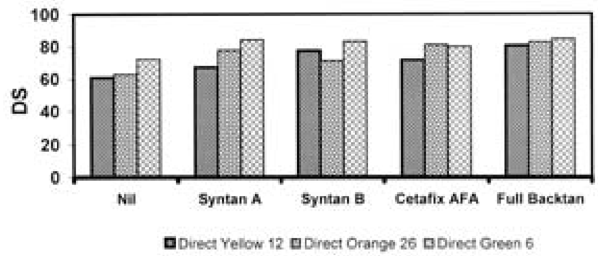

Figure 8. Effect of aftertreatments on wool at 70°C.

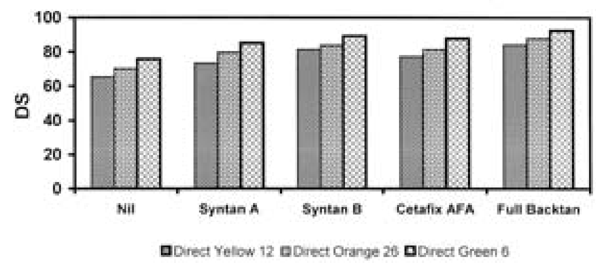

Figure 9. Effect of aftertreatments on wool at 50°C.

This improvement for yellow dye is higher, since this dye belongs to class A, which has low wash fastness property; thus, the full backtan in this case is more effective.

Effect of Syntans on Nylon 6

Although the full backtan is effective in improving the wash fastness of anionic dyes on nylon 6, but, the aftertreatment is nowadays rarely used owing to the toxicity of potassium antimony tartarate and because it can impair the handle and the light fastness of dyeing as well as impart a shade change in dyeing [11]. An aftertreatment with a syntan has mostly replaced the full backtan as a means of improving the wash fastness of anionic dyes on nylon 6. Syntans offer the advantage of being applied in single stage process and do not suffer from the disadvantage displayed by their natural counterpart, however it is generally accepted that an aftertreatment with a syntan is not as effective as an aftertreatment with the full backtan [11].

Aftertreatment with 3% owf of each of the above three syntans improved the wash fastness and reduced the dye loose in washing tests (Figures 6 and 7). The dye stability data for three syntans are shown in Tables 1 to 6 for comparison, which little difference has been observed between three syntans.

Traditional Full Backtan on Wool

Figures 8 and 9 and Tables 7 to 12 show that the full backtan is more effective in improvement of the wash fastness of anionic dyes on wool, which full backtan increases dye stability to higher degree. The effect of full backtan on three direct dyes on wool is similar to nylon 6. Here also yellow dye showed higher degree of improvement.

Effect of Syntans on Wool

Tables 7 to 12 and Figures 8 and 9 demonstrate the effect of syntans in improvement of the wash fastness of three direct dyes on wool, but improvement of the wash fastness was not so significant.

CONCLUSION

This is the first report of application of direct dyes on nylon 6 and wool using the syntans. Four established aftertreatments were used in this work (one commercial syntan, two synthesized syntans and the traditional full backtan). The effect of these aftertreatments was obtained, according to a new approach that is related to wash fastness. The observations recommended that full backtan showed higher degree of improvement wash fastness on wool and nylon 6. Although syntans improved the wash fastness but no obvious differences between these syntans in generally were observed. The results for nylon 6 and wool showed dye stability obtained for direct dye of class A was lower than other two dyes. However, from this investigation it is clear that all four aftertreatments were effective in improvement the wash fastness of the three direct dyes at three different washing temperatures.

ACKNOWLEDGEMENTS

We wish to express our gratitude to the research affairs Division of Isfahan University of Technology (IUT), for financial support. We also thank Mr Saber Rashtak for a gift of CETAFIX AFA from Avocet Dye & Chemical Co. Ltd.

REFERENCES

1. Tomita M., Tokitaka M., Dihydroxy-diphenylsulfone and salicylic acid derivativies in the aftertreatment of dyed nylon, *J. Soc. Dyers. Colour.*, **96**, 297-301, 1980.
2. Cook C.C., Aftertreatments for improving the fastness of dyes on textile fibers, *Rev. Prog. Color.*, **12**, 73-85, 1982.
3. Burkinshaw S.M. (Ed.), Waring D.R., Hallas C., Plenum, New York, Ch. 7, 237-380, 1990.
4. Burkinshaw S.M., Bahojb-allafan B., The development of a metal-free, tannic acid-based aftertreatment for nylon 6,6 dyed with acid dyes-Part 2: Tannic acid, *Dyes Pigments*, **59**, 71-97, 2003.
5. Burkinshaw S.M., Son Y.-A., Aftertreatments of disulfonated 1:2 premetallised acid dyeings on nylon 6,6 using a syntan in conjuction with a complexing agent, *Dyes Pigments*, **70**, 149-155, 2006.
6. Guthri J., Cook C.C., Effect of presence of a syntan on the dyeing properties of nylon, *J. Soc. Dyers. Colour.*, **98**, 6-10, 1982.
7. Burkinshow S.M., Maseka K.D., Improvement of the wash fastness of non-metallised acid dyes on conventional and microfiber nylon 6,6, *Dyes Pigments*, **30**, 21-42, 1996.
8. Feiz M., Improvement of the wash fastness of direct cotton dyes applied to nylon and cotton dyes aftertreatment with synthetic tanning agents, *Iran. Polym. J.*, **6**, 205-219, 1997.
9. Giles C.H., *A Laboratory Course in Dyeing*, Society of Dyers and Colorists, Bradford UK, 98, 1971.
10. Blackburn R.S., Burkinshaw S.M., Aftertreatment of 1:2 metal complex acid dyes on conventional

and microfiber nylon 6,6 with a commercial syntan/cation system, *J. Soc. Dyers. Colour.*, **114**, 96-100, 1998.

11. Burkinshaw S.M., Bahojb-allafan B., The development of a metal-free, tannic acid-based aftertreatment for nylon 6,6 dyed with acid dyes-Part 1: Tannic acid, *Dyes Pigments*, **58**, 205-218, 2003.