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A polyvinyl alcohol aftertreatment for nylon 6,6. Part 2: Complex formation

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Abstract

The effectiveness of a PVA aftertreatment in improving the fastness of acid dyes to repeated washing at 40, 50 and 60 °C was enhanced by the sequential application of an organic titanate, $MgSO_4$ and a protease enzyme. This was attributed to the formation of a large molecular size, low water-solubility complex situated at the surface of the dyed substrate which physically resists diffusion of dye from the dyed fabric during washing. Although aftertreatment with each of four PVA-based aftertreatments reduced the lightness and chroma of the red and, in particular, the yellow dyeings, it had little effect on the colour of black dyeings.

Keywords: Nylon 6,6; Acid dyes; Aftertreatment; PVA; Tannic acid

1. Introduction

Although tannic acid, used either alone [1] or in conjunction with potassium antimony tartrate [2], metal salts [3,4], or protease enzymes [5–7], is very effective in improving the wash fastness of acid dyes on nylon 6,6, as tannic acid imparts a yellowish brown hue to dyeings [2], it was decided to determine if the high M_r gallotannin could be replaced by polyvinyl alcohol (PVA). The first part of this paper [8] showed that the fastness, to repeated washing at 50 °C, of three acid dyes on nylon 6,6 was improved by an aftertreatment with polyvinyl alcohol. Whilst aftertreatment reduced the lightness and chroma of red and, in particular, yellow dyeings, it had little effect on the colour of black dyeings; the extent of this shade change did not increase significantly with increasing amounts of PVA used. Although PVA imparted a yellow colouration to undyed fabric, the extent of this shade change was much lower than that imparted by the same concentration of tannic acid.

Having obtained promising results using PVA as an aftertreatment [8], it was decided to determine the effectiveness of the polymer when used in conjunction with metal salts and protease enzymes, using a repeated wash testing protocol at three temperatures (40, 50 and 60 °C), in recognition of the wide range of washing temperatures commonly used in Northern Europe.

2. Experimental

2.1. Materials

The scoured, knitted nylon 6,6 fabric described earlier [8], which was kindly supplied by Dupont (UK), was used; the three commercial acid dyes (Table 1) that had been previously used [8] were again employed. A sample of the enzyme *Savinase* was kindly provided by Novazyme; *Celvol 540* (87–89% hydrolysed PVA) was obtained from Celanese chemicals, *Tyzor TE* (triethanolamine titanate; **1**) was generously supplied by DuPont (US) and magnesium sulphate was obtained from Aldrich. All other chemicals were laboratory grade reagents.

2.2. Dyeing

The dyes were applied using the equipment and methods described earlier [8]; the pH was adjusted using McIlvaine

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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

Table 2
Colorimetric data for untreated dyeings

Dye	Wash temp/°C	No. of washes	L^*	a^*	b^*	C^*	h^0	$f(k)$
Red K-2G	–	0	39.8	47.5	20.2	51.6	23.0	96.4
	40	5	40.7	48.6	21.5	53.2	23.8	94.7
	50	5	40.4	47.7	20.6	51.9	23.4	93.2
	60	5	41.0	47.5	21	51.9	23.8	89.3
Yellow C-3RL	–	0	67.4	32.9	78.1	84.7	67.1	80.6
	40	5	68.2	31.0	76.0	82.1	67.7	68.9
	50	5	69.6	28.9	73.7	79.2	68.5	55.3
	60	5	72.3	24.6	68.3	72.6	70.1	35.7
Black C-DPL	–	0	20.9	0.2	−4.5	4.5	273.6	188.4
	40	5	21.2	0.1	−4.7	4.7	271.6	183.8
	50	5	22.1	0.1	−4.8	4.8	271.9	170.3
	60	5	23.4	0.1	−5.2	5.2	271.9	151.8

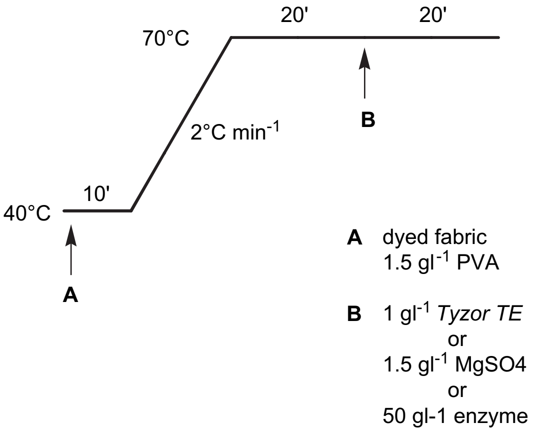


Fig. 1. Two-stage aftertreatment method.

buffer. The dyeings were rinsed thoroughly in tap water and allowed to dry in the open air.

2.3. PVA aftertreatment

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

2.4. Colour measurement

All measurements were carried out using the equipment and procedures described earlier [8].

2.5. Wash fastness

Three ISO wash tests, namely ISO CO6/A2S (40 °C), ISO CO6/B2S (50 °C) and ISO CO6/C2S (60 °C) [9] 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.

3. Results and discussions

The moderate fastness to washing of the three dyes on nylon 6,6 is clearly evident from the reduction in colour strength $f(k)$ (Table 2) which the dyeings underwent as a consequence of their submission to five repeated wash tests. It is also apparent that the reduction in colour strength increased with increasing temperature of wash testing due to the corresponding increase in removal of dye from the dyed samples during wash testing. The colorimetric data presented in Table 2 show that the changes observed for the three dyes can be attributed to loss of dye from the dyeings rather than to changes in the colour of the dyeings; the effect of increasing washing temperature on the extent of dye loss is clear, especially in the case of the yellow dye at 60 °C. Table 3 shows the change in shade of the dyeings that occurred as a result of the five repeated wash tests; all three dyes displayed poor fastness, especially the yellow dye. The increase in shade change that accompanied an increase in wash temperature is attributable to an increase in the amount of dye removed from the dyeings. The extent of staining of adjacent multifibre strip by vagrant dye, as a result of the five, consecutive wash tests is also shown in Table 3.

Table 3
Shade change and staining of adjacent multifibre strip achieved for untreated dyeings

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

Bold = 40 °C; * = 50 °C; () = 60 °C.

Table 4
Colorimetric data for dyeings aftertreated with PVA

Dye	Wash temp/°C	No. of washes	L^*	a^*	b^*	C^*	h^0	$f(k)$
Red K-2G	–	0	39.2	47.5	21.0	51.9	23.8	103.8
	40	5	39.2	47.4	20.9	51.8	23.8	103.3
	50	5	39.5	47.3	21.0	51.8	23.9	101.8
	60	5	40.4	47.6	20.8	52.0	23.5	93.6
Yellow C-3RL	–	0	65.9	32.0	76.1	82.5	67.1	83.2
	40	5	67.5	30.1	74.9	80.8	68.0	69.0
	50	5	68.1	28.1	72.2	77.5	68.7	58.3
	60	5	70.6	23.6	67.6	71.6	70.7	39.3
Black C-DPL	–	0	21.1	0.3	−4.9	4.9	274.1	185.7
	40	5	20.6	0.2	−5.0	5.0	273.1	192.2
	50	5	22.0	0.2	−4.9	4.9	273.2	171.5
	60	5	22.4	0.2	−5.1	5.1	272.4	164.8

Table 6
Colorimetric data for dyeings aftertreated with PVA/*Tyzor*

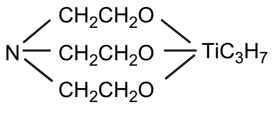
Dye	Wash temp/°C	No. of washes	L^*	a^*	b^*	C^*	h^0	$f(k)$
Red K-2G	–	0	40.2	47.7	20.1	51.7	22.9	93.7
	40	5	41.7	48.2	20.6	52.4	23.1	84.9
	50	5	41.2	48.0	20.5	52.2	23.1	88.0
	60	5	39.5	46.2	19.6	50.2	23.0	96.0
Yellow C-3RL	–	0	66.1	31.9	77.1	83.4	67.4	86.5
	40	5	66.9	30.3	75.2	81.0	68.0	73.7
	50	5	68.6	28.3	73.1	78.4	68.8	58.4
	60	5	69.0	24.7	68.7	72.9	70.1	46.4
Black C-DPL	–	0	20.7	0.1	−4.7	4.7	272.3	191.0
	40	5	21.3	0.1	−4.7	4.7	271.8	182.6
	50	5	21.7	0.1	−4.8	4.8	272.0	176.2
	60	5	22.4	0.1	−5.1	5.1	271.1	166.0

The low staining observed for the adjacent acrylic, polyester and cotton components can be attributed to the 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 are due to the high substantivity of the dyes towards these fibres. The poor fastness of the yellow dyeing towards repeated wash testing is clear. The increased staining of adjacent materials that accompanied an increase in wash temperature (Table 3) can be attributed to a corresponding increase in the amount of dye removed from the dyeings at the temperature at which wash fastness testing was carried out.

Table 4 shows the colorimetric data obtained for dyeings which had been aftertreated with 1.5 g l^{-1} PVA. When these colorimetric data are compared with those obtained for the untreated dyeings prior to wash testing (Table 2) it is clear that aftertreatment reduced the lightness and chroma of the red and, in particular, the yellow dyeing, but had little effect on the colour of the black dyeing. As discussed in the first part of the paper [8], although PVA imparted a yellow colouration to the dyed substrate, the extent of this shade change was much lower than that imparted by similar concentrations of tannic acid. In the context of the effect of the PVA aftertreatment on the fastness of the dyeings, a comparison of the fastness data obtained for the dyeings which had not been aftertreated (Table 3) with those observed for dyeings which had been aftertreated with PVA (Table 5) shows that application of the polymer reduced both the shade change and the extent of staining of adjacent materials for each of the three dyes used at each of the three wash temperatures employed.

As mentioned, tannic acid in conjunction with potassium antimony tartrate [2] metal salts [3,4] or protease enzymes [5–7], is very effective in improving the wash fastness of acid dyes on nylon 6,6. In these two-stage aftertreatments, the gallotannin is firstly applied to the dyed nylon fibre and the tanned fabric is then treated with the metal salt or enzyme from a fresh bath. 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 metal salt or enzyme results in the formation of a large molecular size, low water-solubility 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 [7]. In this context, it was decided to investigate if such a mechanism could be achieved with PVA using metal salts and enzymes.

Organic titanates are widely employed to augment the adhesion properties of coatings, paints, inks and other surface materials; the addition of titanates to PVA microgels provides compounds that are useful as sizes for paper and textiles [10].



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Such titanates, as exemplified by *Tyzor TE* **1** used in this work, cross-link polymers, such as PVA, through the active hydrogen

Table 5
Shade change and staining of adjacent multifibre strip achieved for dyeings aftertreated with PVA

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

Bold = 40 °C; * = 50 °C; () = 60 °C.
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Table 7
Shade change and staining of adjacent multifibre strip achieved for dyeings aftertreated with PVA/*Tyzor*

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

Bold = 40 °C; * = 50 °C; () = 60 °C.

of a suitable polar group (e.g. amino, thiol, hydroxyl, amido or carboxyl) [11]; in the context of PVA, selected organic titanates are referred to as *insolubilisers* in general purpose adhesives employed for bonding paper, textiles, leather, wood, and porous ceramic surfaces [12]. Table 6 shows the colorimetric data obtained for dyeings which had been aftertreated using the two-stage PVA/*Tyzor* aftertreatment. A comparison of these data with those of the untreated dyeings prior to wash testing (Table 2) reveals that aftertreatment reduced the lightness and chroma of the yellow dyeing but had little effect on the colour of the red and black dyeings, as had been observed in the case of an aftertreatment with PVA alone (Table 4). In terms of the effect of the PVA/*Tyzor* aftertreatment on the fastness of the dyeings, a comparison of the shade changes and staining of adjacent materials obtained for dyeings which had not been aftertreated (Table 3) with those for dyeings which had been aftertreated with PVA/*Tyzor* (Table 7) reveals that the two-stage aftertreatment markedly improved the fastness of the three dyes. When the fastness results in Table 7 are compared to those obtained when PVA had been used as an aftertreatment (Table 5), it is evident that the PVA/*Tyzor* aftertreatment was far more effective than PVA alone, at each of the three wash temperatures employed.

The observed enhancement of the effectiveness of PVA in improving the fastness of the dyeings to repeated wash testing imparted by the sequential application of *Tyzor TE* can be attributed to the organic titanate having ‘insolubilised’ the PVA, presumably, by the formation of a metal-complex. Indeed, it is proposed that in this two-stage treatment, the high M_r polymer is adsorbed by virtue of various ionic and nonionic forces of interaction (e.g. hydrogen bonding, dispersion forces, dipole–dipole and electrostatic forces) onto the dyed nylon substrate. Sequential treatment with the organic titanate results in the formation of a large molecular size, low water-solubility 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. Such a mechanism is analogous to that proposed to explain the effectiveness of the aftertreatments involving tannic acid used in conjunction with potassium antimony tartrate [2] metal salts [3,4] and protease enzymes [5–7].

As an alternative to *Tyzor TE*, it was decided to employ $MgSO_4$ as a cross-linker of PVA. Table 8 shows the colorimetric data obtained for dyeings which had been aftertreated using the two-stage PVA/$MgSO_4$ aftertreatment. Comparison of the data in Table 8 with those of the untreated dyeings prior to wash testing (Table 2) shows that, as observed for both PVA and PVA/*Tyzor* aftertreatments, the lightness and chroma of the yellow dyeing were reduced but the colour of the red and black dyeings was little affected by aftertreatment. Comparison of the shade change and staining results obtained for dyeings which had been aftertreated with PVA/$MgSO_4$ (Table 9) with those secured for dyeings which had not been aftertreated (Table 3) reveals that the two-stage aftertreatment markedly improved the fastness of the three dyes. When the fastness results in Table 9 are compared to those obtained when PVA had been used as an aftertreatment (Table 5), it is evident that the PVA/$MgSO_4$ aftertreatment was considerably more effective than PVA alone, at each of the three wash temperatures employed. Furthermore, comparing the results in Table 9 with those obtained using PVA/*Tyzor* (Table 7) shows that the PVA/$MgSO_4$ aftertreatment was comparable to PVA/*Tyzor* in terms of the improvement in the fastness of the three dyes.

In an attempt to develop a metal-free, tannic acid-based aftertreatment for acid dyed nylon, it was found [6] that a protease enzyme could replace the toxic potassium antimony tartrate in the traditional full backtan aftertreatement. It was proposed [1,6,7] that the sequential application of tannic acid and enzyme resulted in the formation of an insoluble,

Table 8
Colorimetric data for dyeings aftertreated with PVA/$MgSO_4$

Dye	Wash temp/°C	No. of washes	L^*	a^*	b^*	C^*	h^0	$f(k)$
Red K-2G	–	0	39.8	47.3	20.2	51.4	23.1	96.5
	40	5	40.6	47.7	20.7	52.0	23.5	91.9
	50	5	40.6	47.6	20.5	51.9	23.2	91.1
	60	5	40.5	46.9	19.7	50.9	22.8	89.4
Yellow C-3RL	–	0	66.3	32.9	77.7	84.4	67.0	87.8
	40	5	67.3	30.6	72.6	78.8	67.1	63.3
	50	5	69.1	28.7	73.3	78.7	68.6	56.7
	60	5	69.8	25.5	69.5	74.0	69.8	45.4
Black C-DPL	–	0	20.8	0.2	−4.7	4.7	272.9	189.9
	40	5	21.2	0.1	−4.7	4.7	272.1	182.9
	50	5	22.0	0.1	−4.8	4.8	272.2	171.6
	60	5	22.3	0.1	−5	5.0	271.3	167.1

Table 9
Shade change and staining of adjacent multifibre strip achieved for dyeings aftertreated with PVA/$MgSO_4$

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

Bold = 40 °C; * = 50 °C; () = 60 °C.

tannic acid/enzyme complex situated at the surface of the dyed substrate and, therefore, that the enzyme successfully replaced the metal salt (potassium antimony tartrate) used in the full backtan. Table 10 shows the colorimetric data obtained for dyeings which had been aftertreated using the two-stage PVA/enzyme system; when these data are compared with those obtained for untreated dyeings prior to wash testing (Table 2), it is clear that, as observed for each of the PVA-based aftertreatments used in this work, the lightness and chroma of the yellow dyeing were reduced but the colour of the red and black dyeings was little affected by aftertreatment. In terms of the fastness of the aftertreated dyeings to repeated wash testing, when the shade change and staining results displayed in Table 11 are compared to those obtained for the untreated dyeings (Table 3) it is apparent that the use of the enzyme in conjunction with PVA improved the effectiveness of the polymer in improving the fastness of the dyeings. In the case of the two-stage tannic acid/enzyme application aftertreatment for acid dyed nylon, 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 situated at the surface of the dyed substrate [7]. It was suggested that tannic acid would 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) and that such interaction would result 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 [7]. Presumably, a similar mechanism can be considered to operate in the case of the two-stage PVA/enzyme aftertreatment employed herein.

Table 10
Colorimetric data for dyeings aftertreated with PVA/enzyme

Dye	Wash temp/°C	No. of washes	L*	a*	b*	C*	h^0	*f*(*k*)
Red K-2G	–	0	40.6	48.5	20.8	52.7	23.2	93.6
	40	5	42.9	49.7	21.7	54.3	23.5	81.4
	50	5	43.2	47.6	19.2	51.4	22.1	71.9
	60	5	41.1	48.0	20.1	52.0	22.7	82.6
Yellow C-3RL	–	0	66.7	31.9	77.3	83.6	67.5	83.1
	40	5	68.1	30.0	75.5	81.3	68.1	67.8
	50	5	68.8	27.4	72.3	77.3	69.2	55.4
	60	5	68.2	22.7	66.6	70.4	71.1	45.4
Black C-DPL	–	0	20.7	0.2	−4.6	4.6	272.8	191.8
	40	5	21.3	0.1	−4.8	4.8	272.1	181.2
	50	5	21.8	0.1	−4.8	4.8	271.9	174.5
	60	5	21.7	0.1	−4.9	4.9	271.8	175.9

However, when the extent of shade change and staining obtained for the PVA/enzyme system (Table 11) is compared to those obtained using PVA/*Tyzor* (Table 7) and PVA/$MgSO_4$ (Table 9), it is apparent that the enzyme system was the least effective of the three two-stage aftertreatments used, especially in the case of repeated washing at 60 °C. Further parts of this paper will describe the nature of the interactions of PVA with the enzyme and with metal salts and organic titanates.

4. Conclusions

The effectiveness of PVA in improving the fastness of acid dyes to repeated washing at 40, 50 and 60 °C was enhanced by the sequential application of an organic titanate, $MgSO_4$ and a protease enzyme. It is proposed that in these two-stage aftertreatments, the high M_r polymer is adsorbed by virtue of various ionic and non-ionic forces of interaction (e.g. hydrogen bonding, dispersion forces, dipole–dipole and electrostatic forces) onto the dyed nylon substrate. Sequential treatment with the organic titanate, metal salt or enzyme results in the formation of a large molecular size, low water-solubility 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. Such a mechanism is analogous to that proposed to explain the effectiveness of the aftertreatments involving tannic acid used in conjunction with potassium antimony tartrate [2] metal salts [3,4] and protease enzymes [5–7]. Further work is needed to establish the precise mechanism by which the PVA/titanate, PVA/$MgSO_4$ and PVA/enzyme systems operate; this will be the focus of a subsequent part of this paper.

Although aftertreatment with each of four PVA-based aftertreatments reduced the lightness and chroma of the red and, in

Table 11
Shade change and staining of adjacent multifibre strip achieved for dyeings aftertreated with PVA/enzyme

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

Bold = 40 °C; * = 50 °C; () = 60 °C.

particular, the yellow dyeings, it had little effect on the colour of black dyeings.

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