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Aftertreatment of disulfonated 1:2 pre-metallised acid dyeings on nylon 6,6 using a syntan in conjunction with a complexing agent

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Abstract

Nylon 6,6 was dyed using three commercial disulphonated 1:2 pre-metallised acid dyes. An aftertreatment with a commercial synthetic tanning agent was applied to the dyeings and the aftertreated dyeings were further treated with a metal salt in an attempt to improve wash fastness properties still further. Untreated, syntanned and syntanned/backtanned specimens were subjected five times to a repeated wash testing protocol. The fastness, to repeated wash testing, of nylon 6,6 which had been dyed with the three dyes was improved, as expected by an aftertreatment with the commercial syntan. Further, significant, improvement in wash fastness was secured by the subsequent treatment of the syntanned fibre with the metal salt. This two-stage, syntan/metal salt aftertreatment raised the level of wash fastness of the 2% omf dyeings to that more closely approaching that expected of the full backtan.

Keywords: Nylon 6,6; Pre-metallised acid dyes; Wash fastness

1. Introduction

In spite of the generally very good wash fastness properties of 1:2 pre-metallised dyes on nylon fibres, an aftertreatment with a natural (full backtan) or synthetic tanning agent (syntan) is often necessary to secure highest levels of fastness to washing, particularly in terms of colour loss in the case of the disulfonated variants.

The classical full backtan aftertreatment, which was devised to improve the characteristically poor wet fastness of non-metallised acid dyes on nylon, comprises the sequential application of tannic acid and potassium antimonyl tartrate (tartar emetic). In this two-stage aftertreatment, the high M_r gallotannin component binds to the protonated amino end groups in the nylon fibre and the sequential treatment with tartar emetic results in the formation of an insoluble, potassium antimonyl tannate complex that is situated at the surface of the dyed substrate and which provides a physical barrier to the diffusion of dye from the dyed fabric during washing. The purpose of the metal salt (potassium antimonyl tartrate) in the traditional full backtan aftertreatment is, therefore, to form a complex with the adsorbed tannic acid in situ at the surface of the dyed nylon 6,6.

Although the full backtan can significantly improve the wet fastness properties of pre-metallised acid dyes on nylon, it is nowadays rarely used owing to the toxicity of tartar emetic and because it can impair the handle and the light fastness of dyeings as well as impart a shade change to dyeings. Consequently, an aftertreatment with

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a syntan has mostly replaced the full backtan as a means of improving the wet fastness of acid dyes on nylon. While syntans have the advantage of being applied in a single process compared with the common, two-bath, full backtanning process and do not suffer from the disadvantages displayed by their natural counterpart, an aftertreatment with a syntan is not as effective as an aftertreatment with the full backtan [1].

It has been demonstrated that the effectiveness of a commercial syntan in improving the wash fastness of various non-metallised acid dyes [2,3] and pre-metallised acid dyes [4,5] on nylon 6,6 can be enhanced by the subsequent application of a selected, polymeric cationic agent to the syntanned, dyed material. It is proposed [1,2] that this two-stage aftertreatment process results in the formation of a large molecular size, low aqueous solubility, complex between the anionic syntan and the cationic compound within the dyed fibre. A two-stage, modified full backtan aftertreatment was devised [6,7] that uses tannic acid and a tin sulfate derived product (*Gallofix*) in which the tin salt forms a metal complex with the tannic acid and avoids the use of the traditional, toxic, potassium antimonyl tartrate. Although the tannic acid/tin sulfate system was found to markedly enhance the wash fastness of both non-metallised and pre-metallised acid dyes on nylon 6,6 [6,7], its widespread usefulness is potentially compromised by the use of the tannic acid component and the concomitant disadvantages associated with handle and shade change described above. As syntans do not display the disadvantages of their natural counterpart and improve wash fastness of pre-metallised acid dyes on nylon 6,6 (albeit to a lesser degree than does a full backtan), the present work was carried out to determine whether the sequential treatment of a commercial syntan with *Gallofix* might enhance the effectiveness of the syntan to an extent that is comparable to that of the full backtan.

2. Experimental

2.1. Materials

Knitted nylon 6,6 fabric of 78f/68 dtex per filament and amino end group (AEG) content of 45 m-eq. kg^{-1} was kindly supplied by Dupont (UK). The fabric was scoured before use by treatment in a solution of 3 g dm^{-3} *Sandozin NIE* (a non-ionic surfactant supplied by Clariant UK) and 1 g dm^{-3} Na_2CO_3 at 60 °C for 30 min. The scoured fabric was rinsed thoroughly in tap water and allowed to dry in the open air. Crompton & Knowles kindly supplied the three commercial disulfonated 1:2 pre-metallised acid dyes, listed in Table 1; the dyes were chosen because they displayed moderate fastness on nylon 6,6 to the repeated washing protocol employed in this work. *Fixogene AXF*, a synthetic tanning agent, was kindly supplied by Uniqema; *Gallofix* was generously provided by Omnichem-Ajinmoto.

Table 1
Disulfonated 1:2 pre-metallised acid dyes used

Commercial name	C.I. generic name
Neutrilan Yellow M-3R	C.I. Acid Yellow 384
Neutrilan Bordeaux M-B	C.I. Acid Violet 90
Neutrilan Navy M-BR	C.I. Acid Blue 193

2.2. Dyeing

A 4 g sample of nylon 6,6 was dyed with 2% omf of each of the three dyes in sealed, stainless steel dye pots of 200 cm^3 capacity, housed in a laboratory-scale, *Zeltex Polycolor PC1000* dyeing machine using a liquor ratio of 20:1; the dyeing method used is shown in Fig. 1. The pH was adjusted using McIlvaine buffers [8]. At the end of dyeing, the dyed samples were removed, rinsed thoroughly in tap water and allowed to dry in the open air.

2.3. Syntan aftertreatment

Dyeings were aftertreated with 2% omf *Fixogene AXF* in sealed, stainless steel dye pots of 200 cm^3 capacity, housed in a laboratory-scale, *Zeltex Polycolor PC1000* dyeing machine using a liquor ratio of 20:1; the aftertreatment method used is shown in Fig. 2. At the end of treatment, the syntanned samples were removed, rinsed thoroughly in tap water and allowed to dry in the open air.

2.4. Backtanning treatment with Gallofix

Syntanned dyeings were treated with 2% omf of *Gallofix* at pH 3.5 (acetic acid) in sealed, stainless steel dye pots of 200 cm^3 capacity, housed in a laboratory-scale, *Zeltex Polycolor PC1000* dyeing machine using a liquor ratio of 20:1; the aftertreatment method used is

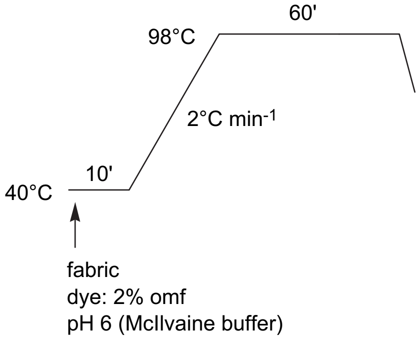

Fig. 1. Dyeing method.

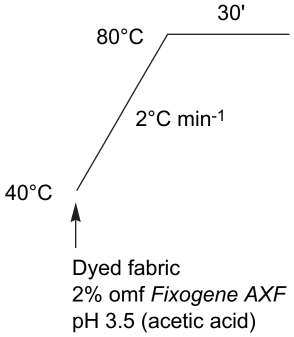

Fig. 2. Syntan aftertreatment.

shown in Fig. 3. At the end of treatment, the samples were removed, rinsed thoroughly in tap water and allowed to air dry.

2.5. Colour measurement

All measurements were carried out using an *X-rite* spectrophotometer interfaced to a PC using D_{65} illumination, 10° standard observer with specular component excluded and UV component included. Each fabric was folded once to give two thickness and an average of four readings was taken each time. The reduction in depth of shade of the dyeings that occurred as a result of washing was calculated using Eq. (1) and expressed as percentage colour loss (L_c) where $\mathrm{fk_u}$ and $\mathrm{fk_w}$ are the weighted K/S values of the unwashed and washed specimens, respectively.

$$L_c = \left[\frac{\mathrm{fk_u} - \mathrm{fk_w}}{\mathrm{fk_u}}\right] \times 100 \qquad (1)$$

2.6. Wash fastness

Wash fastness tests were conducted according to ISO 105:C06/C2 [9] using SDC multifibre as adjacent fabric; the samples were sequentially washed five times.

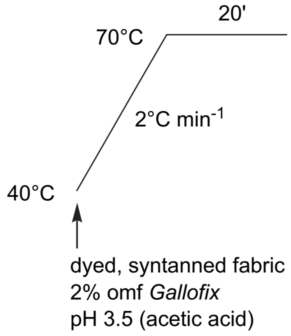

Fig. 3. *Gallofix* treatment.

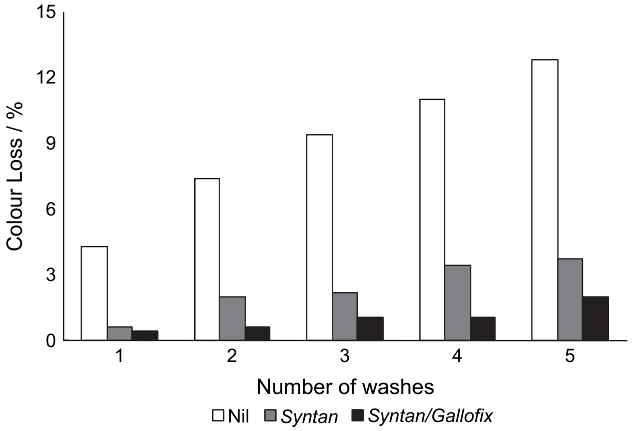

Fig. 4. Colour loss of 2% omf dyeings of C.I. Acid Blue 193.

3. Results and discussion

The three dyes were selected for use because each displayed moderate fastness to washing on the knitted nylon 6,6 fabric substrate employed in this work at the 2% omf depth of shade employed. In the context of the shade change which the dyeings underwent when they were subjected to five, consecutive wash tests, Figs. 4–6 and Tables 2–4 show the data obtained for the three dyes. The moderate fastness of the three dyes to repeat washing is clearly evident, insofar as the dyeings which had not been aftertreated underwent a reduction in colour strength fk due to the loss of dye during washing. It is apparent from Figs. 4–6 that for each dye used, the extent of dye loss increased, progressively, as the number of washes increased. The colorimetric data presented in Tables 2–4 reveal that the shade changes observed for the three dyes are attributable to a loss of dye from the dyeings rather than to changes in the colour of the dyeings. For each dye, in the case of the dyeings which had not been aftertreated, the dyeings displayed much greater colour loss than the corresponding aftertreated dyeings. After one wash, losses of between

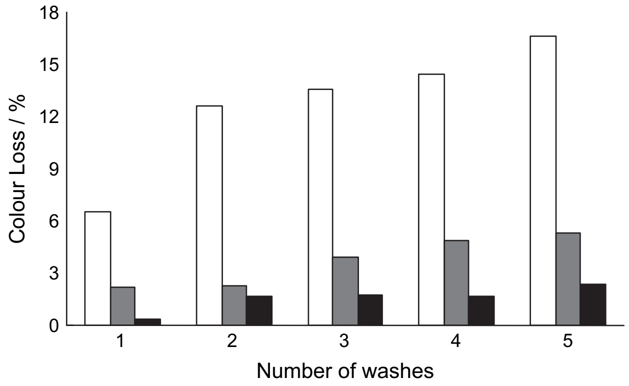

Fig. 5. Colour loss of 2% omf dyeings of C.I. Acid Violet 90; key as in Fig. 4.

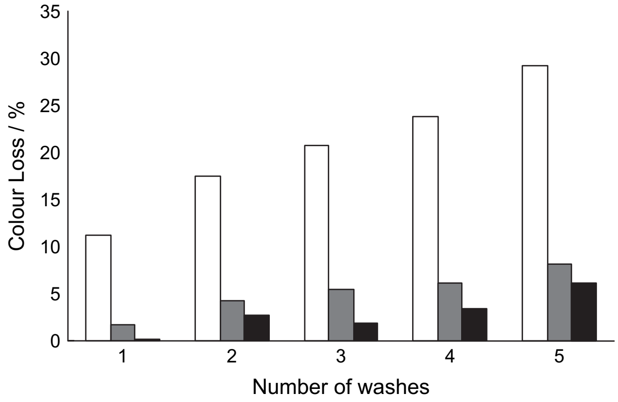

Fig. 6. Colour loss of 2% omf dyeings of C.I. Acid Yellow 384; key as in Fig. 4.

Table 3
Colorimetric data for 2% omf C.I. Acid Violet 90 dyeings

Aftertreatment	Washes	L^*	a^*	b^*	C	h	fk
Nil	0	29.1	41.2	−1.2	41.2	358.4	181.3
	1	29.8	41.4	−1.3	41.4	358.2	169.5
	2	30.6	41.7	−1.5	41.7	357.9	158.5
	3	30.7	41.6	−1.6	41.6	357.8	156.7
	4	30.8	41.7	−1.5	41.7	357.9	155.2
	5	31.1	41.8	−1.2	41.8	357.7	151.2
Fixogene AXF	0	29.8	41.4	−1.4	41.4	358.1	169.8
	1	29.9	41.2	−1.7	41.3	357.6	166.1
	2	30.1	41.6	−1.3	41.6	358.2	165.9
	3	30.2	41.4	−1.4	41.4	358.1	163.1
	4	30.4	41.6	−1.4	41.6	358.1	161.6
	5	30.4	41.6	−1.4	41.6	358.0	160.8
Fixogene AXF/Gallofix	0	28.9	41.1	−1.1	41.0	358.3	181.3
	1	29.1	41.0	−1.2	41.1	358.4	180.6
	2	29.4	41.3	−0.9	41.3	358.8	178.3
	3	29.3	41.2	−1.1	41.2	358.5	178.2
	4	29.3	41.3	−0.9	41.3	358.7	178.3
	5	29.4	41.3	−0.9	41.3	358.7	177.0

4% and 10% were observed; colour loss continued over successive washes and, after five washes in the case of the non-aftertreated yellow dye, a loss of almost 30% was obtained.

As expected, an aftertreatment with the syntan (*Fixogene AXF*) markedly reduced colour loss; this is clearly evident in Figs. 4–6; although the extent of shade change increased progressively as the number of washes increased for each of the three dyes used, the rate of this progressive dye loss was substantially lower than that observed for the non-aftertreated dyeings. The corresponding colorimetric data (Tables 2–4) reveal that the colour of the dyeings was little changed by an aftertreatment with the syntan.

Interestingly, Figs. 4–6 show that the additional treatment of the syntanned dyeings with *Gallofix* enhanced the ability of the syntan to improve fastness to repeated washing. For each of the three dyes under consideration, the extent of colour loss after the first wash test was negligible (0.3% or less). Although the extent of shade change increased progressively as the number of washes increased for each of the three dyes used, the rate of this progressive dye loss was considerably lower than that observed for both the non-aftertreated dyeings and the syntanned dyeings. These findings suggest that tin salt was clearly very effective in enhancing the effectiveness of the anionic syntan in a manner similar to that found for the tannic acid/*Gallofix* system described previously [6,7].

Earlier work [6] reported the effects, on the repeated wash fastness of the same three dyes, of aftertreatments

Table 2
Colorimetric data for 2% omf C.I. Acid Blue 193 dyeings

Aftertreatment	Washes	L^*	a^*	b^*	C	$h°$	fk
Nil	0	27.5	0.8	−16.7	16.7	272.9	140.1
	1	28.0	0.8	−16.9	16.9	272.6	134.1
	2	28.5	0.7	−16.9	16.9	272.4	129.7
	3	28.7	0.7	−17.0	17.0	272.5	126.9
	4	29.0	0.7	−17.0	17.0	272.4	124.7
	5	29.2	0.7	−17.0	17.1	272.5	122.1
Fixogene AXF	0	26.0	0.8	−16.5	16.6	272.9	156.9
	1	26.1	0.8	−16.6	16.6	272.8	155.9
	2	26.3	0.9	−16.6	16.6	272.9	153.8
	3	26.3	0.8	−16.5	16.5	272.6	153.5
	4	26.5	0.9	−16.6	16.6	273.0	151.5
	5	26.5	0.9	−16.6	16.7	273.0	151.0
Fixogene AXF/Gallofix	0	25.2	0.8	−16.3	16.4	272.8	167.8
	1	25.2	0.8	−16.4	16.4	272.9	167.1
	2	25.3	0.9	−16.4	16.5	273.2	166.0
	3	25.2	0.9	−16.5	16.5	273.3	166.8
	4	25.3	0.9	−16.5	16.5	273.3	166.0
	5	25.4	0.9	−16.4	16.5	273.0	164.5

Table 4
Colorimetric data for 2% omf C.I. Acid Yellow 384 dyeings

Aftertreatment	Washes	L^*	a^*	b^*	C	$h°$	fk
Nil	0	58.4	25.0	68.4	72.8	70.0	152.6
	1	59.5	24.6	68.1	72.4	70.2	135.5
	2	60.1	24.3	67.8	72.0	70.3	125.9
	3	60.5	24.1	67.5	71.7	70.3	120.9
	4	60.6	23.9	66.9	71.1	70.3	116.2
	5	61.3	23.6	66.7	70.8	70.5	107.9
Fixogene AXF	0	58.2	25.0	67.9	72.3	69.8	151.0
	1	58.6	24.8	68.3	72.7	70.0	148.4
	2	58.9	24.8	68.4	72.7	70.1	144.7
	3	59.0	24.8	68.1	72.5	70	142.7
	4	59.0	24.7	68.0	72.4	70	141.8
	5	59.2	24.5	68.0	72.3	70.2	138.8
Fixogene AXF/Gallofix	0	58.2	25.3	67.5	72.1	69.4	145
	1	58.4	25.3	67.4	72.0	69.4	144.7
	2	58.6	25.2	67.4	71.9	69.5	141
	3	58.5	25.3	67.3	71.9	69.4	142.2
	4	58.7	25.1	67.3	71.8	69.5	140.1
	5	58.7	25.0	66.8	71.4	69.5	136.2

Table 5
Colour loss (L_c) achieved after five repeated wash tests

Dye	*Fixogene AXF*/cation[a]	*Fixogene AXF*/*Gallofix*	*Tannic acid*/*Gallofix*[a]
C.I Acid Blue 193	4.8	2.0	0.7
C.I Acid Violet 90	3.3	2.4	0.3
C.I Acid Yellow 384	5.9	6.1	3.2

[a] Data from Ref. [6].

with the tannic acid/*Gallofix* full backtan and also with the syntan/cation system. When the results obtained in the current work using the syntan/*Gallofix* system are compared with those reported previously [6] it is evident (Table 5) that the tin salt was more effective than the commercial cation when used in combination with the syntan. However, Table 5 shows that the *Fixogene AXF*/*Gallofix* combination was out-performed by the tannic acid/*Gallofix* aftertreatment in terms of the colour loss achieved from the 2% omf dyeings.

The colour loss that occurs during laundering obviously translates to a change in the shade of a dyeing. Table 6 shows the colour difference (ΔE) between the original (unwashed) dyeings and washed dyeings. Not surprisingly, significant colour loss was associated with greater shade change. The effectiveness of *Fixogene AXF* in reducing shade change is evident as also is the enhanced effectiveness when the syntanning was accompanied by the *Gallofix* combination. The major component of such a shade change is lightness. In the case of the hue and chroma changes (a^* and b^*) that occurred during washing (Figs. 7–9), the arrows lead from initial to final colour change (five washes) to show the direction of the colour change; clearly, the extent of the colour change was small. In the case of C.I. Acid Blue 193, aftertreatment imparted a slight yellowing but the change over five washes predominantly reduced yellowness. For C.I. Acid Violet 90, aftertreatment had little effect, while the main changes upon laundering involved a slight increase in redness. For C.I. Acid Yellow 384, aftertreatment caused the dyeings to be less yellow, while on washing a decrease in chroma occurred. Overall, the observed colorimetric changes were small and the lack of a general trend for all three dyes indicates that the change of shade on aftertreatment and the yellowing over successive washes associated with the use of tannic acid in a full backtan was absent.

Table 7 shows the extent of staining of the adjacent multifibre strip fabric achieved for the three dyes used. As might be expected, staining was mostly observed on the nylon component of the multifibre and, to a lesser extent, on the wool component. All three dyes displayed improved resistance to staining as a result of aftertreatment. The extent of the improvement in staining secured by an aftertreatment with the syntan alone was of the same magnitude as that obtained using the syntan/*Gallofix* system.

In order to explain the observed enhancment, imparted by *Gallofix*, to the effectiveness of the syntan, an explanation can be proposed that is analogous to that which describes the manner in which the metal salt interacted with tannic acid in the tannic acid/*Gallofix* system previously reported [6,7]. As mentioned, in the classical, two-stage, full backtan aftertreatment, the tannic acid component behaves as a high M_r anionic, polyphenolic compound which binds to the protonated amino end groups in the nylon fibre; other forces of interaction, such as H-bonding and ion-dipole forces also will contribute towards tannic acid-fibre substantivity [1]. Subsequent treatment with potassium antimonyl tartrate results in the formation of an insoluble, potassium antimonyl tannate complex situated at the surface of the dyed substrate which provides a physical barrier to the diffusion of dye from the dyed fabric during washing [1,10]. The purpose of the metal salt (potassium antimonyl tartrate) in the traditional full backtan aftertreatment is to form a low solubility complex with the adsorbed tannic acid in situ at the surface of the dyed nylon 6,6. Thus, in terms of the case of the tannic acid/*Gallofix* aftertreatment, the tin salt replaced the potassium antimonyl tartrate as the complexing metal.

A similar mechanism can be proposed to operate in the case of the observed enhancement of the effectiveness of the syntan by *Gallofix*. Firstly, syntans are, typically, water-soluble, anionic polycondensates (of formaldehyde with arylsulfonates and sulfonates of dihydroxydiaryl sulfones [1]) which are adsorbed on to dyed nylon by virtue of ion-ion forces of interaction operating between anionic (sulfonate) groups in the syntan and the terminal amino groups in the nylon substrate; other forces of interaction, such as H-bonding and ion-dipole forces also will contribute towards syntan-fibre substantivity [1,10,11]. Thus, similarities exist in terms of the manner by which syntans and tannic

Table 6
Effect of aftertreatment of colour change (ΔE CIE Lab)

Aftertreatment	ΔE after one wash			ΔE after five washes		
	C.I. Acid Yellow 384	C.I. Acid Violet 90	C.I. Acid Blue 193	C.I. Acid Yellow 384	C.I. Acid Violet 90	C.I. Acid Blue 193
None	1.2	0.8	0.6	3.6	2.2	1.8
Fixogene AXF	0.6	0.4	0.19	1.2	0.7	0.4
Fixogene AXF/Gallofix	0.2	0.1	0.1	0.9	0.5	0.2

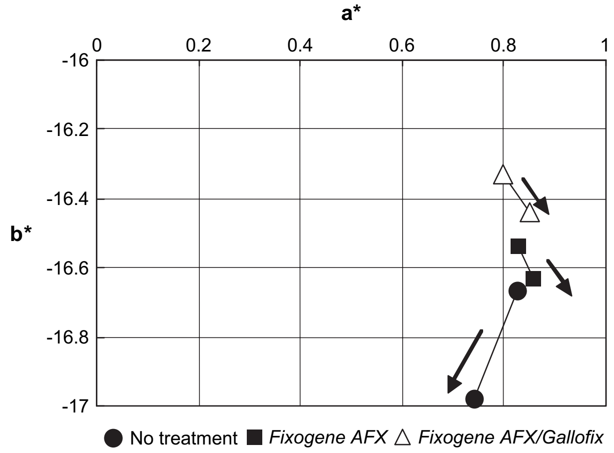

Fig. 7. Colour change after five washes: C.I. Acid Blue 193 (arrows indicate direction from initial to final shade).

acid are adsorbed by dyed nylon fibre. The adsorption of the large M_r syntans follows a BET mechanism [1,11] which results in the formation of multilayers of adsorbed syntan molecules situated at the periphery of the dyed nylon 6,6. Their ability to improve the wet fastness of acid dyes on nylon 6,6 is attributable to the resulting 'layer' of syntan molecules at the fibre surface reducing the diffusion of dye molecules out of the dyed material during washing; thus, similarities exist between the way in which the syntan and the tannic acid improve the wet fastness of acid dyes on nylon. Hence, the mechanism by which *Gallofix* enhanced the syntan can, by analogy to that operating in the case of the tannic acid/*Gallofix* system, be attributed to the formation of a low solubility metal complex with the adsorbed syntan in situ at the surface of the dyed nylon 6,6.

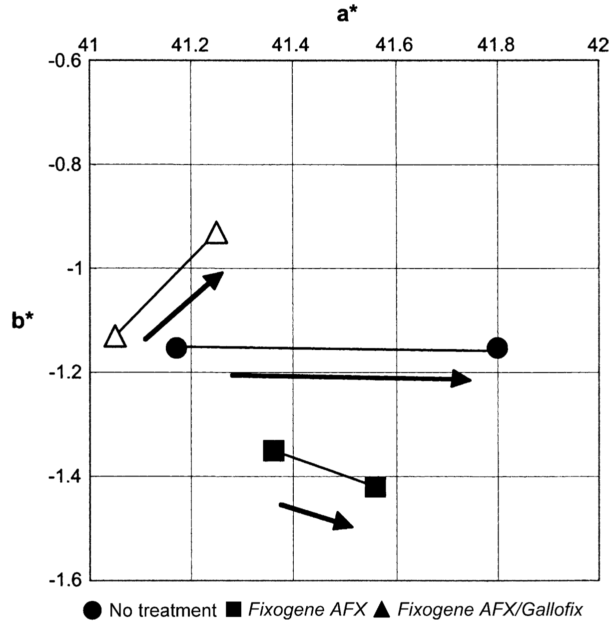

Fig. 8. Colour change after five washes: C.I. Acid Violet 90 (arrows indicate direction from initial to final shade).

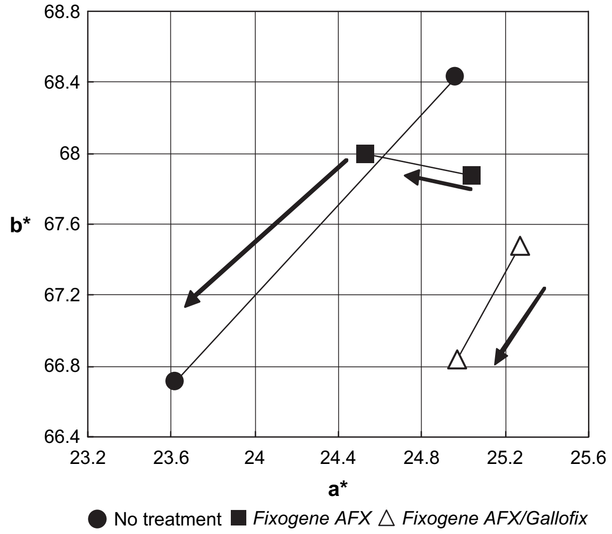

Fig. 9. Colour change after five washes: C.I. Acid Yellow 384 (arrows indicate direction from initial to final shade).

4. Conclusions

The fastness, to repeated wash testing, of nylon 6,6 which had been dyed with three commercial disulfonated 1:2 metal complex acid dyes was improved, as expected by an aftertreatment with a commercial syntan. Further, significant, improvement in wash fastness was secured by the subsequent treatment of the syntanned fibre with *Gallofix*, a proprietary tin formulation. This two-stage, syntan/*Gallofix* aftertreatment raised the level of wash fastness of the 2% omf dyeings to that more closely approaching that imparted by a full backtan.

Table 7
Grey scale assessment of aftertreated 2% omf dyeings on nylon 6,6

Aftertreatment	Acetate	Cotton	Nylon 6,6	Polyester	Acrylic	Wool
C.I. Acid Blue 193						
Nil	5	5	3/4	5	5	4/5
Fixogene AXF	5	5	5	5	5	5
Fixogene AXF/Gallofix	5	5	5	5	5	5
C.I. Acid Violet 90						
Nil	5	5	4	5	5	5
Fixogene AXF	5	5	5	5	5	5
Fixogene AXF/Gallofix	5	5	5	5	5	5
C.I. Acid Yellow 384						
Nil	5	5	3	5	5	4/5
Fixogene AXF	5	5	4/5	5	5	5
Fixogene AXF/Gallofix	5	5	4/5	5	5	5

References

[1] Burkinshaw SM. Chemical principles of synthetic fibre dyeing. London: Blackie; 1995.

[2] Burkinshaw SM, Maseka KD. Dyes Pigments 1996;30:21.

[3] Burkinshaw SM, Maseka KD. ICI surfactants. US Pat 5 350 422; 1994.

[4] Blackburn RS, Burkinshaw SM. J Soc Dyers Colour 1998;114:12.

[5] Blackburn S, Burkinshaw SM. J Soc Dyers Colour 1999;115:102.

[6] Burkinshaw SM, Son Y-A. Dyes Pigments 2001;48:57.

[7] Burkinshaw SM, Son Y-A, Bide MJ. Dyes Pigments 2001;48:209.

[8] Vogel A. A textbook of quantitative inorganic analysis. London: Longmans; 1944.

[9] Standard methods for the determination of the colour fastness of textiles and leather. 5th ed. Society of Dyers and Colourists; 1990.

[10] Cook CC. Rev Prog Col 1982;12:73.

[11] Burkinshaw SM, Maseka KD. Proc AATCC Int Conf 1994.