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The dyeing of silk part 2: Aftertreatment with natural and synthetic tanning agents

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ABSTRACT

Moderate/deep shades on silk were produced using three non-metallised and two pre-metallised acid dyes. Three aftertreatments, namely a syntan, syntan + cation and modified full back tan, improved the fastness of the dyeings to repeated wash testing at 40 °C. However, the extent of this improvement varied for the dyes used. For the two pre-metallised acid dyes and one non-metallised acid dye, the modified full backtan gave marginally superior results whereas for the remaining non-metallised acid dyes, there was little difference in the magnitude of the improvement imparted by the three aftertreatments. In terms of the depth of shade obtained at the end of the five wash tests, the modified backtan gave markedly paler dyeings in the case of the three non-metallised dyes used whilst similar depths of shade were obtained in the case of the two pre-metallised acid dyes, irrespective of aftertreatment used. The aftertreatments also varied in terms of their effects on the hue and chroma of the dyeings, with the modified full backtan generally imparting greatest colour change.

1. Introduction

Silk has been the most revered and prized of all textile fibres for some 5000 years, the characteristic soft handle, excellent drape and unique lustre of cultivated silk being attributable to the fibre's triangular cross-section, smooth surface and fineness. Of the many types of dye towards which silk displays substantivity, the most commonly used are acid dyes, owing to their comparative ease of application and large colour gamut; however, the fastness of the dyes in moderate/deep shades on silk often leaves much to be desired. Furthermore, the fineness of cultivated silk fibres coupled with their smooth, triangular section results in their dyeing behaviour resembling that of microfibre synthetic fibres [1] in that large amounts of dye are required to achieve moderate/deep depths of shade and such dyeings display typically low fastness to wet treatments [2]. Whilst the application of acid dyes to silk has attracted much attention over many decades [3–13], comparatively few publications have concerned their fastness properties, these being mostly concerned with light fastness rather than wash fastness [14–18].

This paper concerns approaches to achieve moderate/deep shades of good wet fastness on cultivated silk. The first part of the paper [19] described how medium/deep shades obtained using four C.I. Solubilised Sulphur dyes on silk fabric displayed good/excellent fastness to washing at 40 °C and little or no sensitivity to oxygen bleach fading. This part of the paper concerns the effects of aftertreatment on the fastness, to repeated washing at 40 °C, of moderate/deep shades on silk, obtained using three non-metallised and two pre-metallised acid dyes.

In this context, as acid dyes display characteristically poor fastness to repeated washing on polyamide fibres, especially in moderate/deep shades [1], it was decided to employ three aftertreatments which are used to improve the wet fastness of acid dyed nylon. Traditionally, the aftertreatment of dyed polyamide fibres is carried out using either a two-stage, tannic acid and potassium antimony tartrate, *full backtan* process or a single-stage *syntan* aftertreatment. However, the full backtan is nowadays rarely used owing to the toxicity of tartar emetic and because it can impart a shade change to dyeings. A modified full backtan aftertreatment has been devised that employs a tin sulfate derived product (*Gallofix*) in which the tin salt forms a metal complex with tannic acid and so avoids the use of the traditional, toxic, potassium antimony tartrate. 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 [20,21]. A method was also developed to enhance the effectiveness of a commercial syntan in improving the wash fastness of non-metallised [22,23] and pre-metallised acid dyes [24,25] on nylon 6,6 by the subsequent

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application of a selected, polymeric cationic agent to syntanned, dyed material. This two-stage 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 [1,22].

In this part of the paper, the three aftertreatments applied to dyed silk were syntan, syntan/cation and modified full backtan (tannic acid/*Gallofix*).

2. Experimental

2.1. Materials

The, deggumed, scoured, *Bombyx mori* silk fabric twill described previously [19] was used. The three non-metallised acid dyes and two 1:2 pre-metallised acid dyes shown in Table 1 were generously provided by Crompton and Knowles and were used without purification. The structure of only one of the dyes, C.I. Acid Blue 193 (**I**), is available [26]. The synthetic tanning agent, *Fixogene AXF* and the cationic fixing agent, *Fixogene CXF* were generously supplied by Uniqema and the tannic acid, *Floctan 1* and the fixing agent *Gallofix* were kindly supplied by Omnichem-Ajinomoto. All other chemicals used were of general laboratory grade.

2.2. Methods

2.2.1. Dyeing

All dyeings were carried out in sealed stainless steel dyepots of 300 cm^3 capacity, housed in a Roaches *Pyrotec* 'S' laboratory dyeing machine using a liquor ratio of 50:1. The methods shown in Figs. 1 and 2 were used for the non-metallised and pre-metallised acid dyes, respectively; McIlvaine buffer solution [27] was used to control the pH of the pre-metallised acid dyebaths. At the end of dyeing, the samples were removed and rinsed in tap water for 10 min.

2.2.2. Aftertreatment

The rinsed dyeings were aftertreated using:

i. a single-stage, syntan (*Fixogene AXF*) treatment (Fig. 3);
ii. a two-stage *syntax* + *cation* (*Fixogene AXF* + *Fixogene CXF*) process in which dyeings which had been aftertreated with the syntan using the method shown in Fig. 3 were rinsed in water and subjected to the treatment depicted in Fig. 4;
iii. a two-stage *modified full back tan* (*Floctan* + *Gallofix*) (Fig. 5) in which McIlvaine buffer solution [27] was used to control pH.

Each of the three aftertreatments was carried out in sealed, stainless steel dyepots of 300 cm^3 capacity, housed in a Roaches *Pyrotec* 'S' laboratory dyeing machine using a liquor ratio of 20:1. At the end of each of the aftertreatments, the sample was removed, rinsed thoroughly in tap water and allowed to dry in the open air.

Table 1
Dyes used.

Commercial name	C.I. Generic name	Type
Nylanthrene Navy C-WG	C.I. Acid Blue 345	non-metallised acid milling
Nylanthrene Orange C-SLF	C.I. Acid Orange 116	
Nylanthrene Rubine 5BLF	C.I. Acid Red 299	non-metallised acid levelling
Neutrilan Navy S-B GR	C.I. Acid Blue 284	monosulfonated
Neutrilan Navy M-BRX	C.I. Acid Blue 193	disulfonated

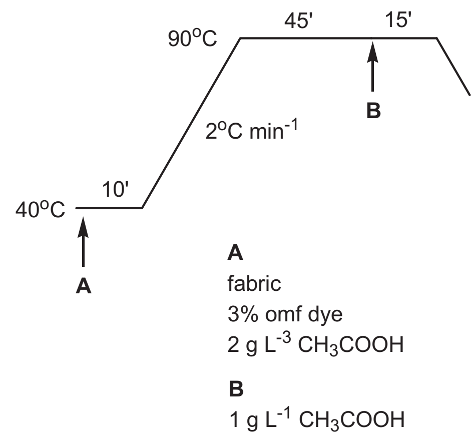


Fig. 1. Dyeing method for non-metallised acid dyes.

2.2.3. Colour measurement

The equipment and techniques described previously [19] were used.

2.2.4. Wash fastness

The dyeings were subjected to five, consecutive ISO C06/A2C (40 °C) wash test methods [28]. At the end of each wash test, the sample was rinsed thoroughly in tap water; a fresh sample of SDC multifibre strip used for each of the five wash tests. The extent to which repeated wash testing reduced the depth of shade of the dyeings was determined using Eq (1) where the subscript 1 refers to the colour strength of the dyeing before washing and the subscript 2 refers to the colour strength of the dyeing after wash #1, #2, … #5, respectively.

$$\%\text{colour loss} = \left(\frac{fk_1 - fk_2}{fk_1}\right) \times 100 \tag{1}$$

3. Results and discussion

As mentioned, whilst acid dyes are commonly used on silk because of their comparative ease of application and large colour gamut, the fastness of the dyes in moderate/deep shades on silk often leaves much to be desired. The five dyes used in this work were selected on the basis that they were typical examples of the

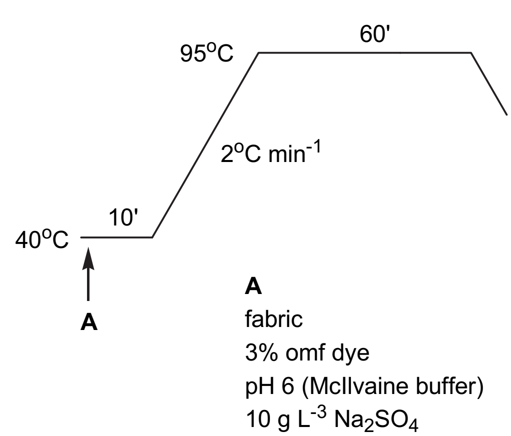


Fig. 2. Dyeing method for pre-metallised acid dyes.

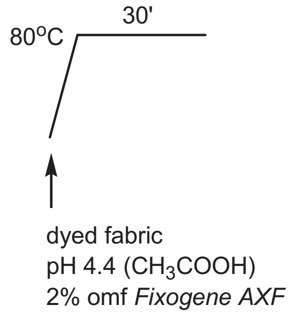


Fig. 3. Syntan Aftertreatment.

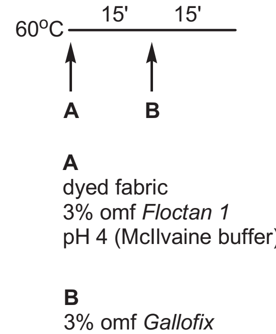


Fig. 5. Modified full backtan aftertreatment.

two main types of acid dye (non-metallised and pre-metallised) and, also, that they furnished moderate/deep shades on the silk fabric used. Although in the Colour Index [26], the application class '*acid dye*' includes both non-metallised and pre-metallised types, these two dye types are considered by both dye makers and dye users as being quite distinct, in terms of their dyeing behaviour, fastness, brilliance of shade, etc. Whilst various classification methods have been devised for the use of acid dyes on wool and nylon [1,29], no such systems apply in the case of silk fibres.

3.1. Non-metallised acid dyes

The differentiation shown in Table 1, for the three non-metallised acid dyes used in this work (i.e., *acid milling* and *acid levelling*) stems from their use on wool and reflects their general levels of wet fastness [29]. Acid levelling dyes are generally of small to moderate M_r and display characteristically superior levelling properties but generally lower levels of wet fastness than their acid milling counterparts [29].

3.1.1. Non-aftertreated dyeings

Fig. 6 shows the colour strength (fk values) obtained for 3% omf dyeings of the three non-metallised acid dyes used (i.e., C.I. Acid Orange 116, C.I. Acid Blue 345 and C.I. Acid Red 299). (results are also shown for dyeings which had been aftertreated with the syntan, the syntan + cation process and the modified full backtan). The colour strength of the dyeings are shown both before and after they had been subjected to five, consecutive wash tests at 40 °C. The corresponding colorimetric data for the dyeings are displayed in Table 2 and the fastness data in Table 3.

It is evident from Fig. 6 that each of the three non-metallised acid dyes furnished moderate/deep shades on the silk fabric. However, the three dyeings displayed only moderate/poor fastness to repeated washing insofar as colour strength decreased with increasing number of washes. A measure of the extent of the reduction in depth of shade that occurred during repeated wash fastness testing is shown by the % colour loss values depicted in Fig. 7, from which it is apparent that at the end of the five, repeated wash tests, the depth of shade had been reduced by ~25, >40% and >50% for the blue, orange and red dyeings, respectively. This reduction in depth of shade imparted by repeated washing can be attributed to dye loss having occurred during each of the five wash tests, this being reflected in the corresponding increased lightness (L^* values) of the dyeings (Table 2) that accompanied repeated wash testing. Unsurprisingly, the vagrant dye that was removed from the dyeings during washing deposited on several of the adjacent multifibre strip materials (Table 3). The comparatively low levels of staining achieved in the cases of the adjacent acrylic and polyester components were anticipated in view of the inherent low substantivity of non-metallised acid dyes towards such types of fibre; also expected, in the context of the substanitivity of the three dyes used, was the very high extent of staining obtained for the adjacent nylon 6,6 and wool fibres, on which this type of dye is used. The moderate levels of staining of the cotton and acetate multifibre components was not unexpected for these non-metallised acid dyes. The colorimetric data obtained for the dyeings before and after wash testing (Table 2) shows that repeated washing had little effect on the colour (hue, h^o and chroma, C^*) of the dyeings.

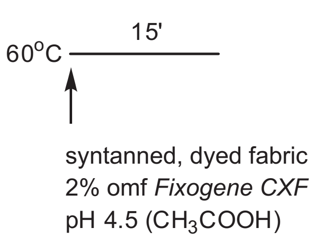


Fig. 4. Syntan/cation aftertreatment.

3.1.2. Syntan aftertreatment

Table 2 shows the colorimetric data obtained for the 3% omf dyeings which had been aftertreated with the syntan. Comparison of this data with that of the dyeings which had not been aftertreated (Table 2) prior to wash testing, reveals that, for each of the three dyes, syntan aftertreatment reduced the chroma and imparted a slight reddish hue to the dyeings. These findings were not surprising in view of the shade changes that can be imparted by such an aftertreatment [1]. The colorimetric data in Table 2 also show that aftertreatment with the syntan increased the lightness of the dyeings, this being mirrored by a corresponding decrease in colour strength (Fig. 6); these findings can be attributed to dye having been desorbed from the dyed silk during the syntan aftertreatment process. Fig. 6 shows that the colour strength of the syntanned dyeings decreased with increasing number of washes, owing to dye loss having occurred during each of the five wash tests. However, it is clear that in the cases of the last three wash tests, the extent of the reduction in the colour strength of the syntanned dyeings was lower than that obtained for the corresponding non-aftertreated dyeings. Indeed, the fk values of the dyeings which had been subjected to five, consecutive wash tests was higher for the syntanned dyeings than those of their non-aftertreated counterparts, for each of the three dyes used, from which it can be concluded that aftertreatment with the syntan improved the fastness of the three dyeings to repeated washing. This was confirmed by the lower extent of staining of adjacent

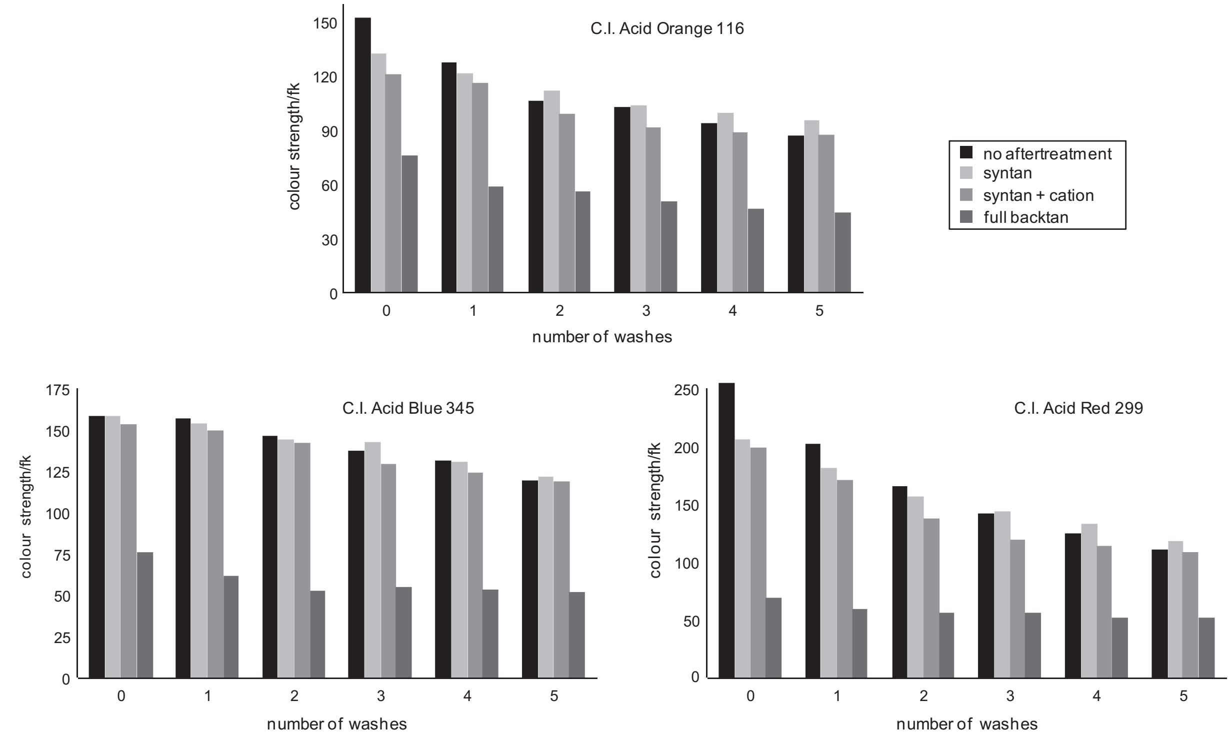


Fig. 6. Colour strength of 3% omf non-metallised acid dyes.

multifibre strip materials recorded for the syntanned dyeings after five washes (Table 3). In terms of the reduction in depth of shade that occurred as a result of repeated wash fastness testing, the % colour loss values displayed in Fig. 7 reveal that syntan aftertreatment reduced the extent of colour loss obtained at the end of the five, repeated wash tests in the cases of C.I. Acid Orange 116 and C.I. Acid Red 299, but had no effect in the case of C.I. Acid Blue 345.

3.1.3. *Syntan + cation aftertreatment*

As discussed, the two-stage, syntan + cation aftertreatment process was developed to enhance the effectiveness of commercial syntans in improving the wash fastness of various non-metallised and pre-metallised acid dyes on nylon. Table 2 and Fig. 6 show that the application of this aftertreatment increased the lightness and reduced the colour strength, respectively, of the dyeings prior to

Table 2
Colorimetric data obtained for 3% omf non-metallised dyes.

Aftertreatment	Number of washes	C.I. Acid Orange 16					C.I. Acid Blue 345					C.I. Acid Red 299				
		*L**	*a**	*b**	*C**	*h*°	*L**	*a**	*b**	*C**	*h*°	*L**	*a**	*b**	*C**	*h*°
nil	0	49.6	43.1	52.2	67.7	50.5	26.0	1.6	−22.3	22.3	274.1	22.0	22.1	−0.5	22.1	358.6
	1	51.6	41.6	52.1	66.6	51.4	25.9	1.9	−21.3	21.4	275.1	24.4	24.5	−1.2	24.5	357.2
	2	53.0	40.1	50.8	64.7	51.8	26.7	1.8	−21.2	21.2	274.9	26.6	25.0	−2.3	25.0	354.8
	3	53.2	39.2	50.4	63.8	52.1	27.6	1.6	−21.4	21.5	274.3	28.5	26.0	−2.9	26.2	353.7
	4	54.1	38.6	49.9	63.1	52.3	28.1	1.5	−21.3	21.4	274.1	30.0	26.1	−3.6	26.4	352.1
	5	55.1	38.3	50.2	62.9	52.7	29.4	1.2	−21.7	21.7	270.3	31.4	26.9	−4.3	27.1	350.9
syntan	0	49.9	42.1	49.9	65.4	49.8	25.5	1.8	−20.1	20.8	275.1	24.2	23.4	−0.3	23.4	359.3
	1	50.8	41.3	49.7	64.8	50.3	26.0	1.8	−19.9	19.9	275.2	25.5	24.1	−1.8	24.2	355.7
	2	51.5	40.8	49.1	63.8	50.3	26.8	1.6	−20.1	20.1	274.6	27.1	24.6	−2.8	24.7	353.5
	3	51.8	39.9	47.9	62.4	50.2	27.0	1.6	−20.0	20.1	274.6	28.3	25.8	−2.7	25.9	354.0
	4	52.7	39.7	48.8	62.9	50.9	28.0	1.5	−19.9	19.9	274.3	29.2	26.3	−3.4	26.5	352.6
	5	53.1	39.5	48.3	62.5	50.7	29.0	1.2	−19.8	19.9	273.5	30.6	26.0	−3.8	26.2	351.6
syntan + cation	0	51.3	41.3	50.5	65.3	50.7	26.0	1.8	−20.0	20.0	275.2	24.7	23.3	−0.2	23.3	359.6
	1	50.8	40.9	48.6	63.5	49.9	26.5	1.7	−21.4	21.4	270.4	26.3	25.1	−2.0	25.2	359.9
	2	53.4	39.8	49.8	63.7	51.3	27.1	1.5	−20.6	20.6	274.2	28.7	25.6	−3.3	25.8	352.6
	3	53.9	39.5	49.0	62.9	51.1	28.3	1.3	−20.8	20.8	273.6	30.5	25.9	−3.9	26.2	351.5
	4	53.7	39.1	47.8	61.8	50.7	28.8	1.1	−20.1	20.1	273.1	31.2	26.2	−3.3	26.3	352.8
	5	54.3	38.4	48.7	62.0	51.5	29.3	1.2	−19.8	19.9	273.5	31.7	26.1	−3.6	26.4	352.2
modified full backtan	0	38.0	21.4	19.7	70.5	42.6	34.0	13.8	−15.6	20.8	311.5	37.7	21.7	−2.0	21.8	354.7
	1	47.8	23.6	23.8	33.5	45.3	37.0	14.1	−15.6	21.0	312.1	40.5	25.7	−0.3	25.7	359.3
	2	49.5	24.8	26.3	36.5	46.6	39.2	14.6	−15.8	21.5	312.8	41.0	25.5	−1.9	25.5	355.7
	3	50.3	23.7	25.0	34.4	46.5	38.8	13.9	−15.6	20.8	311.7	40.9	25.1	−2.1	25.2	355.2
	4	52.1	23.8	26.4	35.0	47.9	39.1	13.2	−15.4	20.2	310.6	41.9	24.9	−2.3	25.0	354.7
	5	52.8	22.9	26.6	35.0	49.3	39.9	9.3	−12.7	15.8	306.2	41.8	24.4	−2.1	24.3	355.1

Table 3
Wash fastness data obtained for 3% omf dyeings.

C.I.	Aftertreatment	Number of washes	Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
Orange 116	nil	1	3/4	3/4	2	4/5	5	4
		5	4/5	4	3	4/5	5	4/5
	syntan	1	4	4	3	5	5	4/5
		5	5	4/5	4	5	5	5
	syntan + cation	1	4/5	4/5	3/4	5	5	5
		5	4/5	4/5	4	5	5	5
	modified full backtan	1	4	5	4	5	5	4/5
		5	4/5	4/5	4	5	5	5
Blue 345	nil	1	4	3/4	2	4/5	5	4/5
		5	4/5	4/5	3	5	5	5
	syntan	1	5	4/5	3	4/5	5	5
		5	5	5	3/4	5	5	5
	syntan + cation	1	4/5	5	3	5	5	5
		5	5	5	4	5	5	5
	modified full backtan	1	5	5	3	5	5	4/5
		5	5	5	5	5	5	5
Red 299	nil	1	2/3	2	1	3	4	3/4
		5	3/4	3	2	4	4/5	4
	syntan	1	3/4	3	2	3/4	4/5	4
		5	3/4	3	2/3	4/5	4/5	4/5
	syntan + cation	1	3/4	3	2	3/4	4/5	4
		5	3/4	3	2/3	4/5	4/5	4/5
	modified full backtan	1	3/4	4	2	4	4/5	3/4
		5	3/4	3	2/3	4/5	4/5	4/5
Blue 284	nil	1	5	4	3	5	5	5
		5	5	4/5	3	5	5	5
	syntan	1	5	5	3	5	5	5
		5	5	5	3/4	5	5	5
	syntan + cation	1	5	5	4	5	5	5
		5	5	5	3/4	5	5	5
	modified full backtan	1	5	5	3/4	5	5	5
		5	5	5	4/5	5	5	5
Blue 193	nil	1	4/5	4	3	5	5	5
		5	5	4/5	3/4	5	5	5
	syntan	1	5	4/5	3/4	5	5	5
		5	5	5	4	5	5	5
	syntan + cation	1	5	4/5	4	5	5	5
		5	5	5	4	5	5	5
	modified full backtan	1	5	5	4/5	5	5	5
		5	5	5	4/5	5	5	5

wash testing. The finding that the extents of the reduction in fk values and increase in L^* values were greater for the syntan + cation aftertreatment than the syntan aftertreatment can be attributed to more dye having been desorbed from the dyed substrate during the two hot, aqueous stages of the syntan + cation process than from the single, hot, aqueous stage of the syntan process. The colorimetric data in Table 2 show that, for each of the three dyes, aftertreatment with the syntan + cation process reduced the chroma and imparted a slight reddish hue to the dyeings, these findings being very similar to those obtained for the application of the syntan alone. In terms of the fastness of the dyeings, Fig. 6 shows that the reduction in colour strength of the syntan + cation treated dyeings that occurred during repeated washing was greater than that achieved for the dyeings which had been aftertreated with the syntan alone. Indeed, the fk values of the syntan + cation aftertreated dyeings which had been subjected to five, consecutive wash tests was more or less the same as that of their non-aftertreated counterparts, for each of the three dyes used. Hence, the colour strength data in Fig. 6 showed that aftertreatment with the syntan + cation process did not improve the fastness of the three dyeings to repeated washing.

However, this observation was not supported by the staining results obtained (Table 3) which showed that the syntan + cation aftertreated dyeings displayed slightly superior fastness after five washes than their non-aftertreated counterparts. This finding might be explained in terms of both the amounts of dye that were removed from the dyeings during the aftertreatment process and the amount of vagrant dye available for redeposition on adjacent multifibre strip materials during wash testing. Aftertreatment with the two-stage, syntan/cation process removed dye from the dyeings, as evidenced by the respective fk and L^* values (Table 2 and Fig. 6). This means that there was less dye present in the case of the syntan + cation aftertreated dyeings and, therefore, less dye was available for removal during wash testing, resulting in less vagrant being available for redeposition onto the adjacent multifibre strip materials (Table 3).

3.1.4. *Modified full backtan aftertreatment*

As recounted, the modified full backtan aftertreatment used, which employs a tin sulfate derived product (*Gallofix*), was devised to avoid the use of the traditional, toxic, potassium antimony tartrate in the traditional full backtan aftertreatment for acid dyes on polyamide fibres. In this two-stage aftertreatment, the gallotannin was firstly applied to the dyed silk and the tanned fabric was subsequently treated with the metal salt.

The colorimetric data (Table 2) show that, for each of the three dyes, aftertreatment with the modified full backtan process reduced the chroma and imparted a marked reddish hue to the

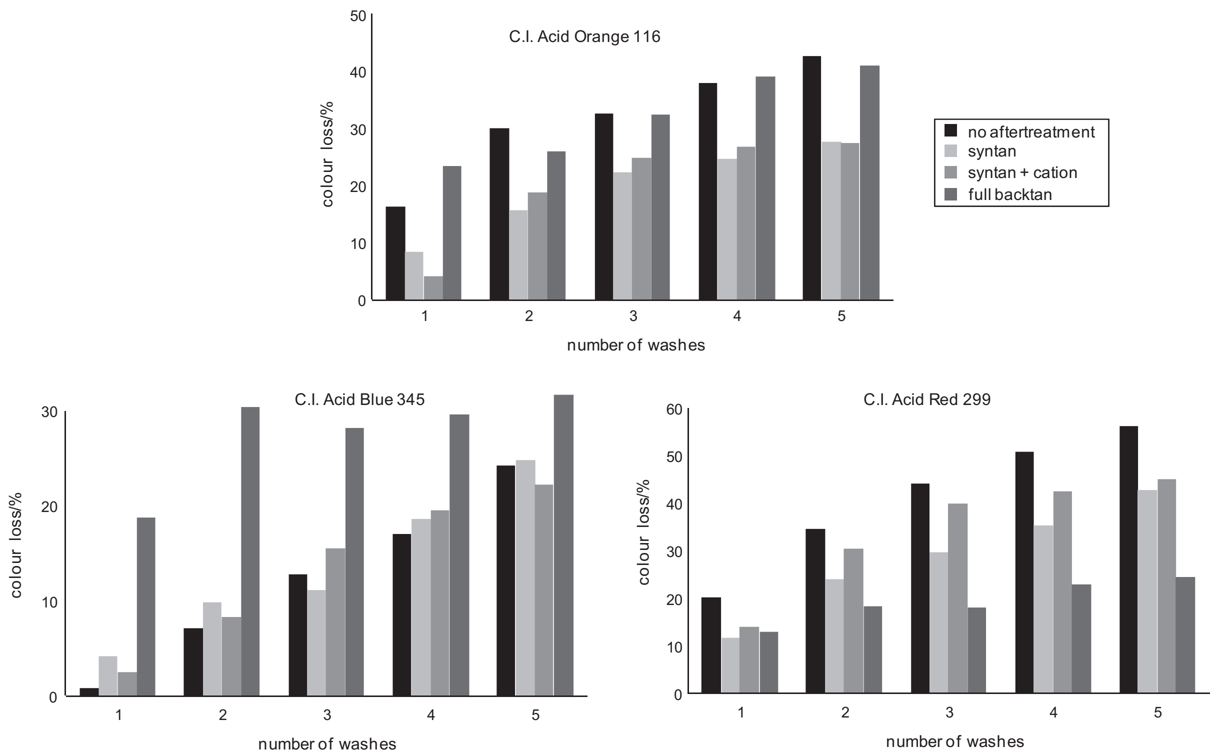


Fig. 7. Colour loss obtained for 3% omf non-metallised acid dyes.

dyeings. These findings were not surprising in view of the well-known shade changes that are associated with the use of the tannic acid component of this aftertreatment [1]. The application of the aftertreatment resulted in marked reductions in colour strength for each of the three dyes used (Fig. 6) prior to wash testing. This can be attributed to dye having been desorbed from the dyed substrate during each of the two hot, aqueous stages of the modified full backtan process. Aftertreatment also brought about a sizeable increase in lightness (Table 2) in the cases of C.I. Acid Blue 345 and C.I. Acid Red 299. In contrast, the L^* of the orange dye was reduced, significantly, by aftertreatment, this resulting from a marked change in the hue and chroma of the dyeing rather than an increase in colour strength of the dyeing. This specificity of action observed for the modified full backtan aftertreatment is discussed below.

In terms of the wash fastness of the dyeings, Fig. 6 shows that the colour strength of the backtanned dyeings was much lower, for each of the five wash tests, than that achieved for the dyeings which had been aftertreated with both the syntan and the syntan + cation processes. Indeed, the fk values of the backtanned dyeings which had been subjected to five, consecutive wash tests were very much lower than those of their non-aftertreated counterparts, for each of the three dyes used. Hence, in terms of depth of shade after wash fastness testing, the colour strength data (Fig. 6) show that aftertreatment with the modified full backtan process did not enable moderate/deep shades to be achieved.

However, the staining results obtained (Table 3) reveal that the backtanned dyeings displayed marginally higher fastness after five washes than their non-aftertreated, syntanned or syntan + cation aftertreated counterparts. This observation can be explained, as above, in terms of both the amounts of dye that were removed from the dyeings during the full backtan aftertreatment and the amount of vagrant dye available for redeposition on adjacent materials during wash testing. Accordingly, aftertreatment with the two-stage, tannic acid/*Gallofix* process removed considerably more dye from the dyeings than was removed by the application of both the syntan and the syntan + cation process, as evidenced by the respective fk and L^* values (Table 2 and Fig. 6). Consequently, much less dye was present on the backtanned aftertreated dyeings and, therefore, considerably less dye was available for removal during wash testing, resulting in far less vagrant dye being available for redeposition onto the adjacent multifibre strip materials. Hence, the lower staining results obtained for the backtanned dyeings (Table 3), which imply that the backtan process was more effective than the syntan or syntan + cation aftertreatments, are erroneous, as these particular grey scale ratings are a consequence of the much lower depth of shade of the backtanned dyeings. Indeed, in the context of the extent to which the depth of shade of the dyeings was reduced during repeated wash fastness testing, the % colour loss values (Fig. 7) obtained show that the modified backtan aftertreatment was less effective than both the syntan and the syntan + cation in the cases of C.I. Acid Orange 116 and C.I. Acid Blue 345, but was the most effective aftertreatment in the case of C.I Acid Red 299. As mentioned, this specificity of effect observed for the modified full backtan aftertreatment is discussed below.

3.2. Pre-metallised acid dyes

Three types of 1:2 pre-metallised acid dye are commercially available, namely *unsulfonated*, *monosulfonated* and *disulfonated*, the three dye types differing in terms of their wash fastness behaviour on polyamide fibres insofar as, depth of shade generally decreases but staining propensity also decreases, with increasing degree of sulfonation of the dyes [24,25].

3.2.1. Non-aftertreated dyeings

Fig. 8 shows the fk values obtained for 3% omf dyeings (both before and after the dyeings had been subjected to five, consecutive wash tests at 40 °C) of the two pre-metallised acid dyes used (i.e., C.I. Acid

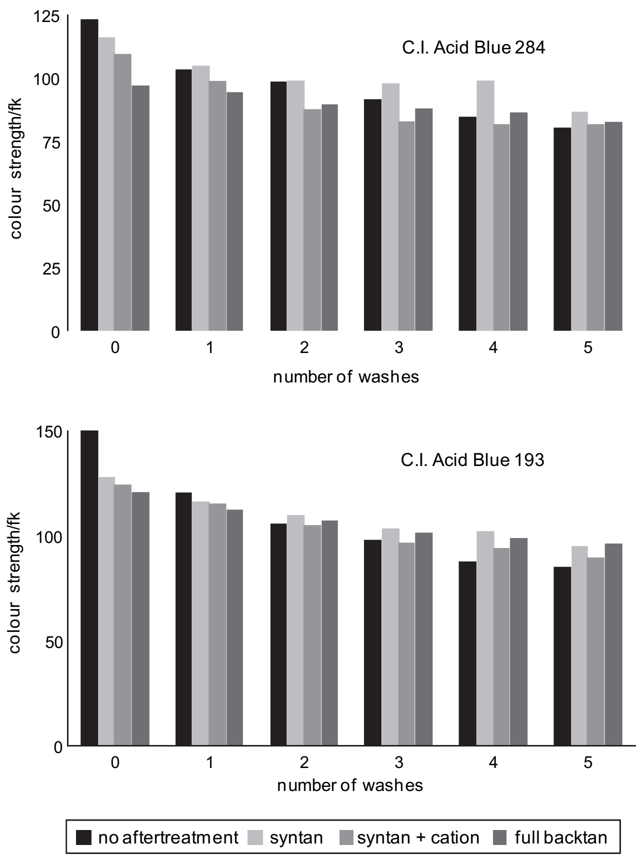


Fig. 8. Colour strength of 3% omf pre-metallised acid dyes.

Blue 284 and C.I. Acid Blue 193). The corresponding colorimetric data for the dyeings are displayed in Table 4 and the fastness data in Table 3.

From Fig. 8 it is clear that each of the pre-metallised acid dyes provided moderate/deep shades on the silk fabric but that both dyeings displayed only moderate/poor fastness to repeated washing insofar as the colour strength of the dyeings decreased with increasing number of washes. At the end of the five, repeated wash tests, the reduction in depth of shade varied from ~35 to 40% (Fig. 9), this being attributable to dye loss having occurred during washing. Such dye loss was reflected in the corresponding increased lightness of the dyeings (Table 4) that accompanied repeated wash testing. The vagrant dye that was removed from the dyeings during washing deposited on the adjacent cotton and nylon components of the multifibre strip material (Table 3) but not on the acetate, acrylic, wool or polyester components, which reflects the substantivity of such pre-metallised acid dyes towards these fibre types. The colorimetric data obtained for the dyeings both before and after wash testing (Table 4) shows that repeated washing had little effect on the hue and chroma of the dyeings.

3.2.2. *Syntan aftertreatment*

Table 4 shows that for both dyes used, syntan aftertreatment had little effect on the hue and chroma of the dyeings, which may be attributed to the moderately deep and relatively dull shades employed in this work. The colorimetric data (Table 4) also show that aftertreatment increased the lightness of the dyeings, this being accompanied by a corresponding decrease in colour strength (Fig. 8); these findings can be attributed to dye having been desorbed from the dyed silk during the syntan aftertreatment process. The fk values in Fig. 6 show that for almost every wash test, the extent of the reduction in the colour strength of the syntanned dyeings was lower than that obtained for the corresponding non-aftertreated dyeings. Hence, aftertreatment with the syntan improved the fastness of the three dyeings to repeated washing, this being confirmed by the lower extent of staining of adjacent materials recorded for the syntanned dyeings after five washes (Table 3). In terms of the reduction in depth of shade that occurred

Table 4
Colorimetric data obtained for 3% omf pre-metallised dyes.

Aftertreatment	Number of washes	C.I. Acid Blue 284					C.I. Acid Blue 193				
		L^*	a^*	b^*	C^*	h^o	L^*	a^*	b^*	C^*	h^o
nil	0	29.4	0.7	−20.7	20.7	271.9	26.3	1.7	−17.1	17.2	275.7
	1	31.8	0.4	−21.1	21.2	271.1	29.2	1.5	−17.8	17.8	274.8
	2	32.4	0.2	−20.9	20.9	270.6	30.9	1.3	−17.5	17.5	274.3
	3	33.3	0.1	−20.5	20.5	270.3	32.0	1.1	−17.5	17.5	273.1
	4	34.5	0.1	−20.5	20.5	270.3	33.5	0.9	−17.6	17.6	272.9
	5	35.1	0.0	−20.4	20.4	272.8	33.9	1.0	−17.5	17.5	273.3
syntan	0	30.2	0.4	−20.6	20.6	271.1	28.7	1.4	−16.7	16.7	274.8
	1	31.6	0.0	−20.6	20.6	272.8	29.6	1.5	−17.1	17.1	275.0
	2	32.4	0.1	−20.7	20.7	270.3	30.4	1.4	−16.9	16.9	274.7
	3	32.5	0.1	−20.3	20.3	270.3	31.2	1.3	−17.0	17.1	274.4
	4	32.3	0.2	−19.9	19.9	272.9	31.4	1.3	−16.9	16.9	274.4
	5	34.0	0.5	−19.3	19.3	271.4	32.4	1.1	−16.8	16.8	273.8
syntan + cation	0	31.0	0.1	−20.9	20.9	270.3	28.4	1.5	−17.0	17.1	275.0
	1	32.3	0.1	−20.3	20.3	270.2	29.7	1.5	−17.3	17.3	274.9
	2	33.9	0.3	−20.0	20.0	270.8	31.0	1.3	−17.2	17.2	274.3
	3	34.7	0.3	−19.9	19.9	270.6	32.1	1.3	−17.1	17.1	274.3
	4	34.8	0.5	−19.4	19.4	271.5	32.5	1.1	−16.9	16.9	273.7
	5	35.1	0.5	−19.5	19.5	271.5	33.2	1.0	−16.6	16.6	273.4
modified full backtan	0	31.9	4.7	−18.8	19.3	284.1	29.2	1.6	−17.3	17.4	275.2
	1	32.4	4.6	−18.8	19.4	283.8	30.2	1.4	−17.5	17.6	274.6
	2	33.0	4.4	−18.5	19.0	283.4	30.8	1.3	−17.2	17.2	274.3
	3	33.3	4.1	−17.8	18.2	282.9	31.5	1.1	−16.6	16.6	273.8
	4	33.6	3.9	−17.5	17.9	282.6	31.9	1.1	−16.8	16.8	273.8
	5	34.2	3.4	−16.5	16.8	281.6	32.3	0.7	−15.8	15.8	272.6

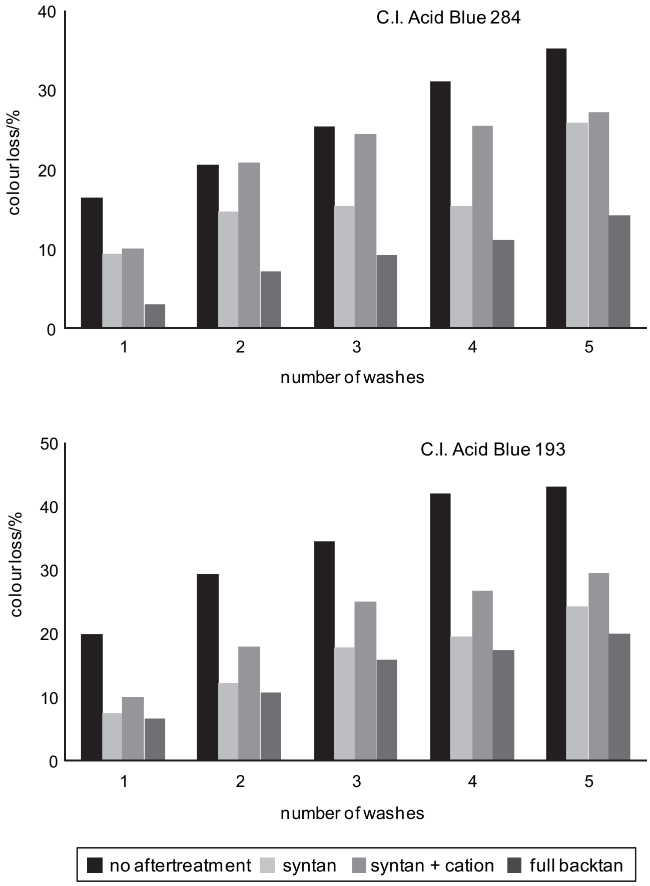


Fig. 9. Colour loss obtained for 3% omf pre-metallised acid dyes.

as a result of repeated wash fastness testing, the % colour loss values displayed in Fig. 9 show that syntan aftertreatment was very effective in reducing the extent of colour loss for both dyes used.

3.2.3. Syntan + cation aftertreatment

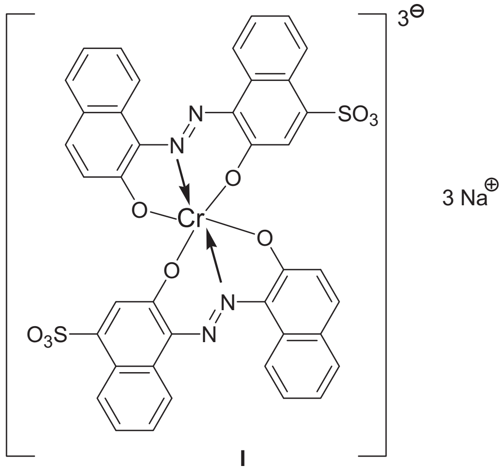
Table 4 and Fig. 8 show that the use of this aftertreatment increased the lightness and reduced the colour strength, respectively, of the dyeings prior to wash testing. The observation that the extents of the reduction in fk and increase in L^* were greater for the syntan + cation aftertreatment than the syntan aftertreatment can be attributed to more dye having been desorbed from the dyed substrate during the two hot, aqueous stages of the syntan + cation process. Table 4 shows that, for both dyes, aftertreatment with the syntan + cation process had little effect on the chroma and hue of the dyeings, as was observed for the syntan aftertreatment, which can be attributed to the moderately deep and relatively dull shades used. In the context of the fastness of the dyeings, Fig. 8 shows that the extent of the reduction in fk of the syntan + cation treated dyeings was greater than that achieved for the dyeings which had been aftertreated with the syntan. Thus, the fk data (Fig. 8) shows that aftertreatment with the syntan/cation process improved the fastness of both dyes to repeated washing. This was supported by the staining results obtained (Table 3) which revealed that the syntan + cation aftertreated dyeings displayed slightly superior fastness after five washes than their non-aftertreated counterparts. Furthermore, in the context of the extent to which the depth of shade of the dyeings was reduced during repeated wash fastness testing, the % colour loss values (Fig. 9) show that the syntan + cation aftertreatment was more effective than the syntan aftertreatment for both dyes.

3.2.4. Modified full backtan aftertreatment

The colorimetric data (Table 4) show that, for C.I. Acid Blue 284, aftertreatment with the modified full backtan process reduced the chroma and imparted a reddish hue to the dyeings. These findings were expected on the basis of the well-known shade changes that can be observed for the tannic acid component of this aftertreatment [1]; however, in the case of C.I. Acid Blue 193, aftertreatment had little effect upon the hue and colour of the dyeing. The application of the aftertreatment resulted in a reduction in colour strength (Fig. 8) and an increase in L^* value for both dyes used prior to wash testing, which can be attributed to dye having been desorbed from the dyed substrate during the two-stage modified full backtan process. In terms of the fastness of the dyeings, Fig. 8 shows that the colour strength of the backtanned dyeings was higher than that obtained for the syntan + cation process in the cases of the last four wash tests and was similar to that achieved for the syntan aftertreatment for the final wash test. Thus, the fk data (Fig. 8) show that aftertreatment with the modified full backtan improved the fastness of both dyes to repeated washing. This finding gained support from the staining results obtained (Table 3), which show that the backtanned dyeings displayed highest fastness after five washes. Furthermore, in terms of the extent to which the depth of shade of the dyeings was reduced during repeated wash fastness testing, the % colour loss values (Fig. 9) clearly show that the modified full backtan aftertreatment was more effective than either the syntan or the syntan + cation aftertreatments for both dyes.

3.2.5. Comparison of results obtained for the two types of dye

The results obtained clearly show that it was possible to obtain moderate/deep shades using both non-metallised and pre-metallised acid dyes on the silk fabric used. It is apparent that prior to aftertreatment, the fastness of the two pre-metallised acid dyes was superior to that of their non-metallised counterparts, in terms of staining (Table 3) of adjacent multifibre strip materials. Furthermore, the staining results in Table 3 also imply that the fastness of the disulfonated dye C.I. Acid Blue 193 was slightly better than that of its monsulfonated counterpart, C.I. Acid Blue 284. As mentioned, the three types of 1:2 pre-metallised acid dye commercially available (*unsulfonated*, *monosulfonated* and *disulfonated*) differ in terms of their wash fastness behaviour on polyamide fibres in that depth of shade generally decreases but staining propensity also decreases, with increasing degree of sulfonation of the dyes [24,25]. This difference in washing behaviour has been ascribed to a difference in the aqueous solubility of the three types of dye; whereas disulfonated variants are more readily removed during washing because of their higher water-solubility, the resulting vagrant dye displays a lower propensity to stain adjacent materials because of this high water-solubility [24,25]. Thus, the staining results obtained for the two pre-metallised acid dyes (Table 3) were as expected. However, when the % colour loss data obtained for the non-metallised acid and pre-metallised acid dyes are compared (Figs. 7 and 9), it is apparent that there were relatively small differences between the two types of dye in terms of the amount of dye that was removed during repeated wash testing, especially as the colour strength of the three non-metallised acid dyeings was higher than that of the two pre-metallised dyeings (Figs. 6 and 8). Thus, although approximately similar levels of dye loss occurred as a result of repeated washing for each of the five dyes used (Figs. 7 and 9), the lower extent of staining obtained for the pre-metallised dyes may be attributable to their comparatively lower substantivity under the aqueous, alkaline washing conditions used, which, in turn, may result from lower water-solubility, larger M_r, etc. Unfortunately, as the structure of only one of the dyes is available (**I**), this proposal cannot be confirmed.



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In terms of the effects imparted by the three aftertreatments used, the results show that each aftertreatment improved the fastness of each of the dyes to repeated wash testing, based on the staining results obtained (Table 3). As such, while these findings were encouraging, bearing in mind that the three aftertreatments used had been devised for use on acid dyed nylon rather than acid dyed silk, it was clear that differences were observed in the behaviour of the five dyes towards the aftertreatments employed that had not been found in the case of non-metallised and pre-metallised dyes on nylon [20–22,24,25].

The extent of wash fastness improvement varied for the dyes used insofar as, for the two pre-metallised acid dyes and C.I. Acid Blue 345, the modified full backtan gave marginally superior results; for the remaining non-metallised acid dyes (C.I. Orange 116 and C.I. Acid Red 299) there was little difference in the improvements imparted by each of the three aftertreatments used. In terms of the depth of shade obtained at the end of the five, consecutive, 40 °C wash tests, the backtan produced markedly paler dyeings in the case of the three non-metallised dyes used (Fig. 6) whereas there was little difference between the fk values of dyeings which had been aftertreated with the syntan and syntan + cation. In contrast, the depth of shade of the two pre-metallised acid dyes was similar for each of the three aftertreatments used (Fig. 8). In addition, differences were obtained in terms of changes in colour and lightness of the dyeings imparted by the aftertreatments. Both syntan and syntan + cation aftertreatments increased the lightness and reduced the colour strength of all of the dyes used, these effects being more pronounced in the case of the two-stage process. The two aftertreatments also reduced the chroma and imparted a slight reddish hue to the non-metallised dyes but had little effect on colour of the pre-metallised dyes. The modified full backtan caused marked reduction in the colour strength of the three non-metallised acid dyes used together with a sizeable increase in lightness in the cases of the red and blue non-metallised dyes, although the L^* of the orange non-metallised dye was reduced, significantly, by aftertreatment, this resulting from a marked change in the hue and chroma of the dyeing rather than an increase in colour strength of the dyeing. The aftertreatment imparted a lower reduction in colour strength and increase in lightness for both pre-metallised dyes and also reduced the chroma and imparted a reddish hue to C.I. Acid Blue 284 dyeings but had no effect on the colour of C.I. Acid Blue 193 dyeings.

Interestingly, the findings reported herein do not entirely agree with those reported [18] for the effects of syntan, syntan/cation and traditional full backtan (tannic acid/tartar emetic) aftertreatments on three non-metallised acid dyes on silk, although this particular work [18] employed different dyes, different syntan, cation and full backtan system to those employed herein and also concerned the desorption of 2% omf dyeings that occurred during a single, 50 °C washing treatment rather than the repeated wash fastness protocol adopted herein.

4. Conclusions

The three aftertreatments improved the fastness of each of the dyes to repeated wash testing. The differences observed in the behaviour of the five dyes towards the aftertreatments employed did not simply divide along the lines of non-metallised versus pre-metallised types, or neither acid milling versus acid levelling nor, indeed, disulfonated versus monosulfonated. As the study used only five dyes and, for the most part, single examples of each of the various dye types selected, the spread of results is therefore small and, perhaps, these findings were to be expected. Nevertheless, some trends were observed of which the marked reduction in the depth of shade of the three non-metallised acid dyes imparted by the modified full backtan (compared to a much lower reduction in fk recorded for the two pre-metallised acid dye) is perhaps the most noticeable, as this implies a fair degree of specificity in terms of the effectiveness of this particular aftertreatment. Clearly, the observed variation in the behaviour of the dyes towards aftertreatment and the marked specificity of action observed for the modified full backtan aftertreatment require further study.

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