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The development of a metal-free, tannic acid-based aftertreatment for nylon 6,6 dyed with acid dyes—part 1: initial studies

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Abstract

A one-bath, two-stage, tannic acid based aftertreatment for nylon 6,6 dyed with acid dyes, in which an enzyme was used to complex tannic acid, has been developed. Four established aftertreatments, namely two commercial syntans, the traditional full backtan and a tannic acid/tin salt system, were chosen as 'references' against which the effectiveness of the developed tannic acid/enzyme sytem was compared. In recognition of the fact that different washing temperatures are employed in Northern Europe, the effectiveness of the various aftertreatments was determined at three washing temperatures, namely 40, 50 and 60 °C, using a repeated wash testing protocol. It was found that each of the four established aftertreatments was highly effective in improving the wash fastness of the three dyes at all three washing temperatures used. The effectiveness of the tannic acid/enzyme system in improving the wash fastness to repeated washing was comparable to that of the four 'reference' aftertreatments. The metal-free, tannic acid/enzyme aftertreatment offers a potentially more environmentally acceptable alternative to the antimony-based and tin-based systems.

Keywords: Nylon 6; 6; Acid dyes; Full backtan; Syntan; Enzyme

1. Introduction

Previous work [1,2] reported the extent to which the wash fastness to repeated washing at 60 °C, of eight commercial 1:2 pre-metallised acid dyes [1] and six non-metallised acid dyes [2] on nylon 6,6 fabric, was improved by an aftertreatment with a newly developed full backtan system that comprised tannic acid and a non-potassium antimonyl tartrate complexing agent. It was found that the extent of wash fastness improvement imparted by the new full backtan system was greater than that given by a commercial syntan. In addition, while backtanning imparted little shade change to the dyeings, the handle of the backtanned fabrics was slightly harsher than that of the syntanned fabric; the light fastness of the dyeings was little changed as a result of the backtanning process.

However, despite the effectiveness of the new backtanning system in improving the wash fastness of acid dyes nylon 6,6, because the non-potassium

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Table 1
Dyes used

Commercial name	Type	C.I. generic name
Nylanthrene Black C-DPL	Non-metallised acid	None ascribed
Neutrilan Red K-2G	Unsulfonated 1:2 pre-metallised	None ascribed
Nylanthrene Yellow C-3RL	Non-metallised acid	Acid Orange 67

antimonyl tartrate complexing agent that was used in the previous work was a tin-derived product, it was decided to develop a non-metal based, full backtan aftertreatment. This paper concerns the effectiveness of such a metal-free full backtan aftertreatment, in improving the fastness to repeated washing of commercial acid dyes on nylon 6,6, compared to that of two commercial syntans, the traditional full backtan (tannic acid/potassium antimonyl tartrate) as well as the recently developed tin sulfate system (tannic acid/*Gallofix*) [1,2]. In recognition of the fact that different washing temperatures are employed in Northern Europe, the effectiveness of the various aftertreatments was determined at three washing temperatures, namely 40, 50 and 60 °C.

2. Experimental

2.1. Materials

Knitted nylon 6.6 fabric of 78f/68 dtex per filament and amino end group (AEG) content of 45 meq. 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. Three commercial acid dyes (Table 1) were kindly supplied by Yorkshire Chemicals; the dyes were chosen because they displayed moderate fastness on nylon 6,6 to the repeated washing protocol employed in this work. Two commercial syntans namely, *Zetesal NR* (Zschimmer & Schwarz) and *Nylofixan MF2N* (Clariant, UK) were applied using the maker's recommended procedures [3]. Commercial samples of *Textan 3* (high M_r gallotannin) and *Gallofix* were generously provided by Omnichem-Ajinomoto. A sample of potassium antimony tartrate (tartar emetic) was obtained from Aldrich and a commercial sample of the enzyme *Savinase* was kindly provided by Novazyme.

All other chemical used were laboratory grade reagents.

2.2. Dyeing

The dyes were applied using the equipment described earlier [1] following the method shown in Fig. 1; the pH was adjusted using McIlvaine buffer [4]. The dyeings were rinsed thoroughly in tap water and allowed to dry in the open air.

2.3. Full backtan aftertreatment

The aftertreatment method is given in Fig. 2; the equipment described earlier [1] was used, the application pH (pH 3) being adjusted using McIlvaine buffer [4] The aftertreated samples were removed, rinsed thoroughly in tap water and allowed to air dry.

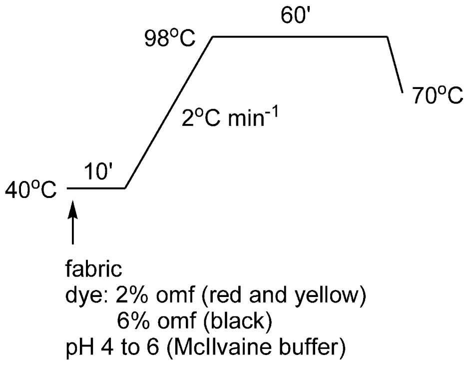

Fig. 1. Dyeing method.

2.4. Gallofix aftertreatment

The aftertreatment method is shown in Fig. 2; the equipment described earlier [2] was used, the pH of application (pH 3) being adjusted using McIlvaine buffer [4]. At the end of treatment, the samples were removed, rinsed thoroughly in tap water and allowed to dry in the open air.

2.5. Enzyme treatment

The aftertreatment method is shown in Fig. 2; the equipment described earlier [2] was used, the pH of application (pH 3) being adjusted using McIlvaine buffer [4]. At the end of treatment, the samples were removed, rinsed thoroughly in tap water and allowed to dry in the open air.

2.6. Syntan aftertreatment

Dyeings were aftertreated (4% omf) using the equipment described earlier [1] following the methods shown in Fig. 3; the pH of application (pH 4) was adjusted using McIlvaine buffer [4]. At the end of treatment, the syntanned samples were removed, rinsed thoroughly in tap water and allowed to air dry.

2.7. Colour measurement

All measurements were carried out using the equipment and procedures described earlier [1].

2.8. Wash-fastness

It was decided that this work should be carried out in recognition of the diverse washing temperatures commonly used in Northern Europe as well as recent trends in wash fastness assessment towards repeated washing testing as opposed to single wash testing. In this context, the wash fastness of the dyed samples was determined at three temperatures (40, 50 and 60 °C). Three, ISO standard wash tests, namely ISO CO6/A2S (40 °C), ISO CO6/B2S (50 °C) and ISO CO6/C2S (60 °C) [5] were used but were modified in that dyeings were subjected to five, consecutive wash tests and, at the end of each wash test, the washed sample was rinsed thoroughly in tap water (but was not dried) and a fresh sample of SDC multifibre strip was used to assess the extent of staining for each of the five wash tests. The extent of the staining of adjacent multifibre strip was expressed in the appropriate staining grey scale whereas the change in shade of the sample after washing was expressed in ΔE CIE $L^*a^*b^*$ units.

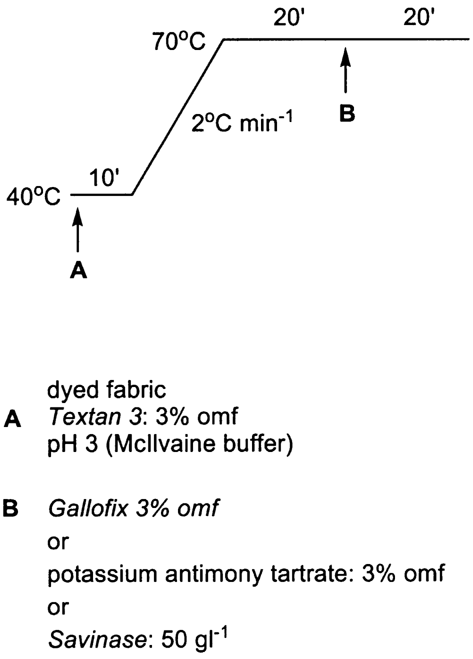

Fig. 2. Tannic acid/metal salt/enzyme treatment.

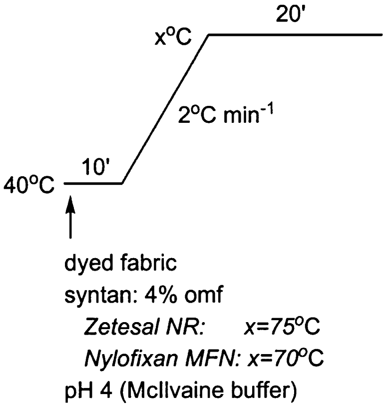

Fig. 3. Syntan treatment.

3. Results and discussion

As mentioned, because washing temperatures vary within Europe, it was decided to use three, common washing temperatures in this work, namely 40, 50 and 60 °C. 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 two different depths of shade employed (2% omf in the cases of the red and yellow dyes and 6% omf in the case of the black dye). In the context of the shade change which the dyeings underwent when they were subjected to five, consecutive wash tests at the three washing temperatures, Tables 2–4 show the colorimetric and colour strength data obtained for the five dyes. The moderate fastness of the three dyes to repeated washing is clearly evident, insofar as the dyeings underwent a reduction in colour strength *f*(*k*) due to the loss of dye during washing. From the *f*(*k*) values shown, it is also apparent that the reduction in colour strength increased with increasing temperature of wash testing; this expected finding can be attributed to a corresponding increase in the extent of removal of dye from the dyed samples during wash testing. The colorimetric data presented in Tables 2–4 reveal that the shade changes observed for the three dyes were attributable to a loss of dye from the dyeings rather than to changes in the colour of the dyeings.

The magnitude of the reduction in colour strength of the dyeings that occurred as a result of repeated washing is evident in Fig. 4 which shows the colour difference (ΔE) obtained between unwashed dyeings and dyeings which had been subjected to five, repeated wash tests. The effect of washing temperature on the extent of the shade change that the dyeings underwent is clearly evident; the yellow dye, in particular, displayed poor fastness to washing at 60 °C.

Table 2
Colorimetric data and wash fastness results for untreated dyeings washed at 40 °C

Dye	No. of washes	L^*	a^*	b^*	C^*	$h°$	$f(k)$
Red K-2G	0	42.2	44.3	17.6	47.7	21.7	91.0
	5	44.0	43.0	18.0	46.6	22.7	78.7
Yellow C-3RL	0	69.9	28.8	71.2	76.8	68.0	66.9
	5	70.5	27.8	68.8	74.6	68.0	50.1
Black C-DPL	0	24.9	−0.3	−3.9	3.9	265.3	180.7
	5	26.5	−0.3	−3.9	3.9	265.6	160.4

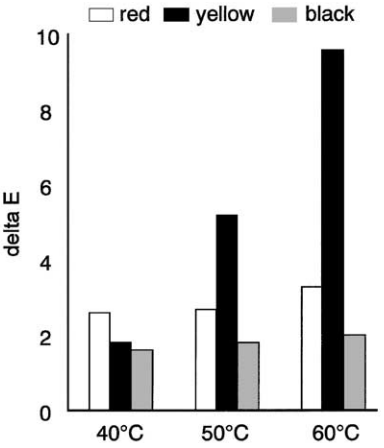

Fig. 4. Colour difference between unwashed and washed dyeings at different washing temperatures.

Table 3
Colorimetric data and wash fastness results for untreated dyeings washed at 50 °C

Dye	No. of washes	L^*	a^*	b^*	C^*	$h°$	$f(k)$
Red K-2G	0	42.2	44.3	17.6	47.7	21.7	91.0
	5	44.5	42.9	18.1	46.5	22.8	76.6
Yellow C-3RL	0	69.9	28.8	71.2	76.8	68.0	66.9
	5	71.4	26.9	66.7	71.9	68.0	48.9
Black C-DPL	0	24.9	−0.3	−3.9	3.9	265.3	180.7
	5	26.7	−0.3	−3.9	3.9	266.1	156.0

Table 4
Colorimetric data and wash fastness results for untreated dyeings washed at 60 °C

Dye	No. of washes	L^*	a^*	b^*	C^*	$h°$	$f(k)$
Red K-2G	0	42.2	44.3	17.6	47.7	21.7	91.0
	5	44.9	42.6	18.4	46.4	23.4	73.2
Yellow C-3RL	0	69.9	28.8	71.2	76.8	68.0	66.9
	5	73.3	24.3	63.3	67.8	69.0	37.5
Black C-DPL	0	24.9	−0.3	−3.9	3.9	265.3	180.7
	5	26.9	−0.3	−3.9	3.9	265.7	153.0

Table 5
Staining of adjacent multifibre strip achieved for untreated dyeings

Dye	No. of washes	Wool	Acrylic	Polyester	Nylon 6,6	Cotton	2° Acetate
Red K-2G	1	**5** 5* (3)	**5** 5* (5)	**5** 5* (5)	**2/3** 1* (1)	**5** 5* (5)	**5** 5* (5)
	5	**5** 5* (4)	**5** 5* (5)	**5** 5* (5)	**3** 2* (1)	**5** 5* (5)	**5** 5* (5)
Yellow C-3RL	1	**5** 2/3* (1/2)	**5** 4* (4)	**5** 4* (3)	**2/3** 1/2* (1)	**5** 4* (4)	**2/3** 1/2* (1)
	5	**5** 3/4* (2/3)	**5** 5* (5)	**5** 4/5* (4)	**3** 2/3* (2)	**5** 4/5* (4/5)	**3** 2/3* (2)
Black C-DPL	1	**4/5** 3/4* (3)	**5** 3* (2/3)	**5** 4/5* (4/5)	**1/2** 1/2* (1)	**5** 5* (4/5)	**5** 5* (5)
	5	**5** 4* (4)	**5** 4/5* (4)	**5** 5* (5)	**2** 2/3* (2)	**5** 5* (5)	**5** 5* (5)

Bold = 40 °C; * = 50 °C; ( ) = 60 °C.

While the nature and magnitude of any shade change which a dyed sample undergoes during washing contribute to the assessment of wash fastness, the extent of any staining of adjacent materials by vagrant dye during washing is an equally important element of wash fastness. Table 5 shows the extent of staining of multifibre strip obtained as a result of the five, consecutive wash tests. The low level of staining achieved in the cases of the adjacent acrylic, polyester and cotton components was anticipated in view of the inherent low substantivity of the three acid dyes towards such fibre types. Also expected, from the viewpoint of the substanitivity of the three dyes used, was the very high extent of staining obtained for the adjacent nylon 6,6 fibre and the moderate staining of the wool component. However, the very high level of staining of the adjacent secondary acetate fibre observed in the case of the yellow dye was unexpected; no explanation for this finding can be offered. The results presented in Table 5 reveal that the extent of staining of the adjacent materials increased, markedly, with increase in washing temperature. In the context of the results displayed in Tables 2–4, this finding can be attributed to a corresponding increase in the amount of dye removed from the dyeings as the temperature at which wash fastness testing was increased.

The four established aftertreatments that were used in this work (two commercial syntans, a traditional full backtan and a tannic acid/tin sulfate system) were chosen as 'references' against which the effectiveness of the developed tannic acid/enzyme system in enhancing the wash fastness of typical acid dyes on nylon 6,6 could be compared. At no time was it the intention of the work to highlight the superiority of one aftertreatment over another in improving wash fastness.

3.1. Traditional full backtan

Aftertreatment of the three dyes with the traditional full backtan markedly improved the wash fastness of each of the dyes to repeated wash fastness, in terms of change in shade of the dyeings (Tables 6–8). Figs. 5–7 show the extent to which the full backtan reduced the shade change of the dyeings in terms of the colour difference obtained after repeated wash testing at the three temperatures used for washing. Comparison of the colorimetric data obtained for the untreated dyeings (Tables 2–4) with those achieved for the full backtanned samples (Tables 6–8) reveals that aftertreatment increased the colour strength and flattened the shade of the dyeings; in the cases of the red and yellow dyeings, aftertreatment also imparted a yellow colour, this being especially

Table 6
Colorimetric data for full backtanned dyeings washed at 40 °C

Dye	No. of washes	L^*	a^*	b^*	C^*	h°	$f(k)$
Red K-2G	0	41.0	43.1	16.4	46.1	20.8	97.7
	5	41.2	43.7	16.4	46.7	20.6	97.2
Yellow C-3RL	0	68.2	27.9	71.3	76.5	68.6	76.0
	5	69.0	27.3	70.0	75.1	68.7	74.6
Black C-DPL	0	23.4	−0.4	−4.0	4.0	264.3	202.5
	5	23.7	−0.4	−3.6	3.6	263.7	200.8

Table 7
Colorimetric data for full backtanned dyeings washed at 50 °C

Dye	No. of washes	L^*	a^*	b^*	C^*	$h°$	$f(k)$
Red K-2G	0	41.0	43.1	16.4	46.1	20.8	97.7
	5	41.3	43.9	16.3	46.8	20.4	96.9
Yellow C-3RL	0	68.2	27.9	71.3	76.5	68.6	76.0
	5	69.3	26.7	68.8	73.8	68.8	74.0
Black C-DPL	0	23.4	−0.4	−4.0	4.0	264.3	202.5
	5	23.9	−0.4	−3.5	3.6	263.5	199.8

Table 8
Colorimetric data for full backtanned dyeings washed at 60 °C

Dye	No. of washes	L^*	a^*	b^*	C^*	$h°$	$f(k)$
Red K-2G	0	41.0	43.1	16.4	46.1	20.8	97.7
	5	41.4	44.1	16.2	47.0	20.2	96.0
Yellow C-3RL	0	68.2	27.9	71.3	76.5	68.6	76.0
	5	70.0	26.0	67.2	72.1	68.8	73.3
Black C-DPL	0	23.4	−0.4	−4.0	4.0	264.3	202.5
	5	24.0	−0.5	−3.4	3.4	261.6	198.7

prevalent for the yellow dyeings. These particular findings were not surprising as it is well known that the full backtan aftertreatment can alter the shade of dyeings [6].

The full backtan was especially effective in reducing the extent of staining of the adjacent multifibre strip during repeated wash testing (Table 9). Comparison of the data for the staining achieved for the untreated dyeings (Table 5) with those obtained for the full backtanned samples (Table 9.) shows clearly how effectively the full backtan aftertreatment reduced staining at each of the three wash temperatures employed.

3.2. Syntans

Although the full backtan is effective in improving the wet fastness of acid dyes on nylon, the aftertreatment is nowadays rarely used owing to the toxicity of potassium antimonyl tartrate and because it can impair the handle and the light fastness of dyeings as well as impart a shade

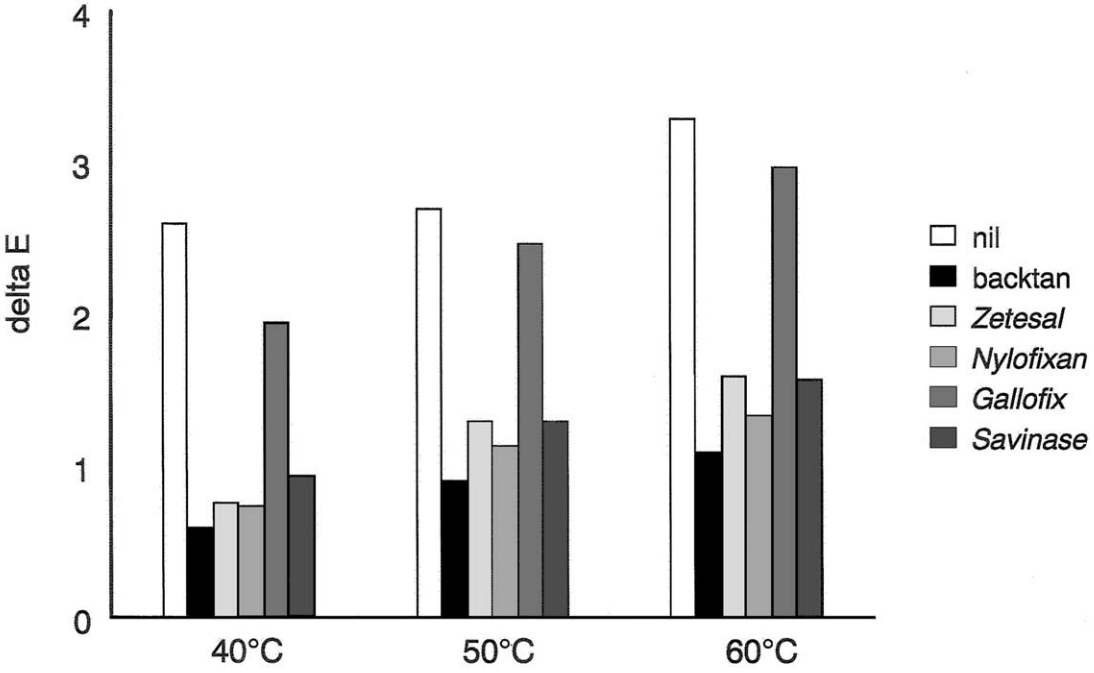

Fig. 5. Effect of aftertreatment on colour difference for red dye.

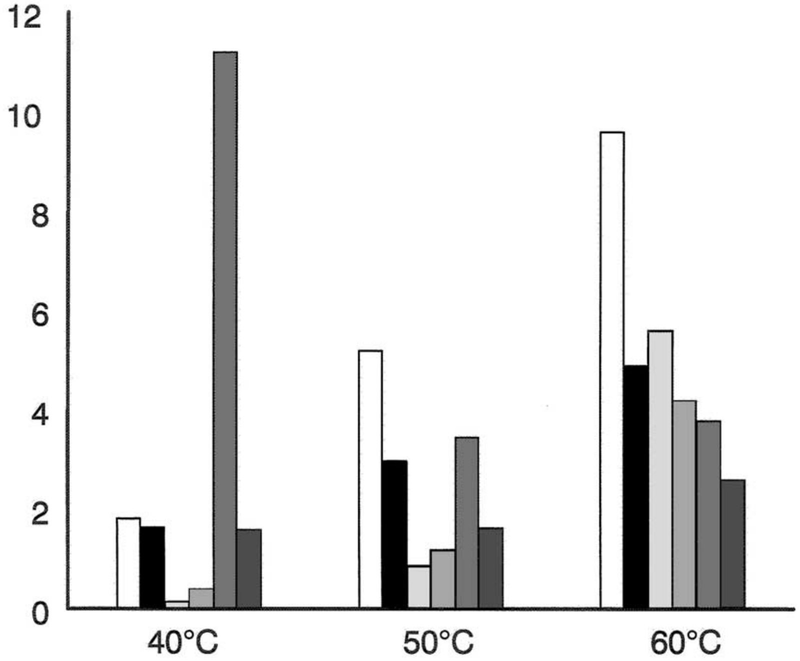

Fig. 6. Effect of aftertreatment on colour difference as for Fig. 5 for yellow dye (legend as for Fig. 5).

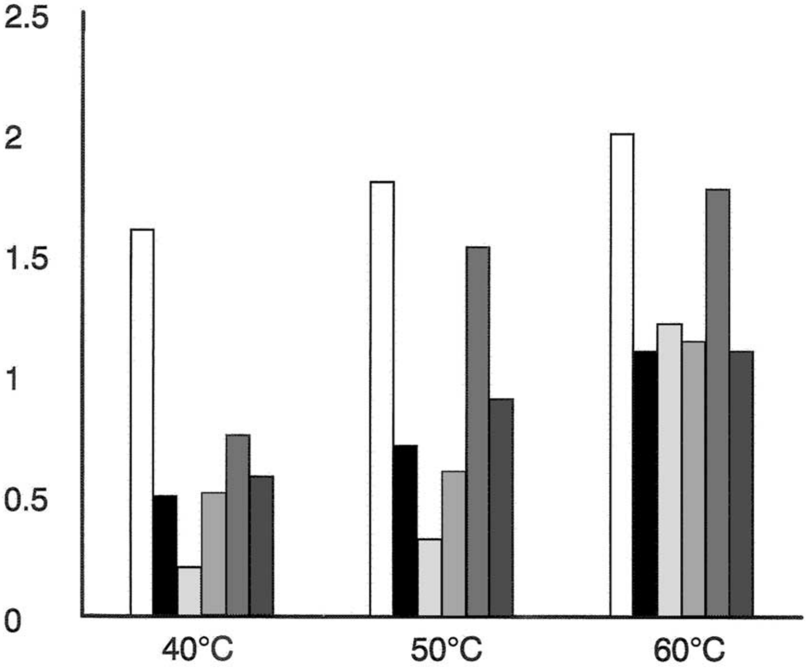

Fig. 7. Effect of aftertreatment on colour difference for black dye (legend as for Fig. 5).

Table 9
Staining of adjacent multifibre strip achieved for backtanned dyeings

Dye	No. of washes	Wool	Acrylic	Polyester	Nylon 6,6	Cotton	2° Acetate
Red K-2G	1	**5** 5* (5)	**5** 5* (5)	**5** 5* (5)	**4/5** 4/5* (2/3)	**5** 5* (5)	**5** 5* (5)
	5	**5** 5* (4/5)	**5** 5* (5)	**5** 5* (5)	**5** 4* (2)	**5** 5* (5)	**5** 5* (5)
Yellow C-3RL	1	**5** 5* (4/5)	**5** 5* (5)	**5** 5* (5)	**5** 5* (4)	**5** 5* (5)	**5** 5* (5)
	5	**5** 5* (4/5)	**5** 5* (5)	**5** 5* (5)	**5** 4/5* (3)	**5** 5* (5)	**5** 5* (5)
Black C-DPL	1	**5** 5* (4/5)	**5** 5* (5)	**5** 5* (5)	**4/5** 4/5* (3/4)	**5** 5* (5)	**5** 5* (5)
	5	**5** 5* (4/5)	**5** 5* (5)	**5** 5* (5)	**5** 4/5* (3/4)	**5** 5* (5)	**5** 5* (4/5)

Bold = 40 °C; * = 50 °C; ( ) = 60 °C.

change to dyeings [6]. An aftertreatment with a synthetic tanning agent (syntan) has mostly replaced the full backtan as a means of improving the wet fastness of acid dyes on nylon. Syntans offer the advantage of being applied in a single stage process and do not suffer from the disadvantages 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 [6].

Aftertreatment with 4% omf of each of the two syntans reduced the extent of shade change of the dyeings (Tables 10–12). When the colorimetric data obtained (Tables 10–12) are compared to those achieved for the untreated dyeings (Tables 2–4), it is evident that aftertreatment with each syntan imparted a yellowness to the shade of the red and yellow dyeings; no such colour change was apparent for the black dyeings. The observed colour changes can be attributed to the well known characteristic of this particular aftertreatment [6]. Figs. 5–7 reveal, in terms of colour difference obtained after repeated wash testing at the three temperatures used, that the two syntans were, overall, very similar to or marginally better than, the full backtan in terms of their ability to reduce the shade change that occurred as a result of repeated washing. The extent of staining of adjacent multifibre strip achieved for the syntanned dyeings (Table 13) was much lower than that obtained for the untreated dyeings (Table 5). However, the reduction in the extent of staining of the adjacent nylon component imparted by syntan aftertreatment (Table 13) was generally lower than

Table 10
Colorimetric data for syntanned dyeings washed at 40 °C

Dye	Syntan	No. of washes	L^*	a^*	b^*	C^*	h°	$f(k)$
Red K-2G	*Zetesal NR*	0	43.4	44.1	16.6	47.1	20.7	81.3
		5	43.5	43.8	17.3	47.1	21.6	81.5
	Nylofixan MFN	0	43.3	44.0	17.9	47.5	22.2	83.9
		5	43.6	43.7	17.3	47.0	21.6	80.5
Yellow C-3RL	*Zetesal NR*	0	70.8	26.9	67.8	73.0	68.4	54.1
		5	70.8	26.8	66.7	71.9	68.1	51.5
	Nylofixan MFN	0	69.7	29.2	70.6	76.4	67.5	65.9
		5	70.1	29.2	70.6	76.4	67.5	64.2
Black C-DPL	*Zetesal NR*	0	20.9	−0.4	−3.8	3.8	263.4	252.4
		5	20.8	−0.3	−3.7	3.7	265.3	255.2
	Nylofixan MFN	0	22.0	−0.3	−4.1	4.1	265.5	228.9
		5	22.4	−0.4	−3.8	3.8	264.6	220.9

Table 11
Colorimetric data for syntanned dyeings washed at 50 °C

Dye	Syntan	No. of washes	L^*	a^*	b^*	C^*	$h°$	$f(k)$
Red K-2G	*Zetesal NR*	0	43.4	44.1	16.6	47.1	20.7	81.3
		5	44.5	44.0	17.0	47.2	21.2	75.4
	Nylofixan MFN	0	43.3	44.0	17.9	47.5	22.2	83.9
		5	44.0	44.4	17.1	47.5	21.1	78.7
Yellow C-3RL	*Zetesal NR*	0	70.8	26.9	67.8	73.0	68.4	54.1
		5	70.4	27.4	67.2	72.6	67.8	54.0
	Nylofixan MFN	0	69.7	29.2	70.6	76.4	67.5	65.9
		5	69.6	29.2	69.2	75.1	67.1	62.4
Black C-DPL	*Zetesal NR*	0	20.9	−0.4	−3.8	3.8	263.4	252.4
		5	20.6	−0.4	−3.7	3.7	264.5	259.6
	Nylofixan MFN	0	22.0	−0.3	−4.1	4.1	265.5	228.9
		5	22.5	−0.3	−3.8	3.8	265.3	220.3

Table 12
Colorimetric data for syntanned dyeings washed at 60 °C

Dye	Syntan	No. of washes	L^*	a^*	b^*	C^*	$h°$	$f(k)$
Red K-2G	*Zetesal NR*	0	43.4	44.1	16.6	47.1	20.7	81.3
		1	44.4	44.6	17.5	47.9	21.4	77.1
	Nylofixan MFN	0	43.3	44.0	17.9	47.5	22.2	83.9
		5	44.6	44.3	17.7	47.7	21.8	75.8
Yellow C-3RL	*Zetesal NR*	0	70.8	26.9	67.8	73.0	68.4	54.1
		5	73.1	25.2	63.0	67.9	68.2	37.5
	Nylofixan MFN	0	69.7	29.2	70.6	76.4	67.5	65.9
		5	70.8	27.9	66.8	72.4	67.4	51.7
Black C-DPL	*Zetesal NR*	0	20.9	−0.4	−3.8	3.8	263.4	252.4
		5	22.1	−0.3	−3.9	3.9	266.1	227.3
	Nylofixan MFN	0	22.0	−0.3	−4.1	4.1	265.5	228.9
		5	23.1	−0.3	−3.8	3.8	265.7	208.9

that achieved using the full backtan (Table 9), especially when washing had been carried out at 50 and 60 °C.

3.3. *Gallofix*

Aftertreatment with the tin-based tannic acid/*Gallofix* system [1,2] reduced the extent of shade change of the dyeings (Tables 14–16) for each of the three washing temperatures used. The colorimetric data clearly shows that aftertreatment with the *Gallofix* system imparted a brownish yellow colour to the shade of the red and yellow dyeings; no such colour change was apparent for the black dyeings. This can be attributed to the dark yellow/brown nature of the tannic acid/*Gallofix* complex, which, presumably, is due to the presence of tin salts.

Figs. 5–7 reveal, in terms of colour difference obtained after repeated wash testing at the three temperatures used, that the tin-based system was, overall, slightly less effective than the full backtan

Table 13
Staining of adjacent multifibre strip achieved for syntanned dyeings

Dye	Syntan	No. of washes	Wool	Acrylic	Polyester	Nylon 6,6	Cotton	2° Acetate
Red K-2G	*Zetesal NR*	1	**5** 5* (4)	**5** 5 (5)	**5** 5* (5)	**4/5** 4* (2/3)	**5** 5* (5)	**5** 5 (4/5)
		5	**5** 5* (4)	**5** 5 (5)	**5** 5* (5)	**5** 4/5* (2)	**5** 5* (5)	**5** 5 (4/5)
	Nylofixan MFN	1	**5** 5* (5)	**5** 5 (5)	**5** 5* (5)	**4/5** 4* (3)	**5** 5* (5)	**5** 5* (5)
		5	**5** 5* (5)	**5** 5* (5)	**5** 5* (5)	**5** 4* (2)	**5** 5* (5)	**5** 5* (5)
Yellow C-3RL	*Zetesal NR*	1	**5** 5* (3)	**5** 5* (5)	**5** 5* (5)	**5** 5* (2)	**5** 5* (4/5)	**5** 5*(3)
		5	**5** 5* (2/3)	**5** 5* (5)	**5** 5* (5)	**5** 4/5* (1/2)	**5** 5* (4/5)	**5** 4/5* (2/3)
	Nylofixan MFN	1	**5** 5* (3)	**5** 5* (5)	**5** 5* (5)	**5** 4/5* (2)	**5** 5* (4/5)	**5** 5* (3)
		5	**5** 5* (2/3)	**5** 5* (5)	**5** 5* (5)	**5** 4/5* (1/2)	**5** 5* (4/5)	**5** 4/5* (2/3)
Black C-DPL	*Zetesal NR*	1	**5** 5* (4)	**5** 5* (5)	**5** 5* (5)	**4/5** 4/5* (4)	**5** 5* (4/5)	**5** 5* (4/5)
		5	**5** 5* (4)	**5** 5* (5)	**5** 5* (5)	**5** 4/5* (3)	**5** 5* (4/5)	**5** 5* (4/5)
	Nylofixan MFN	1	**5** 5* (4)	**5** 5* (5)	**5** 5* (5)	**4/5** 4/5* (4/5)	**5** 5* (5)	**5** 5* (5)
		5	**5** 5* (4)	**5** 5* (5)	**5** 5* (5)	**5** 4/5* (3/4)	**5** 5* (5)	**5** 5* (4/5)

Bold = 40 °C; * = 50 °C; ( ) = 60 °C.

and the two syntans in its ability to reduce the shade change that occurred as a result of repeated washing. The very large ΔE value obtained for the yellow dyeing when washed at 40 °C can be attributed to the marked yellow/brown colour imparted to the dyeing by the aftertreatment. The extent of staining of adjacent multifibre strip achieved for the *Gallofix* treated dyeings (Table 17) was much lower than that obtained for the untreated dyeings (Table 5). Furthermore, the extent of the staining of the adjacent nylon component imparted by *Gallofix* aftertreatment (Table 17) was, overall, better than that achieved using the full backtan (Table 9) and the two syntans (Table 13), especially when washing had been carried out at 60 °C.

Table 14
Colorimetric data for tannic acid/*Gallofix* treated dyeings washed at 40 °C

Dye	No. of washes	L^*	a^*	b^*	C^*	h°	$f(k)$
Red K-2G	0	44.6	43.5	16.3	46.5	20.6	73.1
	5	42.9	42.6	16.0	44.6	21.1	80.2
Yellow C-3RL	0	67.4	27.9	70.6	75.9	68.4	79.2
	5	62.3	22.0	62.5	66.3	70.6	82.7
Black C-DPL	0	22.5	−0.4	−4.2	4.2	265.1	219.8
	5	21.9	−0.2	−3.8	3.8	267.0	231.7

Table 15
Colorimetric data for tannic acid/*Gallofix* treated dyeings washed at 50 °C

Dye	No. of washes	L^*	a^*	b^*	C^*	h°	$f(k)$
Red K-2G	0	44.6	43.5	16.3	46.5	20.6	73.1
	5	46.5	41.2	15.4	42.7	19.7	58.3
Yellow C-3RL	0	67.4	27.9	70.6	75.9	68.4	79.2
	5	66.0	25.3	66.8	71.4	69.3	74.8
Black C-DPL	0	22.5	−0.4	−4.2	4.2	265.1	219.8
	5	21.1	−0.3	−3.6	3.6	265.5	247.6

3.4. *Development of metal-free aftertreatment*

The term ‘tannin’ was first proposed by Seguin [7] to describe water soluble agencies, that were present in certain vegetable tissues (such as oak

Table 16
Colorimetric data for tannic acid/*Gallofix* treated dyeings washed at 60 °C

Dye	No. of washes	L^*	a^*	b^*	C^*	h°	$f(k)$
Red K-2G	0	44.6	43.5	16.3	46.5	20.6	73.1
	5	43.0	41.0	16.0	44.6	21.0	79.4
Yellow C-3RL	0	67.4	27.9	70.6	75.9	68.4	79.2
	5	65.8	25.9	67.8	72.6	69.1	79.3
Black C-DPL	0	22.5	−0.1	−4.2	4.2	265.1	219.8
	5	20.8	−0.1	−3.8	3.8	268.3	253.2

Table 17
Staining of adjacent multifibre strip achieved for tannic acid/*Gallofix* treated dyeings

Dye	No. of washes	Wool	Acrylic	Polyester	Nylon 6,6	Cotton	2° Acetate
Red K-2G	1	**5** 5* (5)	**5** 5* (5)	**5** 5* (5)	**5** 4/5* (3/4)	**5** 5* (5)	**5** 5* (4/5)
	5	**5** 5* (5)	**5** 5* (5)	**5** 5* (5)	**5** 4/5* (3/4)	**5** 5* (5)	**5** 5* (5)
Yellow C-3RL	1	**5** 5* (3/4)	**5** 5* (5)	**5** 5* (5)	**5** 4/5* (3/4)	**5** 5* (5)	**5** 5* (4)
	5	**5** 5* (3/4)	**5** 5* (5)	**5** 5* (5)	**5** 4/5* (2/3)	**5** 5* (5)	**5** 5* (3)
Black C-DPL	1	**5** 5* (4)	**5** 5* (5)	**5** 5* (5)	**4/5** 4/5* (3/4)	**5** 5* (5)	**5** 5* (4)
	5	**5** 5* (4/5)	**5** 5* (5)	**5** 5* (5)	**5** 4/5* (4)	**5** 5* (5)	**5** 5* (4/5)

Bold = 40 °C; * = 50 °C; ( ) = 60 °C.

bark), which converted animal skin into leather. Although tannins have enjoyed considerable textile use over many years, this usage has been confined mostly to their commixture with metal salts. The earliest textile applications of natural tannins included the dyeing of cotton and silk with dyewoods, wherein the tannin was used to ‘fix’ the metal salt (e.g. $CuSO_4$) that was employed as a mordant for the dye [6]. Following the introduction of *Mauvein* in 1856, tannins were utilised as mordants to increase the uptake of cationic dyes onto cotton. Cotton was firstly treated with tannin extract and then with a metal salt solution prior to dyeing, so as to impart adequate wash and light fastness to the dyeings: of the various metals used (Fe, Al, Cu, Pb, Sn), salts of antimony were found to yield dyeings of highest fastness and, of these, it was found that potassium antimony tartrate (tartar emetic) was the most effective. Further development of this approach led to dyed cotton or silk being aftertreated with either tannin alone or tannin in conjunction with potassium antimonyl tartrate (a process known as *backtanning*) or other metal salts such as $SnCl_4$ to improve the fastness of the dyeing.

The classical full backtan aftertreatment, which was originally developed to improve the characteristically poor wet fastness of acid dyes on nylon, entailed successive treatments with tannic acid, potassium antimonyl tartrate and stannous chloride; this method was simplified by the omission of the use of stannous chloride [8]. In this typically two-stage system, the gallotannin component behaves as a high M_r acid which binds to the protonated amino end groups in the nylon fibre and the sequential treatment with potassium antimonyl tartrate 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.

Thus, the purpose of the metal salt (potassium antimonyl tartrate) in the traditional full backtan aftertreatment is to form a complex with the adsorbed tannic acid in situ at the surface of the dyed nylon 6,6. In order to develop a metal-free, full backtan aftertreatment, an alternative was required for the metal (potassium antimonyl tartrate) complexing agent. With this in mind, attention focussed on the well known fact that natural vegetable tannin extracts comprise a heterogenous group of generally amorphous materials that are precipitated by a solution of gelatin, albumen or alkaloids [9]. Initial investigations [10] revealed that although gelatin and various amino acids offered promise as alternative metal-free complexing agents for tannic acid, a decision was made to pursue the use of enzymes.

Enzymes have enjoyed considerable use in the textile industry for many years in the textile industry; they also enjoy widespread use as functional ingredients in detergents for domestic laundering and dishwashing. A wide variety of these highly specific, extremely effective, biological catalyts are available commercially, such as, for example, amylases that are used in desizing, cellulases which are employed in denim finishing and the bio-polishing of cellulosic fibres, proteases which enjoy use in leather, silk and wool processing and pectinases which are used in the biopreparation of cellulosic fibres. For this work, a commercial sample of the protease enzyme *Savinase* was selected for use. Furthermore, since no reference could be found pertaining to the use of an enzyme in conjunction with tannic acid for the improvement of the fastness of acid dyes on nylon, it was decided, for this part of the work, to apply the enzyme in the same manner (i.e. using the same application conditions) that had been used for the full backtan and tannic acid/*Gallofix* (Fig. 2).

Aftertreatment of the three dyes with the two-stage tannic acid/*savinase* treatment markedly improved the wash fastness of each of the dyes to repeated wash fastness, in terms of change in shade of the dyeings (Tables 18–20). Figs. 5–7 show the extent to which the aftertreatment reduced the shade change of the dyeings in terms of the colour difference obtained after repeated wash testing at the three temperatures used for washing. Figs. 5–7 also reveal, in terms of colour difference obtained after repeated wash testing at the three temperatures used, that the enzyme system was almost comparable to the full backtan in its ability to reduce the shade change that occurred as a result of repeated washing. Comparison of the colorimetric data obtained for the untreated dyeings (Tables 2–4) with those achieved for the *Savinase* treated samples (Tables 18–20) reveals that aftertreatment flattened the shade of the dyeings and, in the cases of the red and yellow dyeings, imparted a yellow colour. These particular findings may be attributed to tannic acid component in view of the well known fact that this compound can alter the shade of dyeings [6]. In terms of the extent of staining of adjacent multifibre strip achieved for the tannic acid/*Savinase* treated dyeings, Table 21 shows that aftertreatment markedly reduced staining when compared to that obtained for the untreated dyeings (Table 5). Furthermore, the reduction in the extent of staining of the adjacent nylon component imparted by the enzyme treatment (Table 21) was of the order of that obtained using the tannic acid/*Gallofix* aftertreatment (Table 17), at each of the three temperatures used for washing.

Thus, the newly developed tannic acid/enzyme system markedly improved the fastness of the dyeings to repeated washing at each of the wash temperature used and, overall, in terms of ability to reduce the extents of both shade change and staining of adjacent materials that occurred as a result of

Table 18
Colorimetric data for tannic acid/*Savinase* treated dyeings washed at 40 °C

Dye	No. of washes	L^*	a^*	b^*	C^*	$h°$	$f(k)$
Red K-2G	0	41.2	43.5	16.6	46.6	20.9	92.8
	5	41.8	42.8	16.4	45.8	21.0	91.3
Yellow C-3RL	0	68.2	28.0	73.6	78.7	69.2	70.5
	5	69.2	27.7	72.4	77.5	69.1	69.1
Black C-DPL	0	23.7	−0.2	−3.6	3.6	266.8	197.2
	5	24.2	−0.2	−3.3	3.3	266.5	192.1

Table 19
Colorimetric data for tannic acid/*Savinase* treated dyeings washed at 50 °C

Dye	No. of washes	L^*	a^*	b^*	C^*	$h°$	$f(k)$
Red K-2G	0	41.2	43.5	16.6	46.6	20.9	92.8
	5	42.1	42.6	16.3	45.6	21.0	90.2
Yellow C-3RL	0	68.2	28.0	73.6	78.7	69.2	70.5
	5	69.8	28.1	73.9	79.1	69.2	67.8
Black C-DPL	0	23.7	−0.2	−3.6	3.6	266.8	197.2
	5	24.6	−0.2	−3.5	3.5	266.7	195.0

Table 20
Colorimetric data for tannic acid/*Savinase* treated dyeings washed at 60 °C

Dye	No. of washes	L^*	a^*	b^*	C^*	$h°$	$f(k)$
Red K-2G	0	41.2	43.5	16.6	46.6	20.9	92.8
	5	42.3	42.4	16.3	45.4	21.0	89.8
Yellow C-3RL	0	68.2	28.0	73.6	78.7	69.2	70.5
	5	69.8	27.6	71.6	77.0	69.0	68.3
Black C-DPL	0	23.7	−0.2	−3.6	3.6	266.8	197.2
	5	24.8	−0.2	−3.4	3.4	266.6	193.9

Table 21
Staining of adjacent multifibre strip achieved for tannic acid/*Savinase* treated dyeings

Dye	No. of washes	Wool	Acrylic	Polyester	Nylon 6,6	Cotton	2° Acetate
Red K-2G	1	**5** 5* (3/4)	**5** 5* (5)	**5** 5* (5)	**4/5** 4/5* (3)	**5** 5* (4)	**5** 5* (5)
	5	**5** 5* (5)	**5** 5* (5)	**5** 5* (5)	**5** 4/5* (3/4)	**5** 5* (5)	**5** 5* (5)
Yellow C-3RL	1	**5** 5* (4)	**5** 5* (5)	**5** 5* (5)	**5** 5* (3)	**5** 5* (4)	**5** 5* (4)
	5	**5** 5* (4)	**5** 5* (5)	**5** 5* (5)	**5** 5* (2/3)	**5** 5* (5)	**5** 5* (3/4)
Black C-DPL	1	**5** 5* (4)	**5** 5* (5)	**5** 5* (4/5)	**4/5** 4* (3)	**5** 5* (4)	**5** 5* (5)
	5	**5** 5* (5)	**5** 5* (5)	**5** 5* (4/5)	**5** 5* (4)	**5** 5* (5)	**5** 5* (5)

Bold = 40 °C; * = 50 °C; ( ) = 60 °C.

Table 22
Handle imparted by aftertreatment

Aftertreatment	Harsh	Harsher
Full backtan		✓
Zetesal NR	✓	
Nylofixan MFN	✓	
Tannic acid/*Gallofix*		✓
Tannic acid/*Savinase*		✓

repeated washing, gave results that were comparable to the four established aftertreatments.

3.5. Handle

Table 22 shows that each of the five aftertreatments used were judged to have impaired the handle of the dyeings and that the impairment of handle was judged to be slightly greater in the cases of the three tannic acid-based aftertreatments.

4. Conclusions

As mentioned, the four established aftertreatments that were used in this work (two commercial syntans, the traditional full backtan and the tannic acid/tin sulfate system) were chosen as 'references' against which the effectiveness of the developed tannic acid/enzyme system could be compared. At no time was it the intention of the work to highlight the superiority of one aftertreatment over another in improving wash fastness. The shade change and staining results obtained show that all four aftertreatments were highly effective in improving the wash fastness of the three dyes at all three washing temperatures used.

The findings of this initial study indicate that the effectiveness of the newly developed, tannic acid/enzyme system in improving the wash fastness to repeated washing, was comparable to that of the four established aftertreatments. As mentioned, the aim of this work was to develop a metal-free, tannic acid-based aftertreatment; clearly, this offers a potentially more environmentally acceptable alternative aftertreatment to the full backtan and the tin-derived (*Gallofix*) systems. As also mentioned, the decision to use an enzyme was made on the supposition that it would form a complex with the adsorbed tannic acid *in situ* and, as such, replace the potassium antimonyl tartrate in the traditional full backtan aftertreatment or the tin salt used in the *Gallofix* system. Further work is needed to establish the precise mechanism by which the tannic acid/enzyme system operates; this will be the focus of a subsequent part of this paper.

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