Available online at www.sciencedirect.com

ScienceDirect

Dyes and Pigments 79 (2008) 48–53

www.elsevier.com/locate/dyepig

A tannic acid/ferrous sulfate aftertreatment for dyed nylon 6,6

S.M. Burkinshaw*, N. Kumar

The University of Leeds, Leeds LS2 9JT, UK

Received 6 November 2007; received in revised form 9 January 2008; accepted 10 January 2008
Available online 18 January 2008

Abstract

Both a single-stage and a two-stage aftertreatment using tannic acid in conjunction with ferrous sulfate improved the fastness to repeated washing at 60 °C of two acid dyes on nylon 6,6 most likely via the formation of a low solubility, large molecular size, iron tannate complex within the periphery of the dyed fibre. The iron tannate complex imparted a slight greyish-brown colour to dyeings, although this did not affect the $\lambda_{\max}$ of the dyeings and also increased the colour strength of the dyeings. Neither the single-stage nor the two-stage aftertreatment affected the light fastness of dyeings but both aftertreatments reduced rub fastness.

Keywords: Nylon 6,6; Acid dyes; Aftertreatment; Tannic acid; Ferrous sulfate; Repeated wash fastness

1. Introduction

Vegetable tannin extracts contain a variety of amorphous materials that include large M_r polyphenolic *tannins*, such as the hydrolysable gallotannin, *tannic acid* and less-complex, *non-tannins*, such as flavones and gums. As tannins are large M_r, water-soluble phenolic compounds, they undergo typical phenolic reactions, notably the chelation of metal ions, in which context, tannins have been used on textiles for several hundreds of years, as exemplified by the dyeing of cotton and silk with dyewoods, in which the tannin 'fixed' the metal salt (e.g. $CuSO_4$) that was employed as a mordant for the dye. Perkin used tannins as mordants to increase the uptake of cationic dyes (e.g. *Mauveine*) onto cotton by firstly applying tannin to the cotton and then 'fixing' the tannin by the application of a metal (Fe, Al, Cu, Pb or Sn) salt [1]. Contemporary textile uses for natural tannins include the application of tannic acid in stain resistant treatments for nylon carpets and aftertreatments to improve the wet fastness of dyeings on nylon fibres. In the latter context, as many acid dyes display low/moderate wet fastness on nylon fibres, dyeings are often aftertreated with tannic acid in conjunction with a complexing agent, traditionally a metal salt, such as potassium antimony tartrate, in the classical 'full backtan aftertreatment' [1] in which the gallotannin is first applied to the dyed material and is 'fixed' *in situ* by the subsequent application of the metal salt. Owing to the toxicity of antimony compounds, alternative complexing agents have been investigated, including, recently reported, tin salts [2] and enzymes [3]. The combination of tannins with iron salts has enjoyed varied applications over many centuries, such as the use of tannic acid and iron sulfate in the preparation of iron gall inks, the conservation of rusted artefacts using tannic acid to convert the iron oxide in rust to the stable, blue/black coloured iron tannate and, from a dyeing perspective, the use of *copperas* ($FeSO_4 \cdot 7H_2O$) in conjunction with tannins to produce greyish-brown shades on cotton, silk and wool, which has been practised since medieval times.

This paper concerns the feasibility of improving both the wet fastness and depth of shade of black acid dyes on nylon 6,6 using an aftertreatment comprising tannic acid and iron(II) sulfate.

---

* Corresponding author.
E-mail address: s.m.burkinshaw@leeds.ac.uk (S.M. Burkinshaw).

0143-7208/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2008.01.004

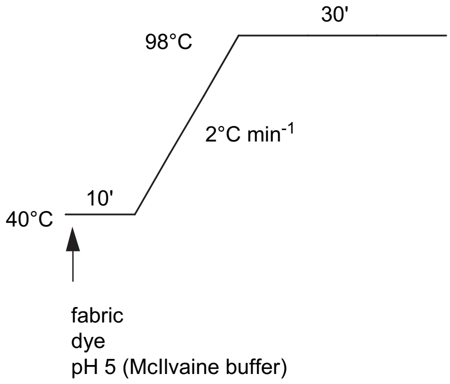

Fig. 1. Dyeing method.

2. Experimental

2.1. Materials

The scoured, knitted nylon 6,6 fabric described earlier [4], which was kindly supplied by *Dupont(UK)*, was used. Commercial samples of *Nylanthrene Black C-DPL* (C.I. Acid Black 172; Yorkshire Colours) and *Nylosan Black N-WL* (no C.I. Generic Name ascribed; Clariant); tannic acid and ferrous sulfate were obtained from Aldrich. All other chemicals were laboratory grade reagents.

2.2. Dyeing

This was carried out in sealed, stainless steel dye pots of 300 cm^3 capacity, housed in a Roaches *Pyrotec S* infrared, laboratory-scale dyeing machine using a liquor ratio of 20:1. The dyeing method used is shown in Fig. 1; the pH was adjusted using McIlvaine buffer. At the end of dyeing, the dyed sample was removed and rinsed in tap water for 10 min.

2.3. Aftertreatment

Dyeings were aftertreated with 3% omf tannic acid and 3% omf ferrrous sulfate using both a two-stage (Fig. 2) and a single-stage (Fig. 3) method. The aftertreated samples were rinsed in cold water and allowed to dry in the open air.

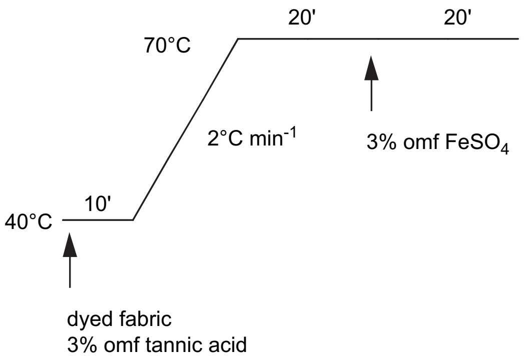

Fig. 2. Two-stage method.

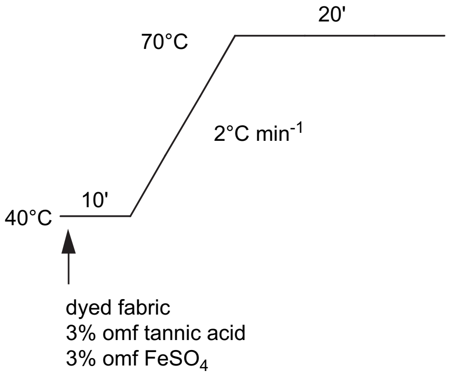

Fig. 3. Single-stage method.

2.4. Colour measurement

All measurements were carried out using an *X-rite* spectrophotometer interfaced to a PC using D_{65} illumination, 10° standard observer with specular component excluded and UV component included. Each fabric was folded once to give two thicknesses and an average of four readings was taken each time.

2.5. Wash fastness

Wash fastness tests were conducted according to the standard ISO 105:C06/C2 [5] method which 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.

2.6. Light fastness

The fastness of the dyeings to light was determined using the ISO BO2 method [5].

Table 1
Colourimetric data for untreated dyeings

Dye	% omf	No. of washes	L^*	a^*	b^*	C^*	h^0	λ_{max}
Nylanthrene Black C-DPL	0.5	0	48.9	−0.4	−6.8	6.8	266.2	580
		5	51.4	−0.3	−6.6	6.6	266.7	580
	1	0	39.6	0.1	−6.5	6.5	269.5	580
		5	39.4	0.0	−6.5	6.5	270.4	580
	2	0	25.5	0.2	−5.5	5.5	272.3	580
		5	26.2	0.2	−5.5	5.5	272.7	580
	4	0	19.1	0.4	−4.4	4.5	275.1	580
		5	19.3	0.4	−4.5	4.5	275.2	580
Nylosan N-WL	2	0	26.3	−2.4	−4.7	5.3	242.8	580
		5	26.1	−2.5	−5.3	5.8	244.6	580
	4	0	19.1	−1.3	−4.2	4.4	252.2	580
		5	20.0	−1.5	−4.6	4.9	252.1	580

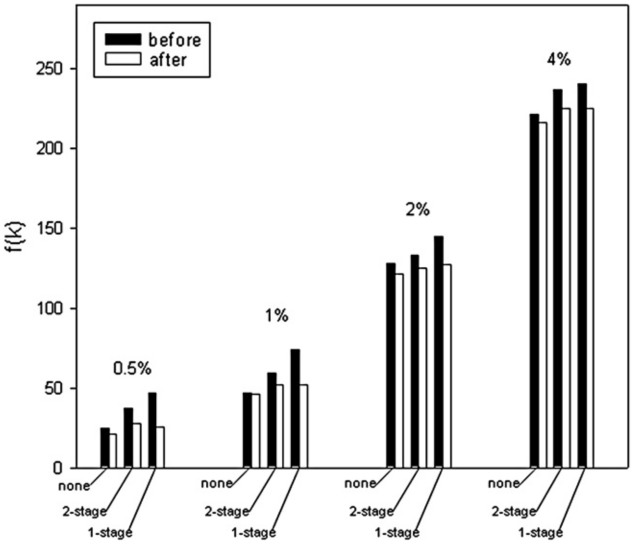

Fig. 4. Effect of colour treatment on colour strengths of *Nylanthrene Black C-DPL* before and after five repeated washes.

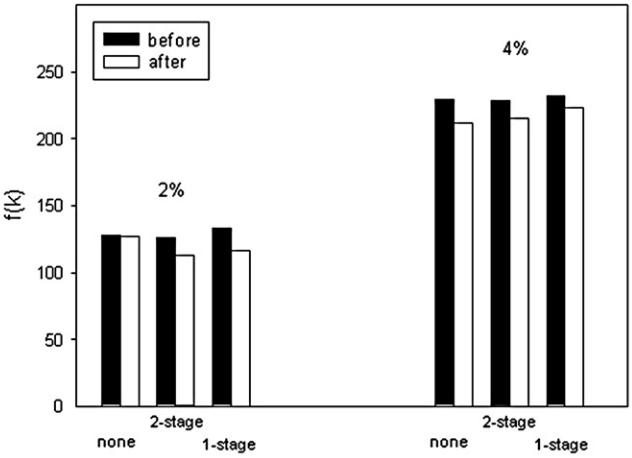

Fig. 5. Effect of colour treatment on colour strengths of *Nylanthrene Black N-WL* before and after five repeated washes.

2.7. Rub fastness

Both the dry and wet rub fastness of the dyed samples was determined using the ISO 105: X12 test method [5].

3. Results and discussion

Although black shades are popular on virtually every type of fibre, the attainment of such dyeings on nylon 6,6 can be problematic owing to the well-known propensity of all types of dye, particularly non-metallised acid dyes, to display only low/moderate fastness to wet treatments on polyamide, especially in deep shades [1]. The two acid dyes used herein were selected on the basis that they provided dyeings of only moderate wet fastness.

Table 1 shows the colourimetric data obtained for 0.5%, 1%, 2% and 4% omf dyeings of *Nylanthrene Black C-DPL* both before and after the five, consecutive wash fastness tests at 60 °C, which had not been aftertreated. It is apparent that for each of the four concentrations of dye used, repeated washing reduced the depth of shade, as evidenced by an increase in lightness ($L*$ value) but the colour (hue, h^0 and chroma, $C*$) of the dyeings was little affected; the λ_{max} of the dyeings was unchanged by repeated washing. The corresponding $f(K/S)$ values for the non-aftertreated dyeings, before and after repeated washing, are shown in Fig. 4; the extent to which subjecting each of the dyeings to five repeated wash tests at 60 °C reduced colour strength is clear. Table 1 also shows the colourimetric data secured for untreated, 2% and 4% omf dyeings of *Nylosan Black N-WL* before and after five repeated wash fastness tests at 60 °C; the corresponding colour strength values are displayed in Fig. 5. As observed previously for *Nylanthrene Black C-DPL*, each dyeing underwent a reduction in depth of shade, as evidenced by an increase in lightness and colour strength, although the colour of the dyeings was little affected by repeated wash testing; the λ_{max} of the dyeings was unchanged.

The wash fastness of the 0.5%, 1%, 2% and 4% omf dyeings of *Nylanthrene Black C-DPL* as well as 2% and 4% omf dyeings of *Nylosan Black N-WL* to repeated fastness testing at 60 °C are shown in Table 2. The extent of the shade change that the dyeings underwent is evident; the finding that shade change increased slightly with increasing amount

Table 2
Wash fastness achieved for untreated dyeings

Dye	% omf	No. of washes	Change in shade	Wool	Acrylic	Polyester	Nylon 6,6	Cotton	2^0 Acetate
Nylanthrene Black C-DPL	0.5	1	4/5	5	5	5	4/5	5	4/5
		5	3/4	5	5	5	5	5	5
	1	1	4/5	5	5	5	4	5	4
		5	4	5	5	5	4/5	5	5
	2	1	4/5	5	5	5	3	5	4
		5	3/4	5	5	5	4	5	5
	4	1	4	5	5	5	2/3	5	4
		5	3/4	5	5	5	4	5	5
Nylosan N-WL	2	1	4/5	5	5	5	3/4	5	4/5
		5	3/4	5	5	5	4	5	5
	4	1	4	5	5	5	2	5	4
		5	3/4	5	5	5	3/4	5	5

Table 3
Wash fastness achieved using two-stage aftertreatment

Dye	% omf	No. of washes	Change in shade	Wool	Acrylic	Polyester	Nylon 6,6	Cotton	2^0 Acetate
Nylanthrene Black C-DPL	0.5	1	4	5	5	5	5	5	4/5
		5	3	5	5	5	5	5	5
	1	1	4/5	5	5	5	4/5	5	4
		5	4	5	5	5	5	5	5
	2	1	5	5	5	5	4	5	4/5
		5	4/5	5	5	5	4/5	5	5
	4	1	5	5	5	5	3/4	5	4
		5	4/5	5	5	5	4/5	5	5
Nylosan N-WL	2	1	4/5	5	5	5	4	5	5
		5	4	5	5	5	4/5	5	5
	4	1	5	5	5	5	3	5	5
		5	4/5	5	5	5	3/4	5	5

of dye applied was expected and reflects the moderate fastness properties of the two dyes used. While the magnitude of any shade change which a dyed sample undergoes during washing contributes to the assessment of wash fastness, the extent of any staining of adjacent materials by vagrant dye during washing is an equally important element of wash fastness. Table 2 shows the extent of staining of multifibre strip obtained as a result of the five, consecutive wash tests. The low level of staining achieved in the cases of the adjacent acrylic, wool, polyester, 2^0 acetate and cotton components was anticipated in view of the inherent low substantivity of the two acid dyes towards such types of fibre; also expected, in the context of the substanitivity of the two dyes used, was the very high extent of staining obtained for the adjacent nylon 6,6 fibre. Table 2 reveals that 2% and 4% omf dyeings of *Nylosan Black N-WL* displayed lower fastness to repeated washings than did 2% and 4% omf dyeings of *Nylanthrene Black C-DPL* (Table 2), despite the dyeings being of similar colour strength at each of the two respective depths of shade (Figs. 4 and 5). This can be attributed to *Nylanthrene Black C-DPL* being a 1:2 Cr metal-complex dye whereas *Nylosan Black N-WL* is a mixture of metal-complex and non-metallised acid dyes [6] and the fact that non-metallised acid dyes exhibit lower wet fastness on nylon than their metallised counterparts.

Aftertreatment using the two-stage, tannic acid–ferrous sulfate process improved the fastness of each of the two dyes at each of the various depths of shade employed, as shown by a comparison of the data in Tables 2 and 3, in terms of both shade change and, more importantly, the extent of staining of the adjacent nylon 6,6 component of the multifibre strip. In order to explain the observed improvement in wash fastness imparted by the tannic acid/ferrous sulfate aftertreatment, an explanation can be proposed that is analogous to that which describes the manner in which potassium antimony tartrate [1] is believed to interact with tannic acid in the full backtan aftertreatment. In the classical, two-stage, full backtan, the tannic acid component behaves as a high M_r anionic, polyphenolic compound which binds to the protonated amino end groups in the nylon fibre; other forces of interaction, such as H-bonding and ion–dipole forces also will contribute towards tannic acid–fibre substantivity. Subsequent treatment with potassium antimony tartrate results in the formation of a low solubility, potassium antimony tannate complex situated at the surface of the dyed substrate which provides a physical barrier to the diffusion of dye from the dyed fabric during washing [1]. The purpose of the metal salt (potassium antimony tartrate) in the traditional full backtan aftertreatment is to form a low solubility complex with the adsorbed tannic acid *in situ* at the surface of the dyed nylon 6,6. In the case of the tannic acid/ferrous sulfate aftertreatment used herein, it seems reasonable to suggest that the iron salt replaced the potassium antimony tartrate as the complexing metal, resulting in the formation of a low solubility, iron tannate complex at the surface of the dyed substrate.

Table 4
Colourimetric data achieved using two-stage aftertreatment

Dye	% omf	No. of washes	L^*	a^*	b^*	C^*	h^0	λ_{max}
Nylanthrene Black C-DPL	0.5	0	43.2	0.4	−6.1	6.1	274.5	580
		5	47.8	−0.3	−4.1	4.2	264.6	580
	1	0	36.2	0.4	−6.0	6.0	273.9	580
		5	38.3	0.0	−4.7	4.7	269.0	480
	2	0	25.1	0.5	−5.3	5.4	275.3	580
		5	25.9	0.2	−4.8	4.8	272.6	580
	4	0	18.4	0.4	−4.1	4.2	276.0	580
		5	19.0	0.4	−4.1	4.1	275.7	580
Nylosan N-WL	2	0	26.3	−2.1	−4.7	5.1	247.3	580
		5	27.8	−2.6	−4.7	5.4	241.0	580
	4	0	19.2	−1.1	−4.0	4.2	254.1	580
		5	19.8	−1.5	−4.6	4.8	251.8	580

The improved fastness imparted by the two-stage, tannic acid–ferrous sulfate process to the two dyes was of particular significance in the case of *Nylanthrene Black C-DPL* dyeings, as the aftertreatment also increased the depth of shade of each of the four dyeings used, as evidenced by the higher $f(K/S)$ values shown in Fig. 4. In this context, a comparison of the colourimetric data obtained for the untreated dyeings (Table 1)

Table 5
Colourimetric data for 3% omf tannic acid + 3% omf $FeSO_4$ aftertreatments applied to undyed nylon 6,6

Aftertreatment	L^*	a^*	b^*	C^*	h^0	$f(K/S)$
Single-stage	59.3	1.7	−7.6	7.8	282.9	13.7
Two-stage	58.4	2.3	−5.5	6.0	293.2	14.6

Table 6
Wash fastness achieved using single-stage aftertreatment

Dye	% omf	No. of washes	Change in shade	Wool	Acrylic	Polyester	Nylon 6,6	Cotton	2^0 Acetate
Nylanthrene Black C-DPL	0.5	1	3/4	5	5	5	5	5	4/5
		5	2/3	5	5	5	5	5	5
	1	1	4	5	5	5	4/5	5	4/5
		5	3	5	5	5	5	5	5
	2	1	4/5	5	5	5	4	5	4/5
		5	4	5	5	5	4/5	5	5
	4	1	5	5	5	5	3	4/5	4/5
		5	4/5	5	5	5	4/5	5	5
Nylosan N-WL	2	1	4/5	5	5	5	3/4	5	5
		5	4	5	5	5	4	5	5
	4	1	5	5	5	5	2/3	5	4/5
		5	4/5	5	5	5	3	5	5

and those which had been aftertreated using the two-stage process (Table 4) reveals that, in the case of *Nylanthrene Black C-DPL*, aftertreatment imparted a slight redness to the dyeings and also reduced the chroma (purity) of the dyeings marginally; however, the extent of this colour change was small, as shown by the fact that the $\lambda_{\max}$ of the dyeings was unchanged by aftertreatment. The enhanced colour strength obtained for the dyeings of *Nylanthrene Black C-DPL* can be attributed to the formation of a dark-coloured complex between the tannic acid and ferrous sulfate. As mentioned, the combination of tannins with iron salts is an ancient practice, as demonstrated by the production of greyish-brown shades on cotton, silk and wool using *copperas* ($FeSO_4 \cdot 7H_2O$) in conjunction with tannins. Table 5 shows both the colour and colour strength obtained when both the two-stage and the single-stage aftertreatments had been applied to undyed nylon 6,6 fabric. It is clear that greyish-brown shades were produced and that there was a small difference between the two aftertreatments in terms of colour strength, with the two-stage process having producing a slightly more reddish hue. In the case of *Nylosan Black N-WL*, comparison of the results in Tables 1 and 4 reveals that the two-stage aftertreatment had little effect on the colour of the dyeings whilst Fig. 5 shows that aftertreatment did not increase the colour strength of the dyeings. The latter finding differs from that obtained for *Nylanthrene Black C-DPL* for which improved wash fastness was accompanied by an increase in colour strength of the dyeings.

The single-stage aftertreatment method (Fig. 3) was devised as an attempt to shorten the two-stage aftertreartment process. A comparison of the data in Tables 1 and 6 shows that the single-stage, tannic acid–ferrous sulfate process improved the wash fastness of both dyes at each of the various depths of shade employed, in terms of shade change and staining of the adjacent nylon 6,6 component of the multifibre strip. This suggests that the admixture of the gallotannin and iron salt resulted in the formation of a low solubility, iron tannate complex which was adsorbed onto the dyed substrate. This is further supported by the observation (Figs. 4 and 5) that the single-stage aftertreatment enhanced the colour strength of the dyeings, especially in the case of *Nylanthrene Black C-DPL*. A comparison of the colourimetric data obtained for the single-stage aftertreatment (Table 7) with those for the untreated dyeings (Table 1) reveals that aftertreatment imparted a slight redness to the dyeings and also reduced the chroma of the dyeings marginally; however, the extent of this colour change was small, as demonstrated by the fact that the $\lambda_{\max}$ of the dyeings was unchanged by aftertreatment. Further comparison of the colourimetric data secured for the single-stage aftertreatment (Table 7) with those obtained for the two-stage aftertreated dyeings (Table 4) shows that the colour imparted

Table 7
Colourimetric data achieved using single-stage aftertreatment

Dye	% omf	No. of washes	$f(K/S)$	L^*	a^*	b^*	C^*	h^0	$\lambda_{\max}$
Nylanthrene Black C-DPL	0.5	0	46.9	40.1	0.5	−7.0	7.0	274.6	580
		5	26.2	48.5	−0.3	−4.4	4.4	265.6	580
	1	0	73.6	33.2	0.6	−6.7	6.7	275.1	580
		5	51.5	38.3	0	−5.2	5.2	269.9	580
	2	0	145.1	24.1	0.3	−5.5	5.6	273.6	580
		5	127.0	25.7	0.1	−5.1	5.1	272.1	580
	4	0	240.6	18.3	0.4	−4.1	4.1	276.1	580
		5	225.0	19.0	0.3	−4.2	4.2	275.1	580
Nylosan N-WL	2	0	133.1	25.6	−2.1	−4.6	5	246.4	580
		5	116.1	27.5	−2.6	−4.7	5.4	241.2	580
	4	0	232.2	19.0	−1.2	−4.1	4.3	253.9	580
		5	223.5	19.4	−1.5	−4.6	4.9	251.6	580

Table 8
Light fastness achieved for *Nylanthrene Black C-DPL*

Dye/% omf	Treatment	Rating
0.5	None	5
	Two-stage	5
	Single-stage	5
1	None	5
	Two-stage	5
	Single-stage	5
2	None	5
	Two-stage	5
	Single-stage	5
4	None	5
	Two-stage	5
	Single-stage	5

Table 9
Rub fastness results for *Nylanthrene Black C-DPL*

Dye/% omf	Treatment	Dry		Wet	
		Change in shade	Staining	Change in shade	Staining
2	None	4	5	4	5
	Two-stage	5	4/5	4/5	3/4
	Single-stage	4/5	3/4	3	2/3
4	None	4/5	5	4/5	5
	Two-stage	4/5	4/5	4	4/5
	Single-stage	4	3/4	4/5	3

to the dyeings by the two different aftertreatments was very similar.

The finding that the wash fastness improvement imparted to dyeings *Nylanthrene Black C-DPL* by both the single-stage and two-stage aftertreatments was accompanied by an increase in colour strength, whereas no such increase in $f(K)$ was obtained for *Nylosan Black N-WL* can be attributed to the former dye being a homogenous 1:2 metal–complex compared to *Nylosan Black N-WL* being a mixture [6] of a metal-complex dye and acid dye.

Table 8 shows that neither the single-stage nor the two-stage aftertreatment affected the light fastness of *Nylanthrene Black C-DPL* dyeings whereas both aftertreatments reduced rub fastness (Table 9). The finding that the rub fastness of dyeings which had been aftertreated using the single-stage process were generally lower than those obtained for dyeings which had received the two-stage aftertreatment (Table 9) can be attributed to a difference in the extent to which the low aqueous solubility iron tannate complexes were able to diffuse within the dyed fibre. In the case of the single-stage process, the large molecular size complex that was formed within the application liquor can be anticipated to display very low diffusional behaviour and, therefore, will have deposited mostly at the periphery of the dyed fibre, resulting in low rub fastness. In contrast, the complex that was generated *in situ* within the fibre, by the sequential application of tannic acid and ferrous sulfate during the two-stage process, will have been able to diffuse to a greater extent within the fibre resulting in higher rub fastness.

4. Conclusions

The fastness to repeated washings at 60 °C of two acid dyes on nylon 6,6 was improved by the application of tannic acid in conjunction with ferrous sulfate, using both a single-stage and a two-stage aftertreatment process. It is proposed that a low water solubility, large molecular size, iron tannate complex was formed that occupied peripheral regions of the dyed fibre thereby resisting the desorption of dye from the dyed substrate during repeated wash testing. The iron tannate complex imparted a slight greyish-brown colour to dyeings, although this did not affect the λ_{max} of the dyeings and also increased the colour strength of the dyeings. Whilst neither the single-stage nor the two-stage aftertreatment affected the light fastness of dyeings, both aftertreatments reduced rub fastness.

References

[1] Burkinshaw SM. Chemical principles of synthetic fibre dyeing. Glasgow: Chapman and Hall; 1995. 223pp.

[2] Burkinshaw SM, Son Y-A. The aftertreatment of acid dyes on nylon 6,6 fibres. Part 1 – 1:2 Pre-metallised acid dyes. Dyes and Pigments 2001;48: 57–69.

[3] Bahojb-Allafan B, Burkinshaw SM. 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;60:102.

[4] Bahojb-Allafan B, Burkinshaw SM. 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;58:205–18.

[5] Methods of test for colour fastness of textiles and leather. 5th ed. Bradford: Society of Dyers and Colourists; 1990.

[6] Nikolaides N, personal communication.