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The development of a metal-free, tannic acid-based aftertreatment for nylon 6,6 dyed with acid dyes. Part 4: tannic acid

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Abstract

A single-bath, single-stage aftertreatment for nylon 6,6 dyed with acid dyes has been developed that involves the application of tannic acid at pH 6. The effectiveness of the aftertreatment was determined, employing a repeated washing protocol, using five commercial acid dyes on nylon 6,6. It was found that the high M_r gallotannin was very effective in improving the fastness of all five acid dyes to repeated washing at 40 °C; however, the aftertreatment was less effective in the cases of repeated washing at 50 °C and 60 °C. Nevertheless, the metal-free, tannic acid aftertreatment offers a potentially more environmentally acceptable alternative to traditional antimony-based aftertreatments.

Keywords: Nylon 6,6; Acid dyes; Full backtan; Tannic acid; Enzyme

1. Introduction

This paper reports work carried out to develop of a metal-free, tannic acid-based aftertreatment for acid dyed nylon, with the aim of providing a potentially more environmentally acceptable aftertreatment to the traditional full backtan. The first part of the paper [1] showed that a newly developed, tannic acid/enzyme aftertreatment was comparable to three established aftertreatments (syntan, full backtan and a modified full backtan) in improving the fastness to repeated washing of three acid dyes on nylon 6,6. In the second part of the paper [2], the optimum application conditions for the tannic acid/enzyme system were determined and a particular tannic acid/enzyme aftertreatment was shown to be more effective than the full backtan aftertreatment in improving the wash fastness of five acid dyes on nylon 6,6. The third part of the paper [3] concerned the effectiveness of four protease enzymes when used in combination with tannic acid, in improving the fastness to repeated washing of five commercial acid dyes on nylon 6,6.

As the purpose of this work was to develop a metal-free, tannic acid-based aftertreatment as an alternative to the traditional full backtan, although the tannic acid/enzyme aftertreatment thus far developed appears to offer an environmentally acceptable alternative to metal-based aftertreatments, the tannic acid/enzyme system

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comprises two stages, namely the application of tannic acid followed by the application of the enzyme. As a consequence, a decision was made to examine the possibility of developing a single stage aftertreatment that used tannic acid alone.

This part of the paper concerns the application of tannic acid as an aftertreatment of nylon 6,6 which had been dyed with five commercial acid dyes. As in previous parts of the paper [1–3], three washing temperatures (40 °C, 50 °C and 60 °C) were employed, using a repeated wash fastness testing protocol, in recognition of the fact that different washing temperatures are commonly used in Northern Europe.

2. Experimental

2.1. Materials

The scoured, knitted nylon 6.6 fabric described earlier [1], which was kindly supplied by Dupont (UK), was used; the five commercial acid dyes (Table 1) that had been previously used [2] were again employed. A commercial sample of Textan 3 (tannic acid) was kindly provided by OmniChem-Ajinomoto and a commercial sample of the enzyme Savinase was generously supplied by Novazyme.

All other chemical used were laboratory grade reagents.

2.2. Dyeing

The dyes were applied using the equipment and methods described earlier [2]; the pH was adjusted using McIlvaine buffer [2]. The dyeings were rinsed thoroughly in tap water and allowed to dry in the open air.

2.3. Tannic acid treatment

Tannic acid was applied to dyed nylon 6,6 using an exhaust method in sealed stainless steel pots of 300 cm^3 capacity housed in a Roaches *Pyrotec S* laboratory scale infrared dyeing machine employing a liquor ratio of 1:20 (Fig. 1) the pH of application being adjusted using McIlvaine buffer [1]. The backtanned samples were rinsed in running water and allowed to dry in the open air.

2.4. Colour measurement

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

2.5. Wash fastness

The wash fastness of the dyed samples to five, consecutive wash tests was determined at three temperatures (40 °C, 50 °C and 60 °C), using the modified, ISO standard wash tests (ISO CO6/A2S (40 °C), ISO CO6/B2S (50 °C) and ISO CO6/C2S (60 °C)) described earlier [1]. The extent of the

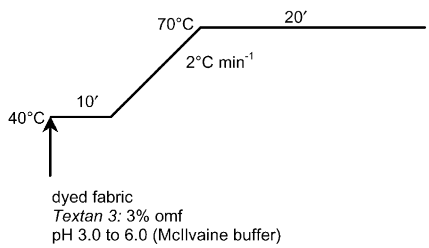

Fig. 1. Tannic acid application method.

Table 1
Dyes used

Commercial name	Type	C.I Generic Name
Neutrilan Red K-2G	Unsulfonated 1:2 per-metallised	Acid Red 278
Nylanthrene Yellow C-3RL	Non-metallised acid	Acid Orange 67
Nylanthrene Blue C-GLF	Non-metallised acid	Acid Blue 281
Nylanthrene Black C-DPL	Non-metallised acid	Acid Black 172
Neutrilan Navy S-BGR	Monosulfonated 1:2 per-metallised	Acid Blue 284

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 CIE $L^*a^*b^*$ ΔE units.

2.6. Light fastness

The fastness of the dyeings to light was determined using the ISO B02 method described earlier [2].

3. Results and discussion

3.1. Untreated dyeings

Tables 2 to 4 shows the colour difference obtained for untreated dyeings which had been subjected to five, consecutive wash tests at 40 °C, 50 °C and 60 °C. The data presented in Tables 2 to 4 are taken from a previous part of the paper [2] and clearly show the moderate fastness to repeated washing of the five dyes used, as evidenced by the reduction in colour strength that occurred because of the loss of dye during washing. The colour strength values also show that the reduction in colour strength increased with increasing temperature of wash testing, which can be attributed to a corresponding increase in the removal of dye from the dyed samples during wash testing.

Table 5 shows the corresponding staining of multifibre strip obtained as a result of the five, consecutive wash tests of the untreated dyeings at each of the three wash temperatures employed; this data is also taken from an earlier part of the paper [2]. The results presented in Table 5 clearly show that the level of staining of the adjacent materials increased, markedly, with increase in washing temperature, which 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.

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

C.I. Acid	Number of washes	L^*	a^*	b^*	C^*	h^o	f(k)
Red 278	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
Orange 67	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
Blue 281	0	42.3	−2.0	−37.9	38.0	267.0	62.7
	5	44.3	−2.9	−36.6	37.0	266.0	52.8
Black 172	0	24.9	−0.3	−3.9	3.9	265.6	180.7
	5	26.5	−0.3	−3.9	3.9	265.6	160.4
Blue 284	0	15.3	2.7	−14.4	14.6	280.6	391.0
	5	15.9	2.7	−15.4	15.6	280.2	373.4

Table 3
Colorimetric data and wash fastness results for untreated dyeings washed at 50 °C [2]

C.I. Acid	Number of washes	L^*	a^*	b^*	C^*	h^o	f(k)
Red 278	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
Orange 67	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
Blue 281	0	42.3	−2.0	−37.9	38.0	267.0	62.7
	5	46.0	−3.1	−36.1	36.2	265.1	47.4
Black 172	0	24.9	−0.3	−3.9	3.9	265.6	180.7
	5	26.7	−0.3	−3.9	3.9	266.1	156.0
Blue 284	0	15.3	2.7	−14.4	14.6	280.6	391.0
	5	16.0	2.7	−15.4	15.7	280.0	367.7

Table 4
Colorimetric data and wash fastness results for untreated dyeings washed at 60 °C [2]

C.I. Acid	Number of washes	L^*	a^*	b^*	C^*	h^o	f(k)
Red 278	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
Orange 67	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
Blue 281	0	42.3	−2.0	−37.9	38.0	267.0	62.7
	5	48.9	−4.0	−34.3	34.5	263.3	37.3
Black 172	0	24.9	−0.3	−3.9	3.9	265.6	180.7
	5	27.3	−0.3	−3.9	3.9	265.7	153.0
Blue 284	0	15.3	2.7	−14.4	14.6	280.6	391.0
	5	16.3	2.6	−15.2	15.4	279.7	355.2

Table 5
Staining of adjacent multifibre strip achieved for untreated dyeings [2]

C.I. Acid	No. of washes	Wool	Acrylic	Polyester	Nylon 6,6	Cotton	2° acetate
Red 278	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)
Orange 67	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)
Blue 281	1	**4** 1/2* (1)	**5** 5* (5)	**4/5** 4/5* (3)	**1/2** 1* (1)	**3/4** 2/3* (2)	**2/3** 1/2* (1)
	5	**4/5** 2/3* (1/2)	**5** 5* (5)	**4/5** 5* (3/4)	**2** 1/2* (1)	**4** 3* (2/3)	**3** 2/3* (2)
Black 172	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)	**2/3** 2/3* (2)	**5** 5* (5)	**5** 5* (5)
Blue 284	1	**5** 3* (2)	**5** 4/5* (4)	**5** 5* (4/5)	**1/2** 1* (1)	**5** 5* (4/5)	**5** 5* (5)
	5	**5** 4* (3)	**5** 5* (5)	**5** 5* (5)	**2/3** 2* (1/2)	**5** 5* (5)	**5** 5* (5)

Bold = 40 °C; * = 50 °C; ( ) = 60 °C.

3.2. *Tannic acid aftertreatment*

In the second part of this paper [2], it was shown that optimal conditions for applying the protease enzyme *Savinase*, in conjunction with tannic acid via a two-stage, single bath aftertreatment method, were 70 °C at pH 6. It was therefore decided to determine the effect of pH on the effectiveness of tannic acid in improving wash fastness, when applied in the absence of either enzyme or metal salt.

Table 6 shows the colorimetric data obtained for dyeings which had been aftertreated with tannic acid and subjected to repeated wash testing at 40 °C. Comparison of this data with that obtained for the untreated dyeings (Table 2) reveals that aftertreatment lowered 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. As previously discussed [1], these latter findings can be attributed to tannic acid having altered the shade of dyeings. Comparison of the data in Table 2 with those in Table 6 also show that aftertreatment with the high M_r gallotannin markedly improved the wash fastness of each of the dyes to repeated wash fastness at 40 °C, in terms of change in shade of the dyeings. The magnitude of the improvement in wash fastness imparted by aftertreatment with tannic acid is manifest in Fig. 2 which shows the colour difference (ΔE) obtained between unwashed dyeings and dyeings which had been subjected to five, repeated wash tests. The magnitude of the difference in the ΔE values for the untreated dyeings and those of the aftertreated dyeings clearly shows the extent to which aftertreatment improved the wash fastness of the dyeings. It is evident from the results presented in Table 6 and Fig. 2 that for each of the five dyes used, the extent of the shade change obtained during washing decreased with increasing pH of application of the tannic acid.

Table 7 shows the corresponding staining of multifibre strip obtained as a result of the repeated five, consecutive wash tests at 40 °C. When the results in Table 7 are compared to the staining results obtained for the untreated dyeings (Table 5), it is clear that tannic acid aftertreatment reduced the extent of staining of adjacent materials. It is evident that the level of staining of the multifibre components was lowest when the high M_r gallotannin had been applied at pH 6.

Tables 8 and 9 show the colorimetric data obtained for dyeings which had been aftertreated with tannic acid and subjected to repeated wash testing at 50 °C and 60 °C, respectively. When compared with the data obtained for the untreated dyeings (Tables 3 and 4), it is evident that aftertreatment markedly improved the wash fastness of

Table 6
Effect of pH of aftertreatment on the colorimetric data and wash fastness results achieved for dyeings washed at 40 °C

C.I. Acid	pH	No. of washes	L^*	a^*	b^*	C^*	h^o	f(k)
Red 278	3.0	0	41.3	43.6	16.7	46.7	21.0	92.4
		5	41.8	42.8	15.9	45.7	20.4	89.9
	4.0	0	41.4	43.6	17.0	46.8	21.3	91.9
		5	41.9	42.9	16.3	45.9	20.8	90.0
	5.0	0	41.8	43.8	17.2	47.1	21.4	91.4
		5	42.2	43.3	16.6	46.4	21.0	90.4
	6.0	0	41.8	44.0	17.4	47.3	21.6	91.2
		5	42.2	43.5	16.9	46.7	21.2	90.4
Orange 67	3.0	0	68.6	28.2	73.5	78.7	69.0	70.0
		5	69.6	27.8	72.3	77.5	69.0	68.0
	4.0	0	68.7	28.3	73.5	78.8	68.9	69.5
		5	69.6	27.9	72.4	77.6	68.9	67.9
	5.0	0	69.0	28.5	73.8	79.1	68.9	68.9
		5	69.6	28.2	72.9	78.1	68.9	67.9
	6.0	0	69.2	28.5	73.9	79.2	68.9	68.2
		5	69.7	28.2	73.1	78.4	68.9	67.5
Blue 281	3.0	0	41.6	−1.7	−38.3	38.3	267.5	63.6
		5	42.5	−2.3	−37.0	37.1	266.4	61.3
	4.0	0	41.7	−1.8	−38.3	38.3	267.3	63.4
		5	42.5	−2.4	−37.2	37.3	266.3	61.6
	5.0	0	41.9	−1.9	−38.1	38.2	267.1	63.1
		5	42.5	−2.4	−37.2	37.3	266.3	61.7
	6.0	0	42.0	−1.9	−38.0	38.1	267.1	62.9
		5	42.6	−2.3	−37.3	37.4	266.5	61.8
Black 172	3.0	0	24.0	−0.3	−3.7	3.7	265.4	193.7
		5	25.0	−0.2	−3.6	3.6	266.8	190.7
	4.0	0	24.2	−0.3	−3.7	3.7	265.4	192.8
		5	25.1	−0.3	−3.6	3.6	265.2	190.1
	5.0	0	24.5	−0.3	−3.8	3.8	265.5	191.4
		5	25.2	−0.3	−3.7	3.7	265.4	189.7
	6.0	0	24.6	−0.3	−3.8	3.8	265.5	190.7
		5	25.1	−0.3	−3.7	3.7	265.4	189.8
Blue 284	3.0	0	14.7	2.4	−13.7	13.9	279.9	394.8
		5	15.1	2.3	−14.4	14.6	279.1	392.7
	4.0	0	14.8	2.4	−13.9	14.1	279.8	394.0
		5	15.2	2.4	−14.5	14.7	279.4	392.3
	5.0	0	15.0	2.6	−14.1	14.3	280.4	393.1
		5	15.3	2.5	−14.6	14.8	279.7	391.7
	6.0	0	15.2	2.6	−14.2	14.4	280.4	392.4
		5	15.5	2.6	−14.6	14.8	280.1	391.5

each of the dyes to repeated wash fastness, in terms of change in shade of the dyeings. Also, aftertreatment with tannic acid flattened the shade of the dyeings and, in the cases of the red and yellow dyeings, aftertreatment also imparted a yellow colour. The extent to which aftertreatment with the high M_r gallotannin reduced the shade change of the dyeings in terms of the colour difference obtained after repeated wash testing at the two washing temperatures is shown in Figs. 3 and 4. The large differences in ΔE values between the untreated dyeings and the aftertreated dyeings clearly shows the extent to which aftertreatment improved the wash fastness of the dyeings at each washing temperature. The corresponding levels of staining that were achieved as a result of repeated wash testing at 50 °C and 60 °C are shown in Tables 10 and 11, respectively. When these staining results are compared to those obtained for the untreated dyeings (Table 5), it is clear that tannic acid aftertreatment was very effective in reducing the extent of staining achieved at both washing temperatures.

The findings that the extents of shade change and staining achieved decreased with increasing pH of application of the tannic acid can be attributed, presumably, to a corresponding reduction in the aqueous solubility of the tannic acid and, as a consequence, an increase in the extent of adsorption of the high M_r gallotannin on the dyed nylon 6,6.

3.3. *Comparison with tannic acid/enzyme and full backtan aftertreatments*

As a means of judging the level of wash fastness imparted by aftertreatment with tannic acid at pH6, it was considered appropriate to compare the results obtained using the two-stage, single bath aftertreatment with tannic acid and enzyme developed earlier [3] as well as the traditional, two-stage, single bath full backtan [2]. Fig. 5 shows the ΔE values obtained for untreated dyeings, between unwashed dyeings and dyeings which had been subjected to five, repeated wash tests at 40 °C for each of the five dyes used. Fig. 5 also shows the corresponding ΔE values obtained for dyeings which had been aftertreated with the full backtan [2], tannic acid/*Savinase* [3] and tannic acid alone (applied at pH 6). The fact that each of the three types of aftertreatment produced lower ΔE values than that of the untreated dyeing is a reflection of their improvement of the wash fastness of the five

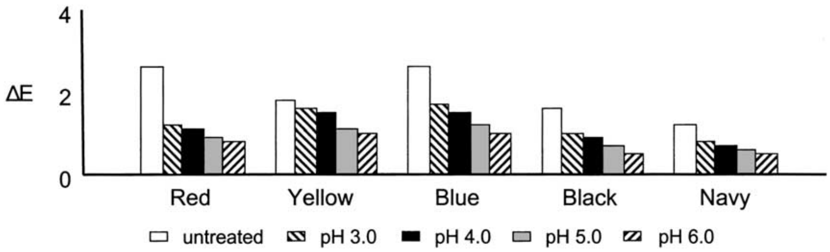

Fig. 2. Effect of pH of application of tannic acid on colour difference obtained after five repeated wash tests at 40 °C.

Table 7
Effect of pH of tannic acid aftertreatment on the staining of adjacent multifibre strip obtained for washing at 40 °C

pH	No. of washes	Wool	Acrylic	Polyester	Nylon 6.6	Cotton	2° acetate
3.0	1	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**4/5** 5* (4) [4/5] {4}	**5** 5* (5) [5] {5}	**5** 5* (4/5) [5] {5}
	5	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (4) [4/5] {4/5}	**5** 5* (5) [5] {5}	**5** 5* (4/5) [5] {5}
4.0	1	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**4/5** 5* (4) [4/5] {4}	**5** 5* (5) [5] {5}	**5** 5* (4/5) [5] {5}
	5	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (4) [4/5] {4/5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}
5.0	1	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**4/5** 5* (4/5) [4/5] {4/5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}
	5	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (4/5) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}
6.0	1	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**4/5** 5* (4/5) [4/5] {4/5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}
	5	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (4/5) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}

Bold = Red 278; * = Orange 67; ( ) = Blue 281 [ ] = Black 172; { } = Blue 284.

dyes used. It is evident that, of the three aftertreatments examined, the tannic acid/enzyme system imparted greatest improvement, overall, in wash fastness and that an aftertreatment with the full backtan was marginally inferior to tannic acid alone in terms of the extent to which wash fastness was improved.

Figs. 6 and 7 show the ΔE values obtained between unwashed dyeings and dyeings which had been subjected to five, repeated wash tests at 50 °C and 60 °C for each of the five dyes used; it is clear that for each dye, aftertreatment with the full backtan [2], tannic acid/*Savinase* [3] and tannic acid alone (applied at pH 6) each markedly improved the fastness of the dyeings to repeated washing. It is apparent that, of the three aftertreatments examined, the tannic acid/enzyme system imparted greatest improvement, overall, in wash fastness and that an aftertreatment with tannic acid alone was marginally poorer than the full backtan in terms of the extent to which wash fastness was improved.

Figs. 8 to 10 show the extent of the staining of adjacent polyester, acrylic and cotton components of multifibre strip, respectively; as discussed previously [2], the low level of staining obtained for these three particular components is attributable to the inherent low substantivity of the three acid dyes towards such fibres. In contrast, the very high extent of staining obtained for the adjacent nylon 6,6 fibre (Fig. 11) and the lower staining of acetate (Fig. 12) and moderate staining of the wool component (Fig. 13) can be explained in terms of the high substantivity of the dyes towards these types of fibre. It is clear that for each dye used, the extent of staining increased with increase in washing temperature, from 40 °C to 60 °C. Although each of the three aftertreatments used reduced the extent of staining, especially in the case of washing at 60 °C, the magnitude of this reduction in staining also decreased with increasing washing temperature. Overall, aftertreatment with the tannic acid/enzyme system imparted greatest improvement in staining, especially in the case of nylon 6,6 component when washed at 60 °C. In general, although the extent of staining achieved for an

Table 8
Effect of pH of aftertreatment on the colorimetric data and wash fastness results achieved for dyeings washed at 50 °C

C.I. Acid	pH	No. of washes	*L**	*a**	*b**	*C**	*h*°	*f*(k)
Red 278	3.0	0	41.3	43.6	16.7	46.7	21.0	92.4
		5	42.3	42.6	15.7	45.4	20.2	88.7
	4.0	0	41.4	43.6	17.0	46.8	21.3	91.9
		5	42.3	42.7	16.0	45.6	20.5	89.0
	5.0	0	41.8	43.80	17.2	47.1	21.4	91.4
		5	42.6	43.1	16.4	46.1	20.8	89.5
	6.0	0	41.8	44.0	17.4	47.3	21.6	91.2
		5	42.5	43.3	16.7	46.4	21.1	89.8
Orange 67	3.0	0	68.6	28.2	73.5	78.7	69.0	70.0
		5	70.0	27.6	72.0	77.1	69.0	67.4
	4.0	0	68.7	28.3	73.5	78.8	68.9	69.5
		5	70.0	27.7	72.1	77.2	69.0	67.2
	5.0	0	69.0	28.5	73.8	79.1	68.9	68.9
		5	69.9	28.0	72.7	77.9	68.9	67.3
	6.0	0	69.2	28.5	73.9	79.2	68.9	68.2
		5	70.0	28.1	73.0	78.2	68.9	67.1
Blue 281	3.0	0	41.6	−1.7	−38.3	38.3	267.5	63.6
		5	43.1	−3.0	−36.6	36.7	265.3	59.0
	4.0	0	41.7	−1.8	−38.3	38.3	267.3	63.4
		5	43.1	−2.9	−36.8	36.9	265.5	59.6
	5.0	0	41.9	−1.9	−38.1	38.2	267.1	63.1
		5	43.0	−2.8	−36.9	37.0	265.7	60.4
	6.0	0	42.0	−1.9	−38.0	38.1	267.1	62.9
		5	42.9	−2.6	−37.0	37.1	266.0	61.0
Black 172	3.0	0	24.0	−0.3	−3.7	3.7	265.4	193.7
		5	25.1	−0.2	−3.4	3.4	266.6	189.3
	4.0	0	24.2	−0.3	−3.7	3.7	265.4	192.8
		5	25.3	−0.3	−3.4	3.4	265.0	189.6
	5.0	0	24.5	−0.3	−3.8	3.8	265.5	191.4
		5	25.3	−0.3	−3.6	3.6	265.2	188.8
	6.0	0	24.6	−0.3	−3.8	3.8	265.5	190.7
		5	25.2	−0.3	−3.6	3.6	265.2	188.9
Blue 284	3.0	0	14.7	2.4	−13.7	13.9	279.9	394.8
		5	15.3	2.2	−14.7	14.9	278.5	391.2
	4.0	0	14.8	2.4	−13.9	14.1	279.8	394.0
		5	15.4	2.3	−14.8	15.0	278.8	391.0
	5.0	0	15.0	2.6	−14.1	14.3	280.4	393.1
		5	15.5	2.5	−14.8	15.0	279.6	391.3
	6.0	0	15.2	2.6	−14.2	14.4	280.4	392.4
		5	15.6	2.5	−14.8	15.0	279.6	391.0

Table 9
Effect of pH of aftertreatment on the colorimetric data and wash fastness results achieved for dyeings washed at 60 °C

C.I. Acid	pH	No. of washes	*L**	*a**	*b**	*C**	*h*°	*f*(k)
Red 278	3.0	0	41.3	43.6	16.7	46.7	21.0	92.4
		5	42.8	42.6	15.4	45.3	19.9	88.0
	4.0	0	41.4	43.6	17.0	46.8	21.3	91.9
		5	42.8	42.7	15.7	45.5	20.2	88.1
	5.0	0	41.8	43.8	17.2	47.1	21.4	91.4
		5	42.9	43.1	16.1	46.0	20.5	88.6
	6.0	0	41.8	44.0	17.4	47.3	21.6	91.2
		5	42.8	43.3	16.4	46.3	20.7	89.0
Orange 67	3.0	0	68.6	28.2	73.5	78.7	69.0	70.0
		5	70.7	27.0	71.2	76.2	69.2	66.3
	4.0	0	68.7	28.3	73.5	78.8	68.9	69.5
		5	70.5	27.3	71.7	76.7	69.2	66.1
	5.0	0	69.0	28.5	73.8	79.1	68.9	68.9
		5	70.4	27.7	72.6	77.7	69.1	66.5
	6.0	0	69.2	28.5	73.9	79.2	68.9	68.2
		5	70.4	27.8	72.7	77.8	69.1	66.5
Blue 281	3.0	0	41.6	−1.7	−38.3	38.3	267.5	63.6
		5	44.3	−4.4	−34.9	35.2	262.8	56.7
	4.0	0	41.7	−1.8	−38.3	38.3	267.3	63.4
		5	44.1	−4.2	−35.2	35.5	263.2	57.3
	5.0	0	41.9	−1.9	−38.1	38.2	267.1	63.1
		5	43.7	−3.3	−36.1	36.3	264.8	58.7
	6.0	0	42.0	−1.9	−38.0	38.1	267.1	62.9
		5	43.6	−3.2	−36.2	36.3	264.9	59.1
Black 172	3.0	0	24.0	−0.3	−3.7	3.7	265.4	193.7
		5	25.5	−0.2	−3.4	3.4	266.6	187.6
	4.0	0	24.2	−0.3	−3.7	3.7	265.4	192.8
		5	25.6	−0.2	−3.4	3.4	266.6	187.5
	5.0	0	24.5	−0.3	−3.8	3.8	265.5	191.4
		5	25.7	−0.3	−3.5	3.5	265.1	186.7
	6.0	0	24.6	−0.3	−3.8	3.8	265.5	190.7
		5	25.5	−0.3	−3.6	3.6	265.2	187.1
Blue 284	3.0	0	14.7	2.4	−13.7	13.9	279.9	394.8
		5	15.7	2.2	−14.9	15.1	278.4	388.6
	4.0	0	14.8	2.4	−13.9	14.1	279.8	394.0
		5	15.7	2.2	−15.0	15.2	278.3	388.3
	5.0	0	15.0	2.6	−14.1	14.3	280.4	393.1
		5	15.8	2.4	−14.9	15.1	279.2	388.2
	6.0	0	15.2	2.6	−14.2	14.4	280.4	392.4
		5	15.9	2.4	−14.9	15.1	279.2	388.6

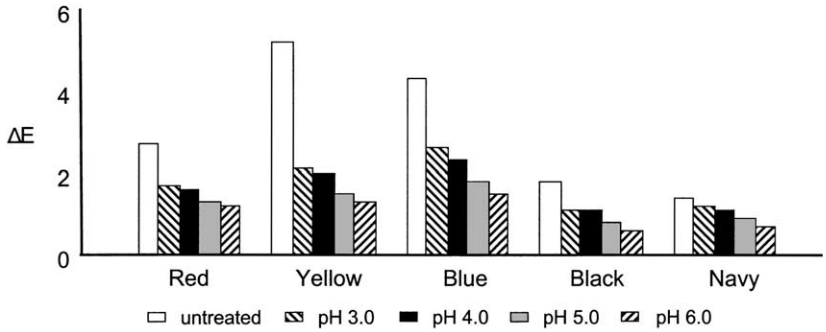

Fig. 3. Effect of pH of application of tannic acid on colour difference obtained after five repeated wash tests at 50 °C (legend as for Fig. 2).

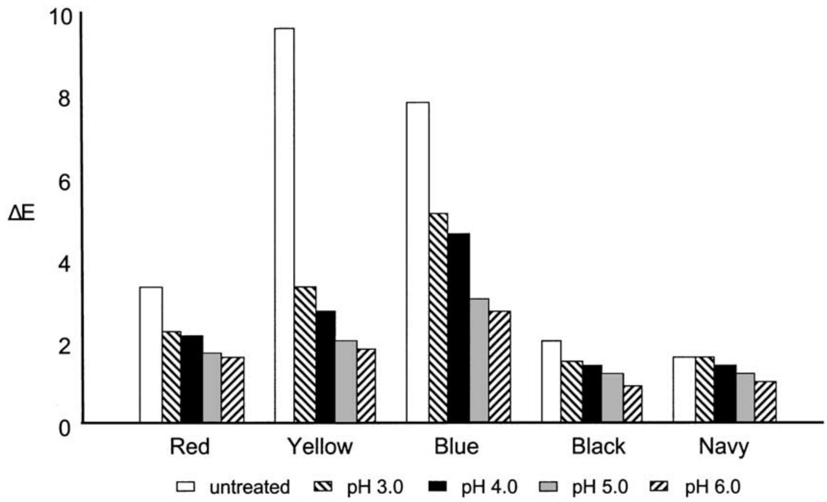

Fig. 4. Effect of pH of application of tannic acid on colour difference obtained after five repeated wash tests at 60 °C (legend as for Fig. 2).

Table 10
Effect of pH of tannic acid aftertreatment on the staining of adjacent multifibre strip obtained for washing at 50 °C

pH	No. of washes	Wool	Acrylic	Polyester	Nylon 6.6	Cotton	2° Acetate
3.0	1	**5** 4* (4) [4] {4}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**3/4** 3/4* (3) [4] {3/4}	**5** 5* (4/5) [5] {5}	**5** 4/5* (4) [5] {5}
	5	**5** 4/5* (4) [4/5] {4/5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**4** 4* (3) [4] {4}	**5** 5* (4/5) [5] {5}	**5** 4/5* (4) [5] {5}
4.0	1	**5** 4/5* (4) [4/5] {4/5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**3/4** 4* (3) [4] {3/4}	**5** 5* (4/5) [5] {5}	**5** 4/5* (4) [5] {5}
	5	**5** 4/5* (4) [4/5] {4/5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**4** 4* (3/4) [4] {4}	**5** 5* (5) [5] {5}	**5** 4/5* (4) [5] {5}
5.0	1	**5** 5* (4/5) [4/5] {4/5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**4** 4/5* (3/4) [4] {4}	**5** 5* (5) [5] {5}	**5** 5* (4/5) [5] {5}
	5	**5** 5* (4/5) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**4/5** 4/5* (4) [4/5] {4}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}
6.0	1	**5** 5* (4/5) [4/5] {4/5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**4/5** 5* (4) [4/5] {4}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}
	5	**5** 5* (4/5) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**4/5** 4/5* (4) [4/5] {4/5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}

Bold = Red 278; * = Orange 67; ( ) = Blue 281 [ ] = Black 172; { } = Blue 284.

Table 11
Effect of pH of tannic acid aftertreatment on the staining of adjacent multifibre strip obtained for washing at 60 °C

pH	No. of washes	Wool	Acrylic	Polyester	Nylon 6.6	Cotton	2° Acetate
3.0	1	**3/4** 3/4* (2) [3/4] {3/4}	**5** 5* (5) [5] {4}	**5** 4/5* (4) [4/5] {4/5}	**2** 2* (1/2) [1/2] {1/2}	**4** 4* (3) [4] {4}	**5** 3* (2) [4] {4}
	5	**4/5** 3* (1) [4] {4}	**5** 5* (5) [5] {5}	**5** 4/5* (3/4) [4/5] {5}	**2** 1/2* (1) [3] {2}	**5** 5* (2) [5] {5}	**5** 2/3* (1) [4] {4}
4.0	1	**3/4** 3/4* (2) [3/4] {3/4}	**5** 5* (5) [5] {4}	**5** 4/5* (4) [4/5] {4/5}	**2** 2/3* (1/2) [1/2] {1/2}	**5** 4/5* (3) [4] {4/5}	**5** 3/4* (2) [4] {4}
	5	**4/5** 3* (1) [4/5] {4}	**5** 5* (5) [5] {5}	**5** 5* (3/4) [4/5] {5}	**2/3** 1/2* (1) [3] {2}	**5** 5* (2/3) [5] {5}	**5** 3* (1) [4/5] {4/5}
5.0	1	**4** 4/5* (2/3) [4] {4}	**5** 5* (5) [5] {4}	**5** 5* (4/5) [4/5] {5}	**3** 3* (2/3) [3] {2}	**5** 5* (4) [4/5] {5}	**5** 4* (3) [4/5] {4/5}
	5	**5** 4* (1/2) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (4) [5] {5}	**3** 3* (1/2) [3/4] {2/3}	**5** 5* (3/4) [5] {5}	**5** 3/4* (2/3) [5] {5}
6.0	1	**4** 4/5* (2/3) [4/5] {4/5}	**5** 5* (5) [5] {4/5}	**5** 5* (4/5) [5] {5}	**3** 3/4* (3) [3/4] {2/3}	**5** 5* (4/5) [5] {5}	**5** 4/5* (3/4) [5] {5}
	5	**5** 4* (1/2) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (4) [5] {5}	**3/4** 3* (2) [3/4] {2/3}	**5** 5* (4) [5] {5}	**5** 4* (3) [5] {5}

Bold = Red 278; * = Orange 67; ( ) = Blue 281 [ ] = Black 172; { } = Blue 284.

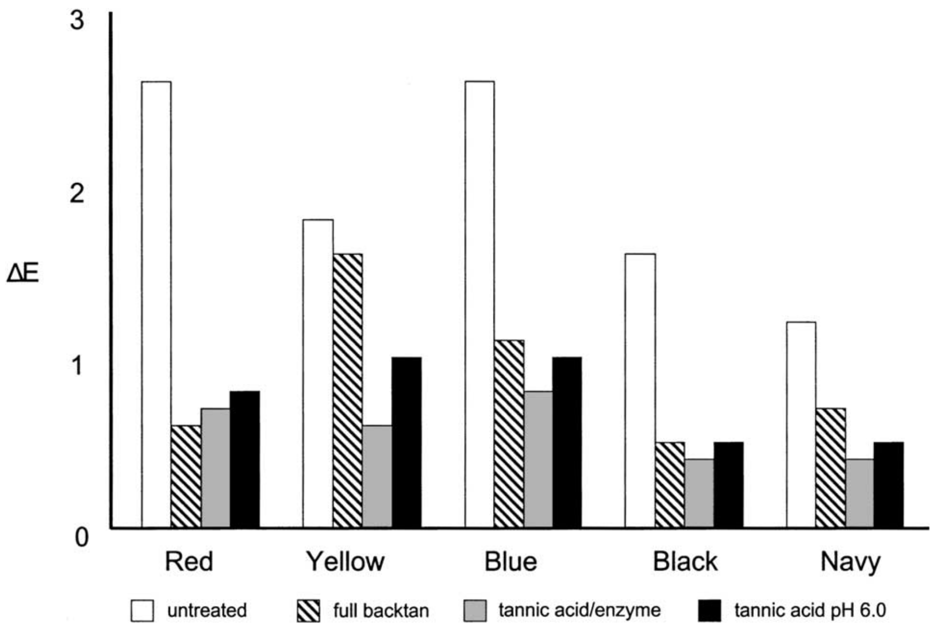

Fig. 5. Colour difference obtained for untreated dyeings and dyeings aftertreated with the full backtan, tannic acid/enzyme and tannic acid alone at pH 6; washed at 40 °C.

aftertreatment with tannic acid alone (applied at pH 6) was comparable to that achieved for the other two aftertreatments when washing had been carried out at 40 °C. However, as the results obtained for the nylon 6,6, acetate and wool components (Figs. 11 to 13) reveal, this was not the case for a wash temperatures of 50 °C and 60 °C, as an aftertreatment with tannic acid alone was not as effective, in reducing staining, as the tannic acid/enzyme system.

3.4. Light fastness

Table 12 shows that the three aftertreatments neither improved nor reduced the light fastness of the dyeings.

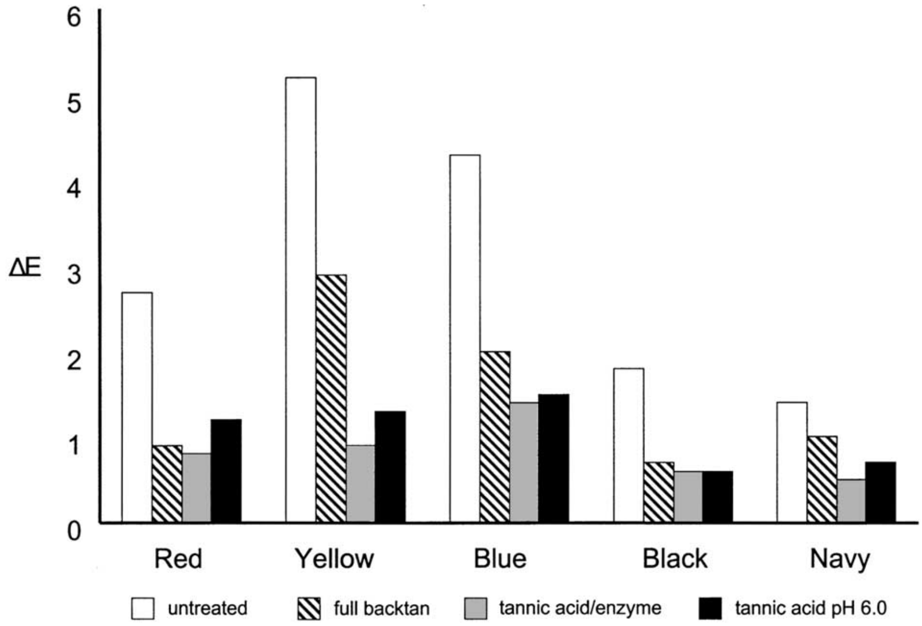

Fig. 6. Colour difference obtained for untreated dyeings and dyeings aftertreated with the full backtan, tannic acid/enzyme and tannic acid alone at pH 6; washed at 50 °C (legend as for Fig. 5).

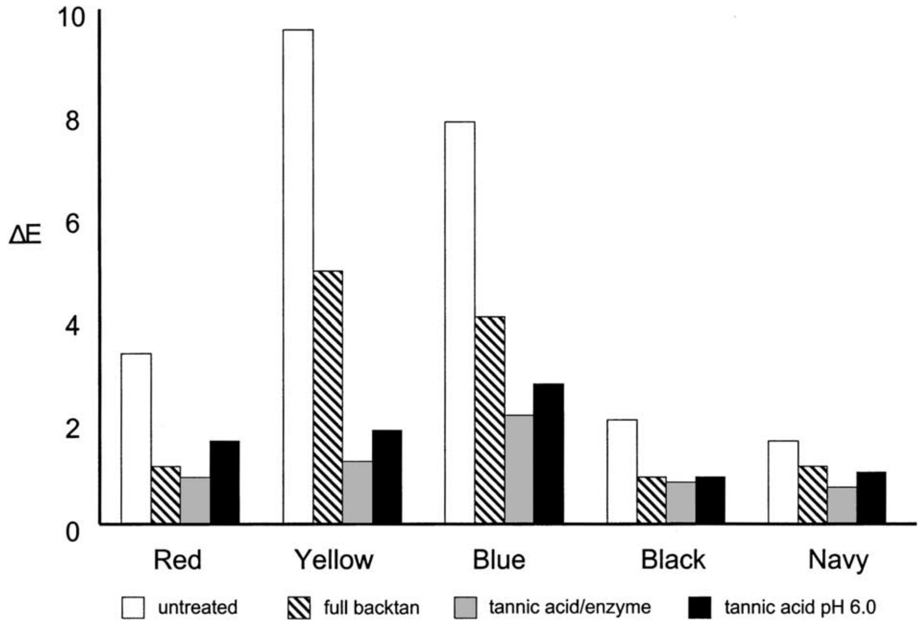

Fig. 7. Colour difference obtained for untreated dyeings and dyeings aftertreated with the full backtan, tannic acid/enzyme and tannic acid alone at pH 6; washed at 60 °C (legend as for Fig. 5).

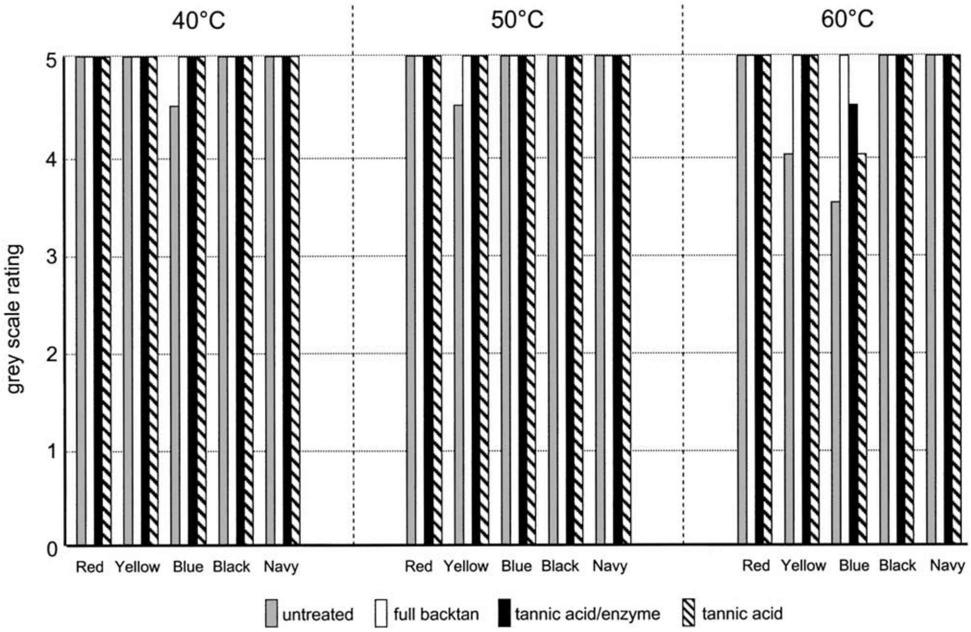

Fig. 8. Staining of adjacent polyester obtained for untreated dyeings and dyeings aftertreated with the full backtan, tannic acid/enzyme and tannic acid alone at pH 6.

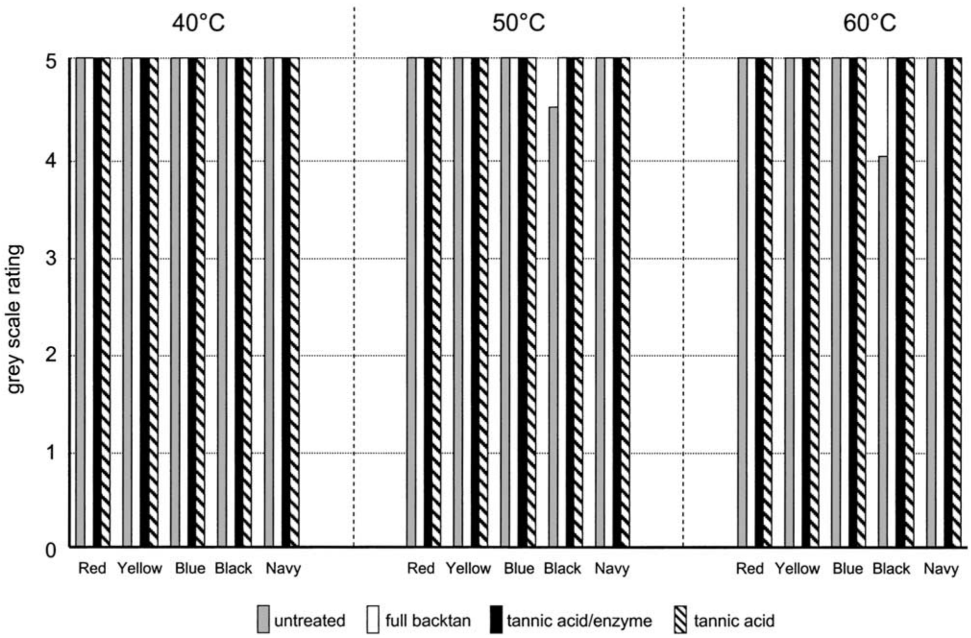

Fig. 9. Staining of adjacent acrylic obtained for untreated dyeings and dyeings aftertreated with the full backtan, tannic acid/enzyme and tannic acid alone at pH 6 (legend as for Fig. 8).

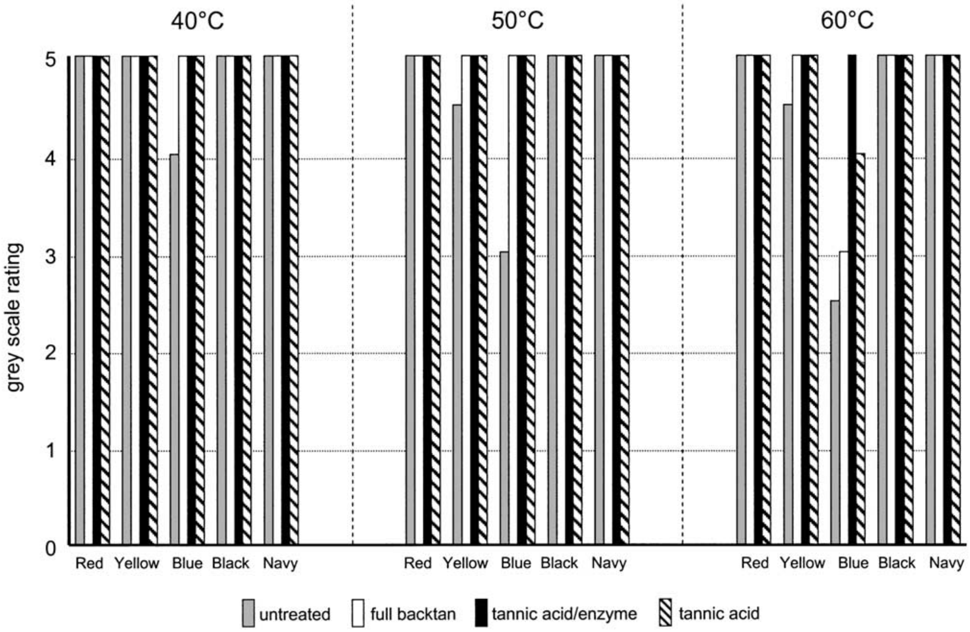

Fig. 10. Staining of adjacent cotton obtained for untreated dyeings and dyeings aftertreated with the full backtan, tannic acid/enzyme and tannic acid alone at pH 6 (legend as for Fig. 8).

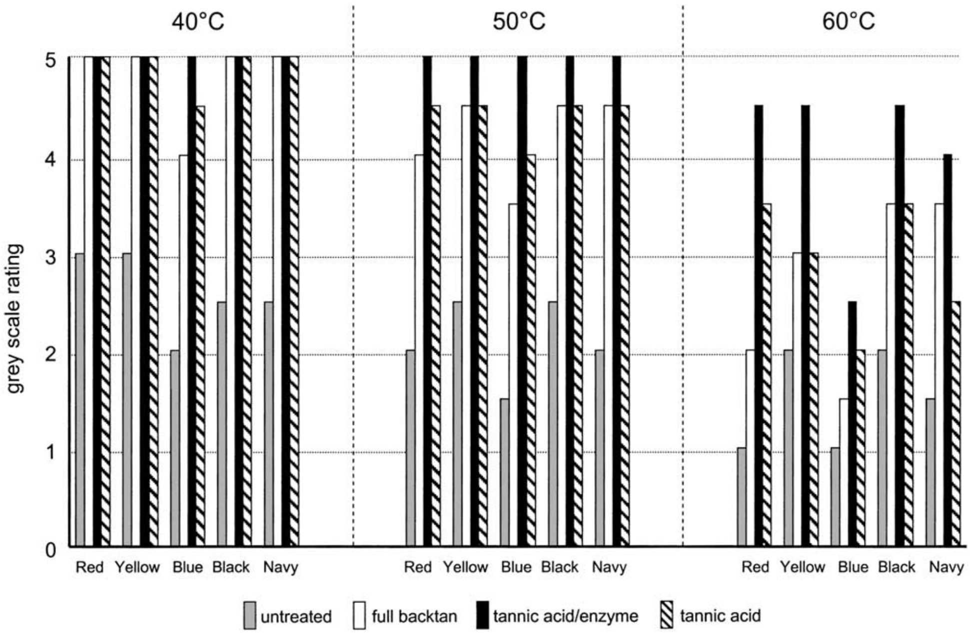

Fig. 11. Staining of adjacent nylon 6,6 obtained for untreated dyeings and dyeings aftertreated with the full backtan, tannic acid/enzyme and tannic acid alone at pH 6 (legend as for Fig. 8).

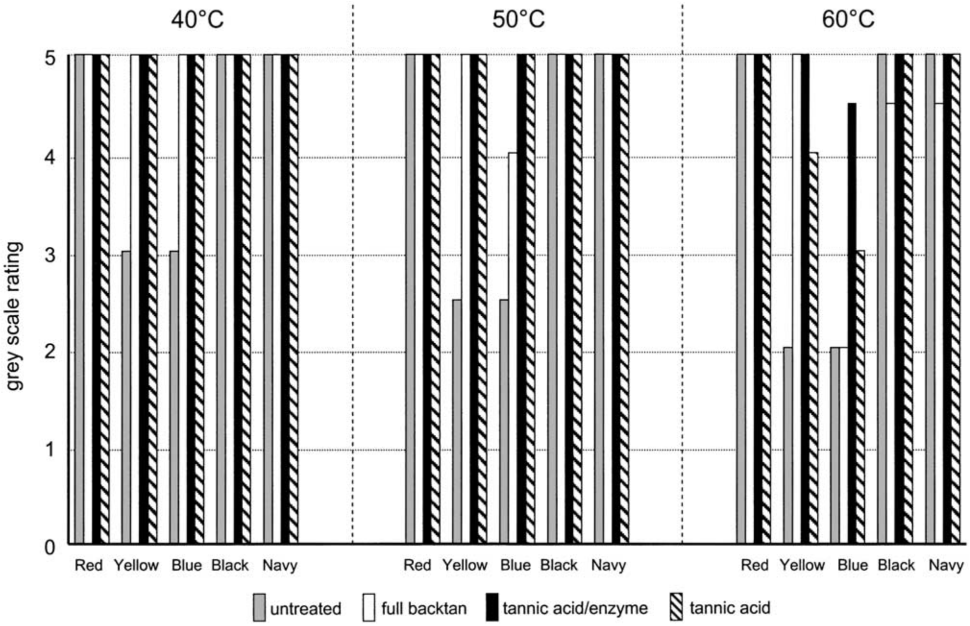

Fig. 12. Staining of adjacent acetate obtained for untreated dyeings and dyeings aftertreated with the full backtan, tannic acid/enzyme and tannic acid alone at pH 6 (legend as for Fig. 8).

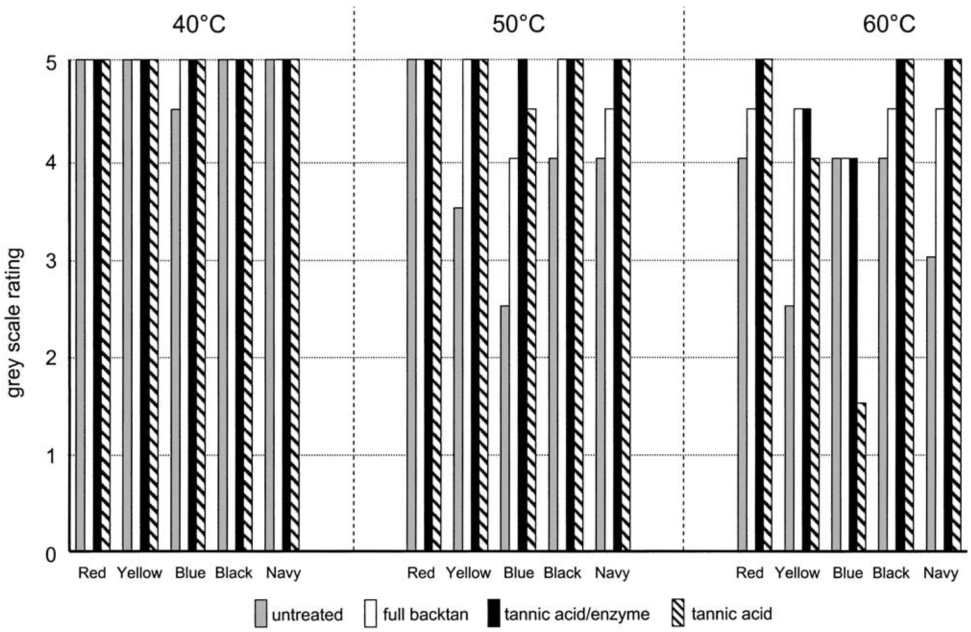

Fig. 13. Staining of adjacent wool obtained for untreated dyeings and dyeings aftertreated with the full backtan, tannic acid/enzyme and tannic acid alone at pH 6 (legend as for Fig. 8).

Table 12
Light fastness results obtained for different aftertreated dyeings

	pH	Red 278	Orange 67	Blue 281	Black 172	Blue 284
Untreated	–	5/6	7	4	5/6	6
Full backtan	–	5/6	7	4/5	5/6	6
Textan 3/Savinase	–	5/6	7	4/5	5/6	6
Textan 3	3.0	5	7	4/5	5/6	6
	4.0	5	7	4	5/6	6
	5.0	5	7	4	5/6	6
	6.0	5/6	7	4/5	5/6	6

4. Conclusions

The application of tannic acid at pH 6 proved to be an effective aftertreatment of dyed nylon 6,6 in terms of the improvement of the fastness of all five acid dyes to repeated washing. However, the effectiveness of the aftertreatment decreased with increasing temperature of washing, from 40 to 50 °C and 60 °C. Nonetheless, while the tannic acid aftertreatment may not be as effective as a tannic acid/enzyme system in improving fastness to washing at 50 °C and 60 °C, it is equally as effective as a tannic acid/enzyme system in the case of washing at 40 °C. Thus, the single-stage, single bath, tannic acid aftertreatment method offers a potentially more environmentally acceptable alternative to the antimony-based, full backtan aftertreatment.

Acknowledgements

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References

[1] Bahojb-Allafan B, Burkinshaw SM. Dyes and Pigments 2002;58:205.
[2] Bahojb-Allafan B, Burkinshaw SM. Dyes and Pigments 2003;59:71.
[3] Bahojb-Allafan B, Burkinshaw SM. Dyes and Pigments 2003;60:91.