ELSEVIER

Dyes and Pigments 47 (2000) 169–175

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

Theoretical and practical aspects of the *Tactel Coloursafe* reactive dyeing system for modified nylon 6,6

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Dedicated to Dr A.T. Peters, whose appreciation of dye chemistry was manifest in the clearest of undergraduate lectures and whose fascination with dye chemistry proved infectious to every one of us (SMB).

Abstract

Three, commercial *Stanalan* reactive dyes were applied to *Tactel Coloursafe* knitted fabric at different pH values and the extents of dye exhaustion and fixation were determined. The three dyes displayed similar characteristics in terms of dye exhaustion and dye fixation. High exhaustion was achieved and this reached a maximum in the region pH 5–6; dye fixation (%*F*) increased with increasing pH of application over the pH region used (pH 3–8). The extent of total fixation (%*T*) followed the same pattern as that of dye fixation (%*F*) in the pH region 3–6 whereas at pH values 7 and 8, total fixation decreased owing to a lowering of dye exhaustion in the same pH region. While unfixed dye was removed from dyeings as a result of a recommended wash-off and syntan aftertreatment, the extent of dye removed was small. Wash-off and syntanning did not markedly alter the colour of the dyeings. The wash fastness of 2% omf dyeings was found to be very good. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Nylon 6,6; Reactive dyes; Dye fixation; Dye exhaustion

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1. Introduction

It is well known that the presence of terminal amino end groups imparts to nylon 6,6 fibre substantivity towards several types of anionic dye, namely *acid* (including pre-metallised acid) *dyes*, *mordant dyes*, *direct dyes* and *reactive dyes*; in addition, *disperse dyes* also are substantive. Of these dye types, anionic dyes and, especially acid (*including pre-metallised acid*) *dyes*, predominate.

Although nylon 6,6 was commercially introduced over 60 years ago, demand for the textile fibre has been enlivened in recent years by the introduction of nylon 6,6 microfibre [1] which is increasingly being used for apparel, sportswear and high performance functional fabrics due to its superior handle, good drapeability and excellent lustre. However, while the dyes used for microfibre nylon 6,6 are the same as for conventional decitex fibre, the dyeing of nylon microfibre presents several problems [1]:

- the greater extent of surface reflection, which is caused by the greater surface area of microfibre, results in identical depth dyeings on microfibre appearing visually paler than those on conventional decitex fibre;

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PII: S0143-7208(00)00073-5

- to achieve the same visual depth of shade, more dye has to be applied to microfibre;
- wash fastness deficiencies associated with conventional decitex fibres are exacerbated in the case of dyed microfibre;
- although aftertreatment can be used to improve the wet fastness of dyed microfibre, aftertreatment is less effective in the case of dyed microfibre than dyed conventional decitex fibre.

The past few years have witnessed ever-more challenging specifications being imposed for dyed textiles and apparel, particularly in the areas of wet and wash fastness, as a consequence of increased demand from consumers and retailers. Whilst this is true for all types of fibres and fibre blends, microfibre nylon 6,6 presents the dyer with a major challenge in terms of achieving high levels of wet fastness in moderate and deep shade depths. Recently, the dyeing of nylon 6,6 with reactive dyes has attracted interest [2–8] through the launch of the joint Du Pont/DyStar dyeing system that utilises Du Pont Tactel Coloursafe®, a modified nylon 6,6 fibre and the DyStar Stanalan® range of modified vinyl sulphone dyes [9]. One major achievement of the *Tactel Coloursafe* dyeing system is the provision of dyeings of high wet fastness on both conventional and microfibre nylon 6,6 [8].

The purpose of the present work was to examine the effect of pH on the exhaustion and fixation of three typical *Stanalan dyes*.

2. Experimental

2.1. Materials

Scoured, circular knitted Tactel *Coloursafe* nylon 6,6 (78f68; 1.14 dtexpf) fabric, was kindly supplied by Du Pont Nylon (UK). Three reactive dyes, namely *Stanalan Dark Red MFFN*, *Stanalan Yellow MFFR* and *Stanalan Brilliant Blue MFFR*, were used. Each dye was kindly supplied by DyStar and was not purified prior to use. A commercial anionic levelling agent, *Levegal SER* and a commercial sample of the syntan, *Mesitol NBSE*, were kindly provided by Bayer (UK). All other reagents used were of general purpose grade.

The composition of the McIlvaine buffers [10] used is given in Table 1.

2.2. Procedures

2.2.1. Dyeing

Dyeings were carried out, using each of the three reactive dyes, employing McIlvaine buffers, in sealed, 300 cm^3 capacity, stainless steel dyepots housed in a Roaches *Pyrotec S* infrared, laboratory scale dyeing machine, using a 25:1 liquor ratio.

Du Pont and DyStar recommend three application methods for the *Stanalan* range of dyes on *Coloursafe* nylon 6,6 (Figs. 1–3). The three dyeing methods differ, in the most part, in terms of the pH used for dyeing. The three pH ranges are used to control the rate of dye uptake for each of three depths of shade applied. Dyeings of 1, 2 and 4% omf were carried out as follows:

dyeing method 1: 1% omf;
dyeing method 2: 2% omf;
dyeing method 3: 4% omf.

Dyeing method 2 was also used to provide 2% omf dyeings at pH 3, 4, 4.5, 5, 7 and 8.

2.2.2. Determination of dyebath exhaustion

The extent of dye exhaustion was determined spectrophotometrically. The absorbance of each dyebath solution was measured using a 1 cm path length quartz cell housed in a Philips PU 8720 UV/visible scanning spectrophotometer both before and after the dyeing process at the λ_{max} of

Table 1
Composition of McIlvaine buffers

pH	0.2 M Na_2HPO_4	0.2 M Citric acid
3.0	20.55	79.45
4.0	38.55	61.45
4.5	45.03	54.97
5.0	51.50	48.50
6.0	63.15	36.85
7.0	82.35	17.65
8.0	97.25	2.75

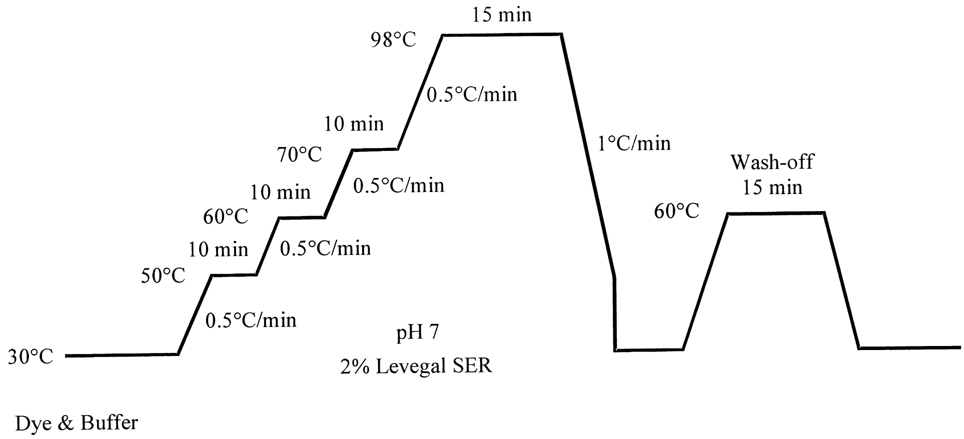

Fig. 1. Dyeing method 1; up to 1.5% omf dye.

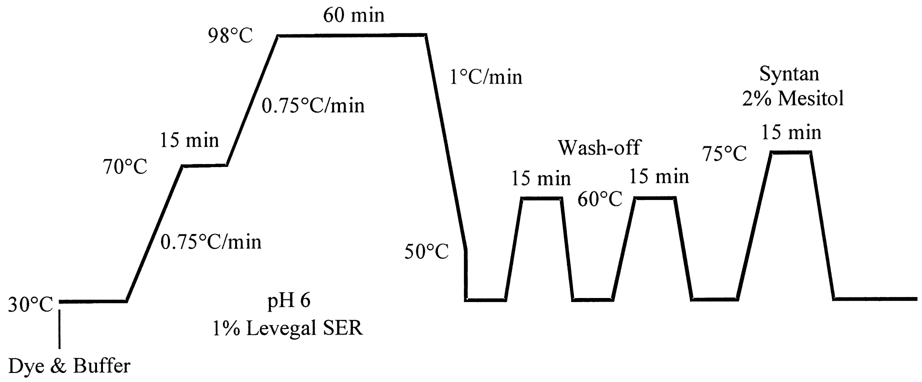

Fig. 2. Dyeing method 2; 1.5–3.0% omf dye.

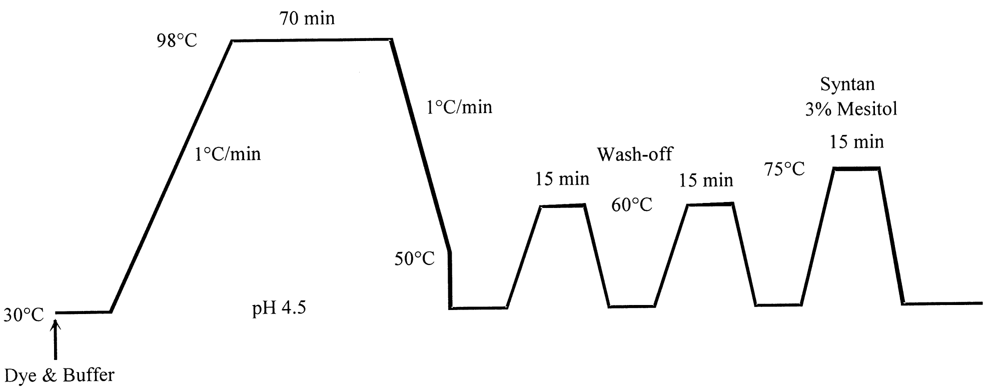

Fig. 3. Dyeing method 3; >3.0% omf dye.

each dye. The percentage dyebath exhaustion (%E) was calculated using Eq. (1), where A_0 and A_f are the absorbances of the dyebath before and after dyeing, respectively.

$$\%E = \left(\frac{A_0 - A_f}{A_0}\right) \times 100 \tag{1}$$

2.2.3. Colour measurement

The reflectance values of the dry samples were measured using an X-Rite *Match Rite* reflectance spectrophotometer interfaced to a personal computer under illuminant D_{65}, using a 10° standard observer, with specular component included and UV component included. The corresponding colour strength (f_k) and colorimetric parameters (L^*, a^*, b^*, C^* and $h°$ values) of the samples were calculated. Each fabric sample was folded twice so as to realise a total of four thicknesses of fabric.

2.2.4. Determination of dye fixation

The extent of covalent fixation of the dye to the fibre was determined for 2% omf dyeings by 'stripping' unfixed dye from the dyed material using 20% aqueous pyridine. This stripping treatment was carried out repeatedly using fresh aqueous pyridine solution until no further dye was removed.

At the end of dyeing, the dyed sample was removed, squeezed over the dyepot, cut into two pieces and allowed to dry in the open air. One half of the dried dyeing was extracted in a soxhlet extraction apparatus. At the end of stripping, the sample was rinsed with water and allowed to dry in the open air.

The extent of fixation (%F) was then calculated using Eq. (2), where the subscripts $_1$ and $_2$ represent, respectively, the f_k values before and after stripping.

$$\%F = \left(\frac{f_{k_1}}{f_{k_2}}\right) \times 100 \tag{2}$$

the extent of total fixation (%T) was calculated using Eq. (3).

$$\%T = \frac{\%E.\%F}{100} \tag{3}$$

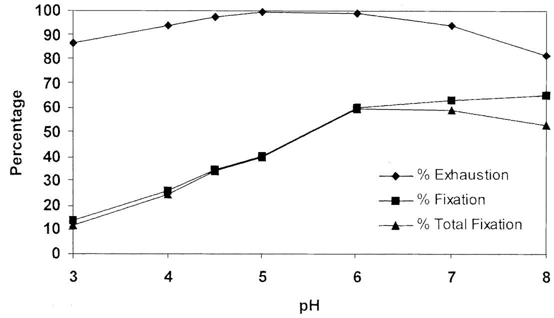

Fig. 5. % Exhaustion, % fixation and % total fixation achieved for 2% omf dyeings of *Stanalan Dark Red MFFN*.

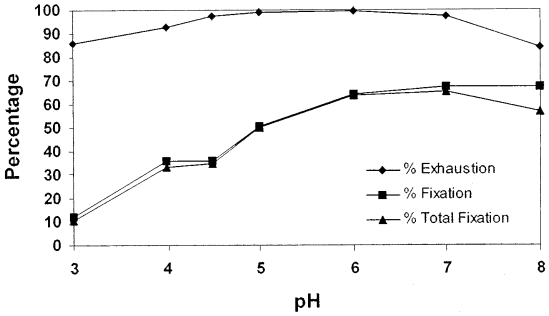

Fig. 4. % Exhaustion, % fixation and % total fixation achieved for 2% omf dyeings of *Stanalan Yellow MFFR*.

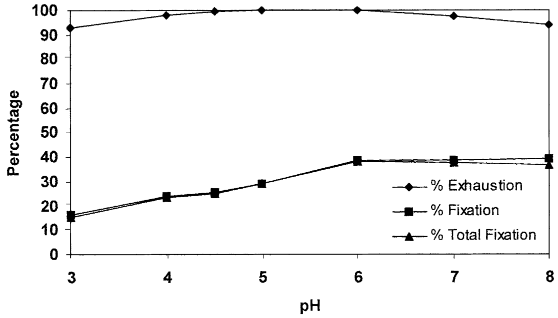

Fig. 6. % Exhaustion, % fixation and % total fixation achieved for 2% omf dyeings of *Stanalan Brilliant Blue MFFR*.

2.2.5. Wash-off

The wash-off procedures used are shown in Figs. 1–3 respectively and depended on the depth of shade used.

2.2.6. Syntan treatment

Du Pont recommends an aftertreatment with the commercial syntan, *Mesitol NBSE*, in the case of dyeings of 1.5% omf and greater, to secure

Table 2
Colorimetric parameters of dyeings

Stanalan	% omf dye	*L**	*a**	*b**	*C**	*h*°
Yellow MFFR	After dyeing					
	1	83.4	9.1	72.9	73.5	82.9
	2	75.4	14.9	77.7	79.1	79.1
	4	76.8	19.5	90.6	92.6	77.9
	After wash-off and syntan aftertreatment					
	1	82.9	9.9	74.5	75.2	82.5
	2	76.5	15.5	79.8	81.3	79.0
	4	76.6	19.8	90.9	93.0	77.7
	After wash fastness testing					
	1	83.8	9.9	75.0	75.7	82.5
	2	76.7	15.9	81.2	82.8	79.0
	4	77.2	20.3	92.7	94.9	77.6
Dark Red MFFN	After dyeing					
	1	43.1	34.7	−20.5	40.3	329.5
	2	33.7	37.0	−19.7	41.9	332.0
	4	26.1	34.2	−14.7	37.3	336.8
	After wash-off and syntan aftertreatment					
	1	45.9	34.2	−20.3	39.7	329.3
	2	34.5	36.8	−20.1	41.9	331.3
	4	26.4	34.9	−16.7	38.7	334.4
	After wash fastness testing					
	1	45.9	35.2	−20.6	40.7	329.6
	2	34.6	37.5	−19.9	42.5	332.0
	4	26.5	35.9	−16.9	39.7	334.8
Brilliant Blue MFFR	After dyeing					
	1	45.8	3.7	−35.6	35.8	276.0
	2	36.9	6.0	−37.3	37.7	279.2
	4	29.4	7.9	−36.0	36.8	282.4
	After wash-off and syntan aftertreatment					
	1	47.0	3.2	−37.1	37.3	275.0
	2	39.0	5.9	−41.7	42.1	278.1
	4	32.4	8.0	−42.0	42.8	280.8
	After wash fastness testing					
	1	48.1	3.1	−38.9	39.1	274.6
	2	39.3	6.0	−42.8	43.2	278.0
	4	34.0	7.4	−42.8	43.4	279.8

Table 3
Wash fastness ratings

Stanalan	% omf dye	Colour change	Adjacent materials					
			Wool	Acrylic	Polyester	Nylon 6,6	Cotton	Sec. acetate
Yellow MFFR	1	4/5–5	5	5	5	5	5	5
	2	4/5–5	5	5	5	5	5	5
	4	4/5–5	5	5	5	4/5–5	4/5-5	5
Dark red MFFN	1	4/5–5	5	5	5	5	5	5
	2	4/5–5	5	5	5	4/5–5	5	5
	4	4/5	5	5	5	4/5	4/5	5
Brilliant Blue MFFR	1	4/5–5	5	5	5	5	5	5
	2	4/5	5	5	5	5	5	5
	4	4/5	5	5	5	5	5	5

optimum wet fastness. This aftertreatment was carried out as shown in Figs. 2 and 3.

2.2.7. *Wash fastness*

The fastness of 1, 2 and 4% omf dyeings to the ISO 105-CO6/B1 washing test was determined [11].

3. Results and discussion

3.1. *Exhaustion, fixation and total fixation*

For this part of the work, dyeings of 2% omf of each of the three dyes were obtained using dyeing method 2. Figs. 4–6 show the effect of application pH on the extents of exhaustion, fixation and total fixation achieved for the three dyes used. In terms of exhaustion, each of the three dyes behaved similarly in that maximum exhaustion occurred in the region pH 5–6. The fact that dye exhaustion was lower at pH 3 and 4 may be due to 'ring-dyeing' caused by the high strike of the anionic dyes (it is assumed that all dyes carried sulfonate groups) on the protonated amino end groups in the substrate. In contrast, the reduction of dye exhaustion observed at pH of 6, 7 and 8 can be attributed to a lowering of the concentration of protonated amino end groups in the fibre and an increase of the concentration of ionised carboxyl groups.

It is clear that for each dye, the extent of dye fixation (%*F*) increased with increasing pH of application over the pH region used (pH 3–8). Presumably, this can be attributed to an increase in the number of unprotonated amino end groups with which the reactive group of the dye was capable of forming a covalent bond. The extent of total fixation (%*T*) followed the same pattern as that of dye fixation (%*F*) in the pH region 3–6; however, at pH values 7 and 8, total fixation decreased owing to a lowering of dye exhaustion in the same pH region.

3.2. *Wash-off and syntan aftertreatment*

Figs. 4–6 show that for each of the three dyes used, while the extent of total dye fixation increased over the pH range used (pH 3–5), maximum dye fixation ranged from slightly below 40% to just over 60%. As a consequence of this incomplete dye fixation, a wash-off treatment is recommended by Du Pont to remove unfixed dye from dyeings; the wash-off treatment suggested for pale dyeings (< 1.5% omf; Fig. 1) is less rigorous than that prescribed for deeper shades (Figs. 2 and 3). Du Pont also advocate the use of a syntan aftertreatment in the case of medium and deep shades (Figs. 2 and 3) as a way of achieving optimum wash fastness. In essence, the aftertreatment is intended to counter the desorption of unfixed dye during subsequent washing and wet treatments.

Table 2 shows the colour strength (f_k values) and the corresponding colorimetric parameters (L^*, a^*, b^*, C^* and h°) of the dyeings, before and after wash-off and syntan treatment as well as after wash fastness testing. It is evident that the extent of dye that was removed as a result of wash-off and syntan treatment was relatively small, decreasing in the order 1% < 2% < 4% omf dye. The colorimetric parameters listed in Table 2 reveal that wash-off and syntanning did not markedly alter the colour of the dyeings.

3.3. *Wash fastness*

Table 2 also shows that for each of the three dyes used, the amount of dye removed from the fibre during the wash fastness test was higher than that removed by wash-off and syntan aftertreatment. Clearly, the colour of the dyeings was not affected by the wash fastness testing. The wash fastness ratings obtained for samples which had been dyed with 1, 2 and also 4% omf of each of the three dyes are displayed in Table 3. The level of fastness achieved for all three dyes can be classified as very good and in some cases as excellent.

4. Conclusions

The three dyes examined behaved similarly in terms of dye exhaustion and dye fixation. In the case of 2% omf dyeings, high exhaustion was achieved and this reached a maximum in the region pH 5–6. The extent of dye fixation (%F) increased with increasing pH of application over the pH region used (pH 3–8), presumably because of the corresponding increase in the number of unprotonated amino end groups to which the reactive dye could fix. The extent of total fixation (%T) followed the same pattern as that of dye fixation (%F) in the pH region 3–6; however, at pH values 7 and 8, total fixation decreased owing to a lowering of dye exhaustion in the same pH region.

While unfixed dye was removed from dyeings as a result of the recommended wash-off and syntan aftertreatment, the extent of dye removed was relatively small. Wash-off and syntanning did not markedly alter the colour of the dyeings. The wash fastness of 2% omf dyeings was found to be very good.

Acknowledgements

The authors would like to thank the State Scholarships Foundation of Greece and Du Pont Nylon (UK).

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