Available online at www.sciencedirect.com

ScienceDirect

Dyes and Pigments 77 (2008) 81−85

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

Polyvinyl alcohol as an aftertreatment. Part 1: Initial studies

S.M. Burkinshaw*, N. Kumar

The University of Leeds, Leeds LS2 9JT, UK

Received 1 July 2006; accepted 14 March 2007
Available online 8 April 2007

Abstract

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. PVA imparted a yellow colouration to undyed fabric but the extent of this shade change was much lower than that imparted by the same concentration of tannic acid.

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

1. Introduction

Although nylon, the first commercially available, wholly synthetic fibre, continues to enjoy widespread textile usage, the relatively low wet fastness of acid dyes on the substrate necessitates the use of an aftertreatment in order to secure satisfactory wet fastness levels. In the classical, two-stage, *full backtan* aftertreatment that comprises tannic acid and potassium antimony tartrate (tartar emetic), the high M_r gallotannin is adsorbed onto the dyed nylon via protonated amino end groups in the nylon fibre and sequential treatment of the tanned dyeing with potassium antimony tartrate results in the formation of an insoluble metal complex *in situ* at the surface of the dyed nylon which physically resists diffusion of dye from the dyed fabric during washing. In view of the marked toxicity of tartar emetic, previous research [1] showed that a 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. The optimum application conditions for the tannic acid/enzyme system were determined [2] and 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, was demonstrated [3]. Subsequently, a single-stage aftertreatment that involved the application of tannic acid was found to be very effective in improving the fastness of 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 [4].

Despite the effectiveness of the new tannic acid and the tannic acid/enzyme systems in improving the wash fastness of acid dyes nylon 6,6, as tannic acid imparts a yellowish brown hue to dyeings [5], it was decided to determine if the high M_r gallotannin could be replaced by a low cost, readily available, water-soluble polymer; in this context, polyvinyl alcohol (PVA) was selected for use. This part of the paper concerns the use of PVA as an aftertreatment of nylon 6,6 which had been dyed with three commercial acid dyes; as the single-stage aftertreatment with tannic acid had been found [4] to be less effective at wash temperatures above 40 °C, it was decided to undertake this initial part of the study using a wash temperature of 50 °C.

2. Experimental

2.1. Materials

Knitted nylon 6.6 fabric of 78f/68 dtex per filament and amino end group (AEG) content 45 meq kg^{-1} was kindly

---

* Corresponding author. Tel.: +44 113 233 3722; fax: +44 113 233 3740.
E-mail address: s.m.burkinshaw@leeds.ac.uk (S.M. Burkinshaw).

0143-7208/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2007.03.008

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

supplied by DuPont (UK). The fabric was scoured before use by treatment in a solution of 3 g dm^{-3} *Sandozin NIN* (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. The three commercial acid dyes used (Table 1), which were kindly supplied by Yorkshire Chemicals, were selected on the basis that they displayed moderate fastness on nylon 6,6 to the repeated washing protocol employed in this work at the 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). A commercial sample of *Textan 3* (tannic acid) was kindly provided by OmniChem-Ajinomoto and *Celvol 540* (87–89% hydrolysed PVA) was obtained from Celanese chemical; all other chemicals were laboratory grade reagents.

2.2. Dyeing

The dyes were applied using the equipment described earlier [1] using the method shown in Fig. 1; the pH was adjusted using McIlvaine buffer [6]. 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. 2; 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. Treatment with nylon 6,6 with tannic acid and PVA

Samples of nylon 6,6 were treated with 1.5, 5 and 10 g l^{-1} tannic acid (at pH 6) or PVA (at pH 4) using the method shown in Fig. 3, the application pH having been adjusted using McIlvaine buffer. The treated samples were removed, rinsed thoroughly in tap water and allowed to air dry.

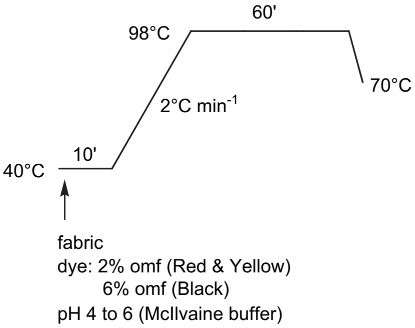

Fig 1. Dyeing method.

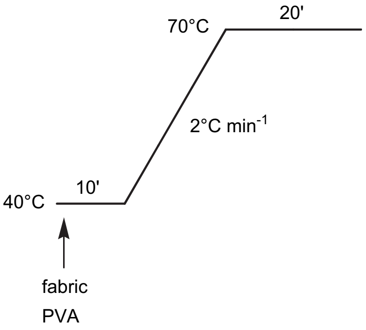

Fig 2. After treatment method.

2.5. Colour measurement

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

2.6. Wash fastness

The wash fastness of the dyed samples was determined using the ISO CO6/B2S (50 °C) test method [7] used but was 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

As mentioned, the three dyes were selected for use because each displayed moderate fastness to washing on the knitted nylon 6,6 fabric substrate used in this work. This is clearly evident from the colorimetric data presented in Table 2 and the reduction in colour strength (*K*/*S* values) which the dyeings underwent (Fig. 4) as a result of having been subjected to five repeated washes; the shade changes observed for the three dyes can be attributable to loss of dye from the dyeings rather

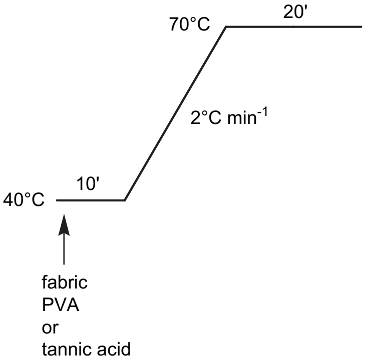

Fig 3. Treatment method.

Table 2
Colorimetric data for untreated dyeings

Dye	No. of washes	L^*	a^*	b^*	C^*	h^0
Red K-2G	0	39.8	47.5	20.2	51.6	23.0
	5	40.4	47.7	20.6	51.9	23.4
Yellow C-3RL	0	67.4	32.9	78.1	84.7	67.1
	5	69.6	28.9	73.7	79.2	68.5
Black C-DPL	0	20.9	0.2	−4.5	4.5	273.6
	5	22.1	0.1	−4.8	4.8	271.9

than to changes in the colour of the dyeings. Table 3 shows the extent of staining, by vagrant dye, of multifibre strip as a result of the five, consecutive wash tests. The lower extent of staining observed for the adjacent acrylic, polyester and cotton components can be attributed to the inherent low substantivity of the three acid dyes towards such fibre types while the 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 results obtained (Tables 2 and 3 and Fig. 4) show that the yellow dye displayed quite poor fastness to repeated washing at 50 °C.

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 antimony tartrate and because it can impair both the handle and light fastness of dyeings as well as impart a shade change to dyeings [5]. As a possible alternative to tannic acid, PVA was chosen in view of the fact that it is a low cost, water-soluble polymer that has excellent film forming, emulsifying and adhesive properties and enjoys manifold applications in paints, paper, plastics, packaging and construction. In particular, its use as a textile size, for a variety of different fibres including polyamides, is very well known.

Table 4 shows the colorimetric data obtained for dyeings which had been aftertreated with 1.5 $g\,l^{-1}$ PVA. In terms of the effect of the PVA aftertreatment on the colour of the dyeings prior to wash testing, a comparison of the colorimetric data in Table 4 with that of the untreated dyeings prior to wash testing (Table 2) reveals that aftertreatment reduced the lightness and chroma of the red and, in particular, of the yellow dyeing but had little effect on the colour of the black dyeing. While this was also observed when higher concentrations of PVA had been used to aftertreat the dyeings (Tables 5 and 6), the extent of the shade change did not increase significantly with increasing amount of PVA used. As mentioned, it is well known that tannic acid imparts a yellowish/brown hue to dyeings [5]; this is exemplified by the results displayed in Table 7, which show the colorimetric data for undyed nylon 6,6 fabric which had been treated with 1.5, 5 and 10 $g\,l^{-1}$ tannic acid. The brown colouration of the white fabric imparted by the gallotannin is clearly evidenced by the higher b^* values of the treated samples; it is also clear that tannic acid treatment reduced, quite markedly, the lightness (L^*) of the fabric; Table 7 shows that the

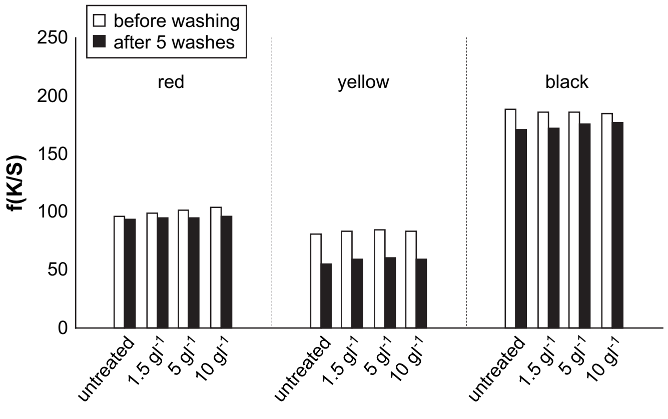

Fig 4. Colour strength of dyeings before and after five repeated washes.

Table 3
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	5	1	5	5
	5	5	5	5	2	5	5
Yellow C-3RL	1	2	5	3/4	1/2	5	1/2
	5	3	5	4/5	2/3	5	2/3
Black C-DPL	1	5	2/3	5	1/2	5	5
	5	5	3/4	5	2	5	5

Table 4
Colorimetric data for dyeings aftertreated with 1.5 $g\,l^{-1}$ PVA

Dye	No. of washes	L^*	a^*	b^*	C^*	h^0
Red K-2G	0	39.2	47.5	21.0	51.9	23.8
	5	39.5	47.3	21.0	51.8	23.9
Yellow C-3RL	0	65.9	32.0	76.1	82.5	67.1
	5	68.1	28.1	72.2	77.5	68.7
Black C-DPL	0	21.1	0.3	−4.9	4.9	274.1
	5	22.0	0.2	−4.9	4.9	273.2

Table 5
Colorimetric data for dyeings aftertreated with 5 $g\,l^{-1}$ PVA

Dye	No. of washes	L^*	a^*	b^*	C^*	h^0
Red K-2G	0	40.0	47.9	21.1	52.4	23.8
	5	40.8	48.0	21.1	52.4	23.6
Yellow C-3RL	0	66.5	33.1	78	84.7	67.0
	5	68.5	29.2	73.5	79.1	68.3
Black C-DPL	0	20.8	0.2	−4.9	4.9	273.3
	5	21.6	0.2	−5.0	5.1	272.8

Table 6
Colorimetric data for dyeings aftertreated with 10 $g\,l^{-1}$ PVA

Dye	No. of washes	L^*	a^*	b^*	C^*	h^0
Red K-2G	0	39.1	47.3	20.7	51.6	23.6
	5	39.4	46.7	20.3	51.0	23.5
Yellow C-3RL	0	66.9	33.0	78.0	84.7	67.1
	5	69.2	28.8	73.7	79.1	68.6
Black C-DPL	0	21.2	0.2	−5.0	5.0	273.1
	5	21.6	0.2	−4.9	4.9	273.1

Table 7
Colorimetric data for nylon 6,6 treated with tannic acid and PVA

Treatment	Conc./g l^{-1}	L^*	a^*	b^*	C^*	h^0	K/S
Nil	–	96.3	−0.3	2.9	2.9	84.1	0.02
Tannic acid	1.5	92.6	0.4	6.2	6.2	86.3	0.07
	5	90.8	0.3	9.4	9.4	88.2	0.2
	10	86.7	1.1	16.2	16.2	86.1	0.2
PVA	1.5	95.0	−0.8	1.7	1.8	115.2	0.02
	5	93.3	−1.4	1.4	1.9	135.1	0.03
	10	93.3	−1.5	1.6	2.2	136.8	0.03

extent of this discolouration increased with increasing concentration of tannic acid applied. Treatment of the undyed nylon fabric with the same concentrations of PVA imparted a yellow colouration to the undyed fabric; the extent of this shade change was lower than that of tannic acid, as shown by the smaller reductions in L^* values and smaller changes in b^* values (Table 7). The nature and magnitude of the shade changes imparted by treatment of the undyed nylon substrate with the two polymers is depicted in the a^*–b^* plot (Fig. 5).

In the context of the effect of the PVA aftertreatment on the fastness of the dyeings to repeated wash testing, a comparison of the colorimetric data (Table 2) and the shade changes obtained for the dyeings which had not been aftertreated (Table 3) with those observed for dyeings which had been aftertreated with PVA (Tables 4–6 and 8–10) shows that application of the polymer improved the fastness of the three dyes and that the extent of staining of adjacent materials decreased with increasing amount of PVA used. A measure of the extent to which aftertreatment with PVA improved the fastness of the dyeings to five repeated washes is provided by the ΔE values between dyeings before and after submission to repeated washes (Table 11); clearly, the largest reduction in ΔE was observed for the yellow dyeings, which was not unexpected in view of the quite poor fastness of this particular dye.

It is believed that tannic acid is adsorbed onto protonated amino end groups in the nylon 6,6 substrate via ion–ion forces; the substantivity of PVA towards nylon 6,6 can, initially, be attributed to H-bonding between the hydroxy groups in the polymer and appropriate polar groups (e.g. NH_2, CONH) in the polyamide substrate. Further work is being carried out to determine the precise nature of the adsorption of PVA on nylon 6,6 which has been dyed with acid dyes.

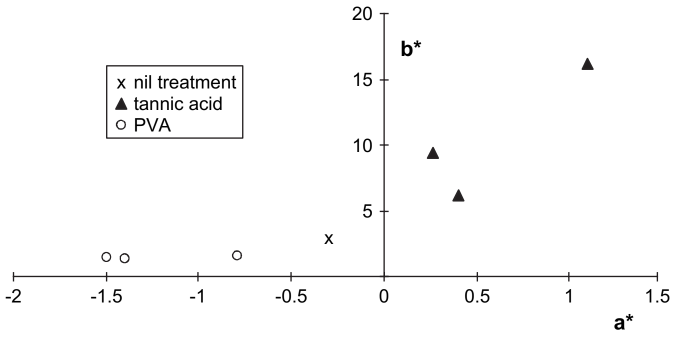

Fig 5. a^*–b^* Diagram for treated and untreated nylon substrate.

Table 8
Staining of adjacent multifibre strip achieved for dyeings aftertreated with 1.5 g l^{-1} PVA

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

Table 9
Staining of adjacent multifibre strip achieved for dyeings aftertreated with 5 g l^{-1} PVA

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

Table 10
Staining of adjacent multifibre strip achieved for dyeings aftertreated with 10 g l^{-1} PVA

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

Table 11
CIE $L^*a^*b^*$ ΔE between dyeings before and after five repeated wash tests

Aftertreatment	*Red K-2G*	*Yellow C-3RL*	*Black C-DPL*
Nil	2.1	6.0	1.1
1.5 g l^{-1} PVA	0.9	4.8	0.9
5 g l^{-1} PVA	0.8	5.4	1.0
10 g l^{-1} PVA	0.7	5.4	0.5

4. Conclusions

While treatment of undyed nylon fabric with PVA imparted a yellow colouration to the substrate, the extent of this shade change was much lower than that imparted by similar concentrations of tannic acid. PVA improved the fastness of the three dyes to repeated washing, the extent of staining of adjacent materials decreasing with increasing amount of PVA used. Although aftertreatment with PVA reduced the lightness and chroma of the red and, in particular, the yellow dyeings, it had little effect on the colour of black dyeings; the magnitude of this shade change did not increase significantly with increasing amounts of PVA applied.

References

[1] Burkinshaw SM, Bahojb-Allafan B. The development of a metal-free, tannic acid-based aftertreatment for nylon 6,6 dyed with acid dyes − part 1: initial studies. Dyes and Pigments 2003;58(3):205−18.

[2] Burkinshaw SM, Bahojb-Allafan B. The development of a metal-free, tannic acid-based aftertreatment for nylon 6,6 dyed with acid dyes − part 2: further studies. Dyes and Pigments 2003;59(1):71−97.

[3] Burkinshaw SM, Bahojb-Allafan B. The development of a metal-free, tannic acid-based aftertreatment for nylon 6,6 dyed with acid dyes − part 3: different enzymes. Dyes and Pigments 2003;60:91−102.

[4] Burkinshaw SM, Bahojb-Allafan B. The development of a metal-free, tannic acid-based aftertreatment for nylon 6,6 dyed with acid dyes − part 4: tannic acid. Dyes and Pigments 2004;62:159−72.

[5] Burkinshaw SM. Chemical principles of synthetic fibre dyeing. London: Blackie; 1995.

[6] Vogel A. A textbook of quantitative inorganic analysis. London: Longmans; 1944.

[7] Standard methods for the determination of the colour fastness of textiles and leather. 5th ed. Society of Dyers and Colourists; 1990.