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The development of a metal-free, tannic acid-based aftertreatment for nylon 6,6 dyed with acid dyes—part 3: different enzymes

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Abstract

A single-bath, two-stage aftertreatment for nylon 6,6 dyed with acid dyes has been developed, in which an enzyme is used to complex tannic acid. The effectiveness of four protease enzymes was determined, employing a repeated washing protocol, using five commercial acid dyes on nylon 6,6. It was found that while each of the four enzymes were very effective, when used in conjunction with tannic acid, in improving the fastness of all five acid dyes to repeated washing at 40, 50 and 60 °C, one particular enzyme was, overall, the most effective. While the chemical structures of the four enzymes used are not available, the nature of their interaction with tannic acid is explained in terms of the general interactions that occur between tannic acid and proteins. It is proposed that the enzymes replace the metal salt (potassium antimonyl tartrate) used in the full backtan aftertreatment and that the sequential application of tannic acid and enzyme results in the formation of an insoluble, tannic acid/enzyme complex that is situated at the surface of the dyed substrate and which provides a physical barrier to the diffusion of dye from the dyed fabric during washing. The 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; Tannic acid; Enzyme

1. Introduction

This paper concerns the development 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 this paper [1] showed that the effectiveness of a newly developed, tannic acid/enzyme aftertreatment in improving the fastness to repeated washing of three commercial acid dyes on nylon 6,6, was comparable to that of established aftertreatments (syntan, full backtan and a modified full backtan) which had been chosen as 'references' against which the developed tannic acid/enzyme system was compared. The second part of the paper [2] described the optimum conditions for

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the application of tannic acid and the particular enzyme and revealed that the effectiveness of the tannic acid/enzyme aftertreatment in improving the fastness to repeated washing of five commercial acid dyes on nylon 6,6 was superior to that of a traditional full backtan aftertreatment.

This part of the paper compares 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 in previous parts of the paper [1,2], the effectiveness of the tannic acid/enzyme systems were determined at three washing temperatures (40, 50 and 60 °C) 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 commercial samples of the enzymes listed in Table 2 were generously supplied by *Novazyme*.

All other chemicals 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. Enzyme treatment

The aftertreatment method is shown in Fig. 1; the equipment described earlier [1] was used, the pH of application being adjusted using McIlvaine buffer as before [1]. At the end of treatment, the samples were removed, rinsed thoroughly in tap 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, 50 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 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 CIEL*a*b* ΔE units.

3. Results and discussion

3.1. Background

In the previous part of this paper [2], it was found that optimal conditions for applying the

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

Table 2
Enzymes used

Enzyme
Savinase
Esperase
Neutrase
Alcalase

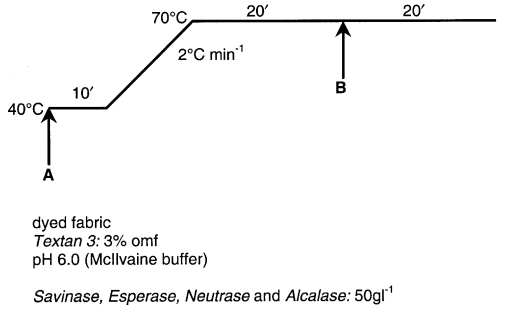

Fig. 1. Tannic acid/enzyme application method.

enzyme *Savinase*, in the two-stage, single bath aftertreatment method used, were 70 °C at pH 6. When applied under these particular conditions, the effectiveness of the tannic acid/*Savinase* aftertreatment in improving the fastness to repeated washing of five commercial acid dyes on nylon 6,6 was superior to that of a traditional full backtan aftertreatment [2]. As a consequence of these findings, it was decided in the present work, to use the tannic acid/*Savinase* aftertreatment as a reference against which the effectiveness of three other protease enzymes would be judged when used in conjunction with tannic acid.

3.2. Untreated dyeings

As previously explained [1], three, common washing temperatures were used in this work, namely 40, 50 and 60 °C, in recognition of the fact that washing temperatures vary within Europe. In this context, Tables 3–5 show the extent of the shade change encountered by the dyeings. The data presented in Tables 3–6 are taken from the 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 $f(k)$ that occurred because of the loss of dye during washing. Also, the $f(k)$ values 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. The colorimetric data presented in Tables 3–5 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 manifest from Fig. 2 which shows the colour difference (delta E) 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 which the dyeings underwent is clearly evident.

Table 6 shows the corresponding staining of multifibre strip obtained as a result of the five, consecutive wash tests. As discussed previously [2],

Table 3
Colorimetric data and wash fastness results for untreated dyeings washed at 40 °C

Dye	Number of washes	L^*	a^*	b^*	C^*	h^o	$f(k)$
Neutrilan 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
Nylanthrene 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
Nylanthrene Blue C-GLF	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
Nylanthrene 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
Neutrilan Navy S-BGR	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 4
Colorimetric data and wash fastness results for untreated dyeings washed at 50 °C

Dye	Number of washes	L^*	a^*	b^*	C^*	h°	$f(k)$
Neutrilan 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
Nylanthrene 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
Nylanthrene Blue C-GLF	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
Nylanthrene Black C-DPL	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
Neutrilan Navy S-BGR	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 5
Colorimetric data and wash fastness results for untreated dyeings washed at 60 °C

Dye	Number of washes	L^*	a^*	b^*	C^*	h°	$f(k)$
Neutrilan 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
Nylanthrene 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
Nylanthrene Blue C-GLF	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
Nylanthrene Black C-DPL	0	24.9	−0.3	−3.9	3.9	265.6	180.7
	5	26.9	−0.3	−3.9	3.9	265.7	153.0
Neutrilan Navy S-BGR	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 6
Staining of adjacent multifibre strip achieved for untreated dyeings

Dye	Number 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)
Blue C-GLF	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 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)	**2/3** 2/3* (2)	**5** 5* (5)	**5** 5* (5)
Navy S-BGR	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.

the low level of staining obtained for the adjacent acrylic, polyester and cotton components is attributable to the inherent low substantivity of the three acid dyes towards such fibre types while the very high extent of staining obtained for the adjacent nylon 6,6 fibre and the moderate staining of the wool component can be explained in terms of the high substantivity of the dyes towards these

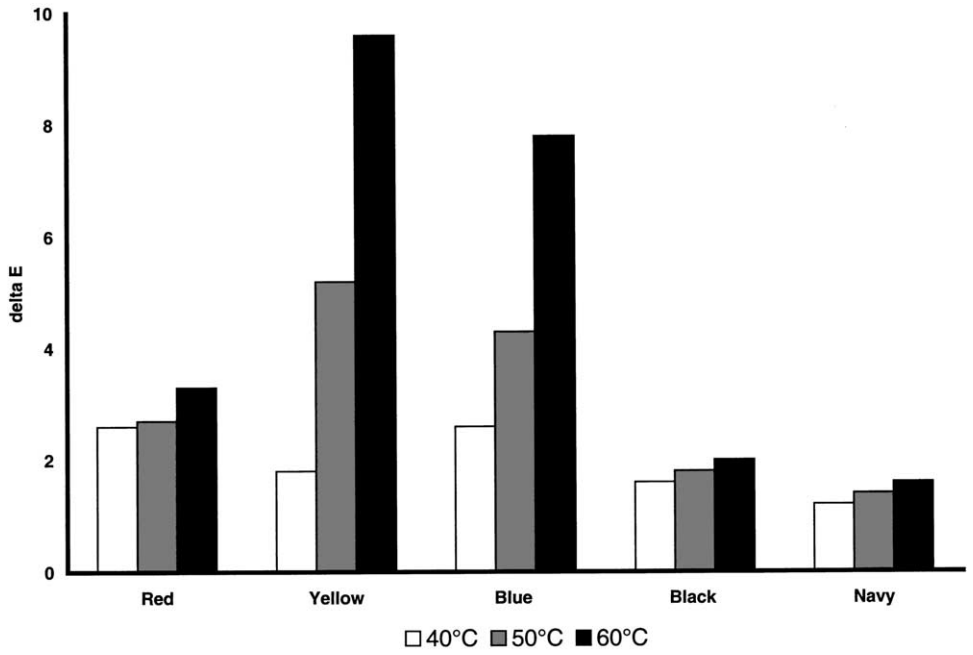

Fig. 2. Colour difference between unwashed and washed dyeings: untreated.

two types of fibre. The results presented in Table 6 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.

3.3. Tannic acid/enzyme aftertreatment

As mentioned, it was decided to use the tannic acid/*Savinase* aftertreatment as a reference against which the effectiveness of three other protease enzymes would be judged when used in conjunction with tannic acid. In this context, Table 7 shows the colorimetric data obtained for dyeings which had been aftertreated with tannic acid/*Savinase* as well as with the three other enzymes and subjected to repeated wash testing at 40 °C. Comparison of these data with that obtained for the untreated dyeings (Table 3) reveals that aftertreatment markedly improved the wash fastness of each of the dyes to repeated wash fastness, in terms of change in shade of the dyeings. Also, it is clear that each of the four tannic acid/enzyme aftertreatments 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. As previously discussed [1], these latter findings can be attributed to tannic acid component of the aftertreatment having altered the shade of dyeings. Fig. 3 shows the extent to which each of the four tannic acid/enzyme systems reduced the shade change of the dyeings in terms of the colour difference obtained after repeated wash testing at 40 °C.

The extent of the staining of adjacent multifibre strip that occurred during repeated wash testing at 40 °C is shown in Table 8. When these staining results are compared to those obtained for the untreated dyeings (Table 6), it is clear that each of the four tannic acid/enzyme systems was very effective in reducing the extent of staining achieved.

Of the four enzymes used, *Savinase* was the most effective in terms of reducing both the extent of shade change (Table 7 and Fig. 3) and staining (Table 8) obtained for repeated washing at 40 °C.

Tables 9 and 10 show the colorimetric data obtained for dyeings which had been aftertreated

Table 7
Effect of different enzymes on the colorimetric data obtained for tannic acid/enzyme aftertreatments washed at 40 °C

Dye	Enzyme	No. of washes	L^*	a^*	b^*	C^*	h^o	$f(k)$
Red K-2G	*Savinase*	0	42.0	43.9	17.2	47.1	21.4	91.4
		5	42.2	43.3	17.0	46.5	21.4	90.9
	Esperase	0	41.6	43.4	16.8	46.5	21.2	92.0
		5	42.0	42.7	16.4	45.7	21.0	91.0
	Neutrase	0	41.7	43.5	16.8	46.6	21.1	92.2
		5	42.1	42.8	16.4	45.8	21.0	91.1
	Alcalase	0	41.8	43.8	17.0	47.0	21.2	91.9
		5	42.1	43.1	16.7	46.2	21.2	91.2
Yellow C-3RL	*Savinase*	0	68.9	28.6	74.6	79.9	68.4	68.9
		5	69.3	28.2	74.4	79.6	69.2	68.5
	Esperase	0	68.6	28.3	74.1	79.3	69.1	69.5
		5	69.2	27.7	73.6	78.6	69.4	68.6
	Neutrase	0	68.8	28.4	74.3	79.5	69.1	69.3
		5	69.3	27.8	73.7	78.8	69.3	68.5
	Alcalase	0	68.8	28.5	74.4	79.7	69.0	69.0
		5	69.3	28.0	74.0	79.1	69.3	68.3
Blue C-GLF	*Savinase*	0	41.9	−2.0	−38.1	38.2	267.0	62.9
		5	42.4	−2.3	−37.5	37.6	266.5	62.0
	Esperase	0	41.6	−1.8	−38.4	38.4	267.3	63.4
		5	42.3	−2.1	−37.7	37.8	266.8	62.2
	Neutrase	0	41.7	−1.9	−38.2	38.3	267.2	63.2
		5	42.3	−2.3	−37.6	37.7	266.5	62.1
	Alcalase	0	41.9	−1.9	−38.2	38.3	267.2	63.0
		5	42.5	−2.2	−37.6	37.7	266.7	62.0
Black C-DPL	*Savinase*	0	24.5	−0.3	−3.8	3.8	265.5	191.2
		5	24.9	−0.3	−3.7	3.7	265.4	190.6
	Esperase	0	24.0	−0.3	−3.7	3.7	265.4	192.8
		5	24.6	−0.3	−3.7	3.7	265.4	191.8
	Neutrase	0	24.2	−0.3	−3.7	3.7	265.4	192.4
		5	24.8	−0.3	−3.7	3.7	265.4	191.4
	Alcalase	0	24.4	−0.3	−4.0	4.0	265.7	191.7
		5	24.9	−0.3	−4.0	4.0	265.7	190.9
Navy S-BGR	*Savinase*	0	15.1	2.6	−14.1	14.3	280.5	393.1
		5	15.2	2.6	−14.5	14.7	280.2	392.6
	Esperase	0	14.5	2.6	−13.5	13.8	280.9	394.7
		5	14.8	2.6	−13.9	14.1	280.6	393.2
	Neutrase	0	14.6	2.5	−13.7	13.9	280.3	394.0
		5	14.9	2.5	−14.1	14.3	280.1	392.5
	Alcalase	0	14.9	2.6	−13.9	14.1	280.6	393.4
		5	15.1	2.6	−14.3	14.5	280.3	392.3

with each of the four tannic acid/enzyme systems and subjected to repeated wash testing at 50 and 60 °C, respectively. When compared with the data obtained for the untreated dyeings (Tables 4 and 5), it is evident that aftertreatment markedly improved the wash fastness of each of the dyes to repeated wash fastness, in terms of change in shade of the dyeings. Also, aftertreatment with each of the four tannic acid/enzyme systems 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. The extent to which each of the four tannic acid/enzyme systems 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. 4 and 5. The corresponding levels of staining that

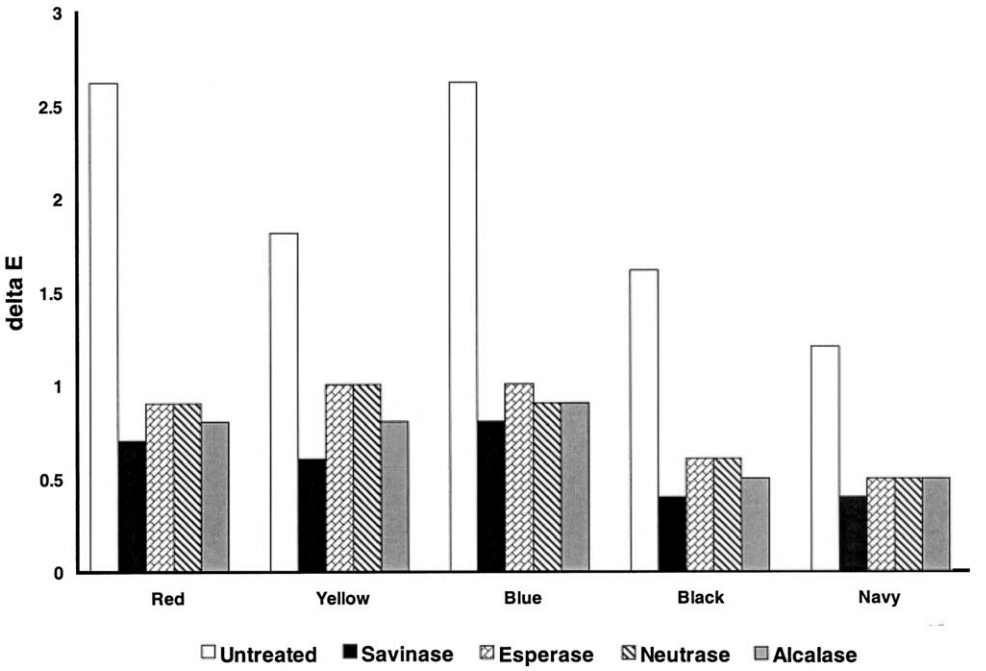

Fig. 3. Comparison of colour difference achieved for dyeings as well as dyeings aftertreated with tannic acid and different enzymes washed at 40 °C.

Table 8
Effect of different enzymes on the staining of adjacent multifibre strip obtained for washing at 40 °C

Enzyme	No. of washes	Wool	Acrylic	Polyester	Nylon 6.6	Cotton	2° Acetate
Savinase	1	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (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* (5) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}
Esperase	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** 5* (4/5) [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}
Neutrase	1	**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	**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] {5}
Alcalase	1	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**5** 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** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}

Bold = *Neutrilan Red K-2G*. * = *Nylanthrene Yellow C-3RL*. ( ) = *Nylanthrene Blue C-GLF*. [ ] = *Nylanthrene Black C-DPL*. { } = *Neutrilan Navy S-BGR*.

was achieved as a result of repeated wash testing at 50 and 60 °C are shown in Tables 11 and 12, respectively. When these staining results are compared to those obtained for the untreated dyeings (Table 6), it is clear that each of the four tannic acid/enzyme systems was very effective in reducing the extent of staining achieved at both washing temperatures.

Of the four enzymes used, *Savinase* was the most effective in terms of reducing both the extent of shade change (Tables 9 and 10 and Figs. 4 and 5) and staining (Tables 11 and 12) obtained for repeated washing at both 50 and 60 °C.

3.4. General discussion

The purpose of this work was to develop a metal-free, tannic acid-based aftertreatment of acid dyes on nylon as an alternative to the tradi-

Table 9
Effect of different enzymes on the colorimetric data obtained for tannic acid/enzyme aftertreatments washed at 50 °C

Dye	Enzyme	No. of washes	L^*	a^*	b^*	C^*	h^o	$f(k)$
Red K-2G	*Savinase*	0	42.0	43.9	17.2	47.1	21.4	91.4
		5	42.3	43.2	17.0	46.4	21.5	90.7
	Esperase	0	41.6	43.4	16.8	46.5	21.2	92.0
		5	42.3	42.6	16.3	45.6	20.9	90.2
	Neutrase	0	41.7	43.5	16.8	46.6	21.1	92.2
		5	42.3	42.6	16.4	45.7	21.0	90.4
	Alcalase	0	41.8	43.8	17.0	47.0	21.2	91.9
		5	42.3	43.0	16.6	46.1	21.1	90.8
Yellow C-3RL	*Savinase*	0	68.9	28.6	74.6	79.9	68.4	68.9
		5	69.5	28.1	74.1	79.3	69.2	68.2
	Esperase	0	68.6	28.3	74.1	79.3	69.1	69.5
		5	69.4	27.6	73.5	78.5	69.4	68.2
	Neutrase	0	68.8	28.4	74.3	79.5	69.1	69.3
		5	69.5	27.7	73.6	78.6	69.4	68.1
	Alcalase	0	68.8	28.5	74.4	79.7	69.0	69.0
		5	69.5	28.0	73.9	79.0	69.2	68.0
Blue C-GLF	*Savinase*	0	41.9	−2.0	−38.1	38.2	267.0	62.9
		5	42.6	−2.6	−37.1	37.2	266.0	61.5
	Esperase	0	41.6	−1.8	−38.4	38.4	267.3	63.4
		5	42.5	−2.5	−37.3	37.4	266.2	61.4
	Neutrase	0	41.7	−1.9	−38.2	38.3	267.2	63.2
		5	42.6	−2.5	−37.1	37.2	266.1	61.5
	Alcalase	0	41.9	−1.9	−38.2	38.3	267.2	63.0
		5	42.7	−2.4	−37.0	37.1	266.3	61.3
Black C-DPL	*Savinase*	0	24.5	−0.3	−3.8	3.8	265.5	191.2
		5	25.1	−0.3	−3.7	3.7	265.4	189.7
	Esperase	0	24.0	−0.3	−3.7	3.7	265.4	192.8
		5	24.7	−0.3	−3.6	3.6	265.2	191.0
	Neutrase	0	24.2	−0.3	−3.7	3.7	265.4	192.4
		5	24.9	−0.4	−3.6	3.6	263.7	190.6
	Alcalase	0	24.4	−0.3	−4.0	4.0	265.7	191.7
		5	25.0	−0.3	−3.8	3.8	265.5	190.1
Navy S-BGR	*Savinase*	0	15.1	2.6	−14.1	14.3	280.5	393.1
		5	15.3	2.6	−14.6	14.8	280.1	392.0
	Esperase	0	14.5	2.6	−13.5	13.8	280.9	394.7
		5	14.9	2.6	−14.0	14.2	280.5	392.0
	Neutrase	0	14.6	2.5	−13.7	13.9	280.3	394.0
		5	15.0	2.4	−14.1	14.3	279.7	391.3
	Alcalase	0	14.9	2.6	−13.9	14.1	280.6	393.4
		5	15.2	2.6	−14.3	14.5	280.3	391.5

tional full backtan. Although the full backtan aftertreatment is highly effective in improving the wet fastness of acid dyes on nylon, it is nowadays used rarely 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 change to dyeings [3].

As discussed [1], the full backtan aftertreatment, which uses a high M_r gallotannin (tannic acid) and potassium antimonyl tartrate (tartar emetic), comprises a two-stage, usually two-bath process in which the gallotannin is firstly applied to the dyed nylon fibre, typically, for 20–30 min at a temperature of 70–90 °C and a pH of 2.5 [3]; the tanned fabric is then treated with potassium antimonyl tartrate from a fresh bath for a further 20 min at 70–90 °C. In this two-stage system, the gallotannin component behaves as a high M_r acid which binds

Table 10
Effect of different enzymes on the colorimetric data obtained for tannic acid/enzyme aftertreatments washed at 60 °C

Dye	Enzyme	No. of washes	L^*	a^*	b^*	C^*	h^o	$f(k)$
Red K-2G	*Savinase*	0	42.0	43.9	17.2	47.1	21.4	91.4
		5	42.4	43.1	16.9	46.3	21.4	90.3
	Esperase	0	41.6	43.4	16.8	46.5	21.2	92.0
		5	42.3	42.4	16.4	45.4	21.2	90.0
	Neutrase	0	41.7	43.5	16.8	46.6	21.1	92.2
		5	42.4	42.5	16.3	45.5	21.0	90.1
	Alcalase	0	41.8	43.8	17.0	47.0	21.2	91.9
		5	42.5	42.9	16.6	46.0	21.2	90.2
Yellow C-3RL	*Savinase*	0	68.9	28.6	74.6	79.9	68.4	68.9
		5	69.8	28.1	73.9	79.1	69.2	67.8
	Esperase	0	68.6	28.3	74.1	79.3	69.1	69.5
		5	69.6	27.5	73.3	78.3	69.4	67.6
	Neutrase	0	68.8	28.4	74.3	79.5	69.1	69.3
		5	69.8	27.6	73.5	78.5	69.4	67.5
	Alcalase	0	68.8	28.5	74.4	79.7	69.0	69.0
		5	69.7	27.9	73.7	78.8	69.3	67.6
Blue C-GLF	*Savinase*	0	41.9	−2.0	−38.1	38.2	267.0	62.9
		5	43.0	−2.9	−36.5	36.6	265.5	60.0
	Esperase	0	41.6	−1.8	−38.4	38.4	267.3	63.4
		5	43.0	−3.0	−36.2	36.3	265.3	58.9
	Neutrase	0	41.7	−1.9	−38.2	38.3	267.2	63.2
		5	42.8	−3.0	−35.9	36.1	265.2	58.8
	Alcalase	0	41.9	−1.9	−38.2	38.3	267.2	63.0
		5	43.3	−2.9	−36.5	36.6	265.5	59.3
Black C-DPL	*Savinase*	0	24.5	−0.3	−3.8	3.8	265.5	191.2
		5	25.3	−0.3	−3.6	3.6	265.2	188.4
	Esperase	0	24.0	−0.3	−3.7	3.7	265.4	192.8
		5	24.9	−0.3	−3.5	3.5	265.1	189.7
	Neutrase	0	24.2	−0.3	−3.7	3.7	265.4	192.4
		5	25.1	−0.4	−3.5	3.5	263.5	189.5
	Alcalase	0	24.4	−0.3	−4.0	4.0	265.7	191.7
		5	25.2	−0.3	−3.7	3.7	265.4	188.9
Navy S-BGR	*Savinase*	0	15.1	2.6	−14.1	14.3	280.5	393.1
		5	15.4	2.5	−14.7	14.9	279.6	391.4
	Esperase	0	14.5	2.6	−13.5	13.8	280.9	394.7
		5	15.0	2.5	−14.1	14.3	280.1	390.8
	Neutrase	0	14.6	2.5	−13.7	13.9	280.3	394.0
		5	15.1	2.4	−14.3	14.5	279.5	390.1
	Alcalase	0	14.9	2.6	−13.9	14.1	280.6	393.4
		5	15.3	2.5	−14.5	14.7	279.8	390.3

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.

To develop a metal-free, full backtan aftertreatment, an alternative complexing agent to potassium antimonyl tartrate was required. While tannic acid and other natural vegetable tannin extracts are precipitated by gelatin, albumen or alkaloids, a decision was made to pursue the use

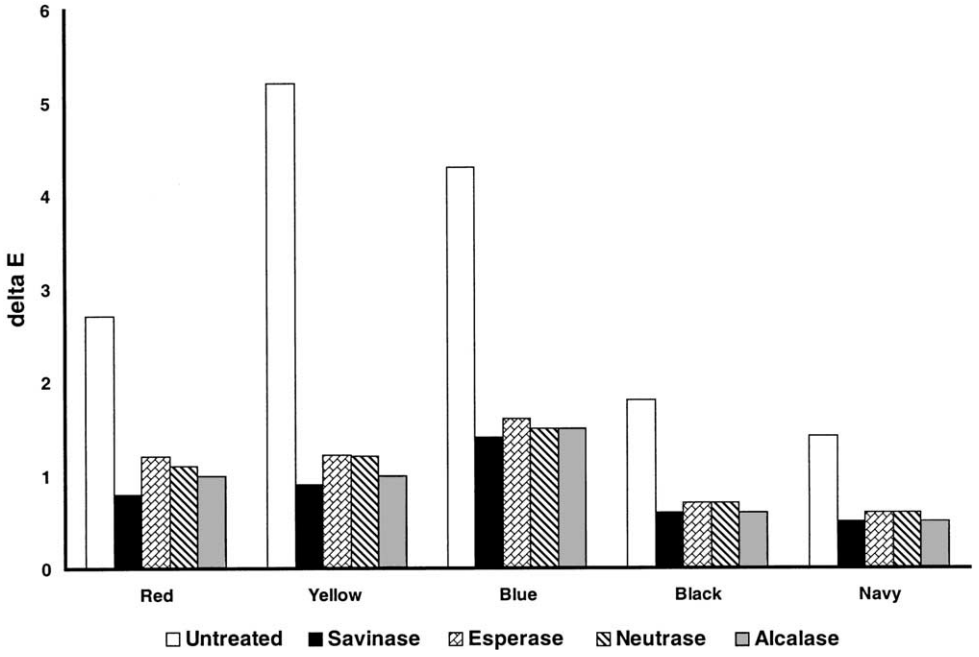

Fig. 4. Comparison of colour difference achieved for untreated dyeings as well as dyeings aftertreated with tannic acid and different enzymes washed at 50 °C.

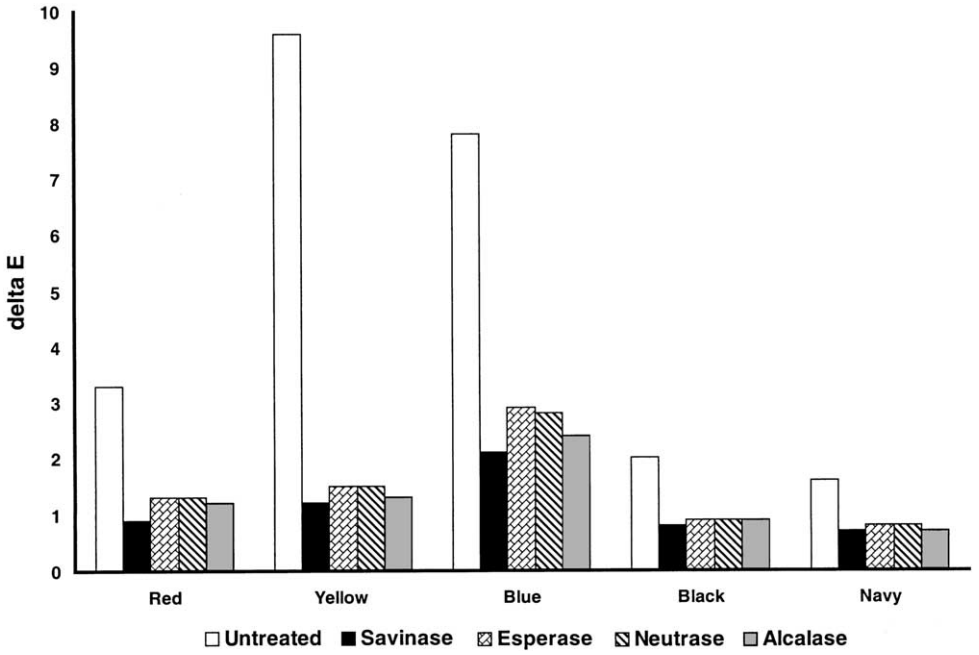

Fig. 5. Comparison of colour difference achieved for untreated dyeings a well as dyeings aftertreated with tannic acid and different enzymes washed at 60 °C.

Table 11
Effect of different enzymes on the staining of adjacent multifibre strip obtained for washing at 50 °C

Enzyme	No. of washes	Wool	Acrylic	Polyester	Nylon 6.6	Cotton	2° Acetate
Savinase	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* (5) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}
Esperase	1	**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** 4/5* (4/5) [5] {5}
	5	**5** 5* (4/5) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**4** 4/5* (4) [4] {4}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}
Neutrase	1	**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** 4/5* (4/5) [5] {5}
	5	**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** 5* (5) [5] {5}
Alcalase	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* (4/5) [5] {5}
	5	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (4/5) [4/5] {4}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}

Legend as for Table 8.

Table 12
Effect of different enzymes of aftertreatment on the staining of adjacent multifibre strip obtained for washing at 60 °C

Enzyme	No. of washes	Wool	Acrylic	Polyester	Nylon 6.6	Cotton	2° Acetate
Savinase	1	**5** 4/5* (4) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**4/5** 4/5* (4) [4] {3}	**5** 5* (5) [5] {5}	**5** 5* (4/5) [5] {5}
	5	**5** 4/5* (4) [5] {5}	**5** 5* (5) [5] {5}	**5** 5* (4/5) [5] {5}	**4/5** 4/5* (2/3) [4/5] {4}	**5** 5* (5) [5] {5}	**5** 5* (4/5) [5] {5}
Esperase	1	**4/5** 4* (3) [4] {4}	**5** 5* (5) [5] {5}	**5** 5* (4/5) [4/5] {5}	**3/4** 3/4* (2/3) [3/4] {3}	**5** 4/5* (4) [4] {4/5}	**5** 4* (3) [5] {5}
	5	**4/5** 4/5* (3) [4] {4}	**5** 5* (5) [5] {5}	**5** 5* (5) [5] {5}	**3** 3* (2) [3] {3}	**5** 5* (3/4) [5] {5}	**5** 4* (3) [5] {5}
Neutrase	1	**4/5** 4* (3) [4] {4}	**5** 5* (5) [5] {5}	**5** 5* (5) [4/5] {5}	**3/4** 3/4* (3) [3/4] {3}	**5** 5* (4) [4/5] {4/5}	**5** 4/5* (3/4) [5] {5}
	5	**4/5** 4/5* (3/4) [4/5] {4/5}	**5** 5* (5) [5] {5}	**5** 5* (4/5) [5] {5}	**3/4** 4* (2) [4] {3}	**5** 5* (4) [5] {5}	**5** 4/5* (4) [5] {5}
Alcalase	1	**5** 4* (4) [4/5] {4}	**5** 5* (5) [5] {4/5}	**5** 5* (4/5) [4/5] {5}	**4** 4* (3/4) [4] {3}	**4** 4* (4/5) [4] {4}	**5** 4* (4) [5] {5}
	5	**5** 4/5* (4) [4/5] {4/5}	**5** 5* (5) [5] {5}	**5** 5* (4) [4/5] {5}	**4** 4/5* (2/3) [4] {4}	**5** 5* (5) [5] {5}	**5** 4/5* (4/5) [5] {5}

Legend as for Table 8.

of enzymes in view of the facts that a wide range of these highly effective, biological catalyts are available commercially and they have enjoyed much use in the textile industry for many years.

Although the chemical structures of the four enzymes used are not disclosed, the nature of their interaction with tannic acid and, in particular, the manner in which the tannic acid/enzyme aftertreatment functions, may be explained in terms of the general interactions that occur between tannic acid and proteins. It is well known that polyphenolic tannins, as represented by tannic acid, contain numerous phenolic and carboxyl groups; it can be anticipated that the latter groups will be ionised at the particular pH value used in the work (i.e pH 6). Tannic acid can be expected to interact with groups, such as amino, hydroxy, carbonyl and chain imino present in the protease enzymes, by virtue of various ionic and non-ionic forces of interaction (e.g. hydrogen bonding, dispersion forces, dipole–dipole and electrostatic forces). It is further proposed that such interaction results in the formation of a tannic acid/enzyme complex of low water solubility, in a manner similar to that experienced in the traditional full backtan. Evidence for such interaction is provided by the observation that when an aqueous solution, at pH 6, of any one of the four enzymes used in this work is added to an aqueous solution of tannic acid, a pale brown coloured precipitate is formed.

In this context, it therefore seems reasonable to suggest that in the two-stage, tannic acid/ enzyme application system used, the tannic acid component binds to the protonated amino end groups in the nylon substrate and the sequential application of enzyme results in the formation of an insoluble, tannic acid/enzyme 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 enzyme replaces the metal salt (potassium antimonyl tartrate) used in the traditional full backtan aftertreatment.

4. Conclusions

Each of the four protease enzymes was very effective, when used in conjunction with tannic acid, in improving the fastness of the five acid dyes to repeated washing at 40, 50 and 60 °C. Although the four enzymes were similar in terms of the reduction in shade change imparted to the dyeings and the reduced level of staining of adjacent materials, *Savinase* was, overall, the most effective of the four enzymes used. Although the chemical structures of the four enzymes used are not available, the nature of their interaction with tannic acid and, in particular, the manner in which the tannic acid/enzyme aftertreatment functions, may be explained in terms of the general interactions that occur between tannic acid and proteins. In this context, it is proposed that the enzymes used replace the metal salt (potassium antimonyl tartrate) employed in the full backtan aftertreatment and that the sequential application of tannic acid and enzyme results in the formation of an insoluble, tannic acid/enzyme complex that is situated at the surface of the dyed substrate and which provides a physical barrier to the diffusion of dye from the dyed fabric during washing.

The two-stage, single bath, tannic acid/enzyme aftertreatment method therefore offers a potentially more environmentally acceptable alternative to the antimony-based, full backtan aftertreatment.

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