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Printing of nylon 6,6 with reactive dyes part I: preliminary studies

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Abstract

Conventional and Coloursafe® modified nylon 6,6 fabrics were printed with reactive dyes from various commercial ranges. Maximum colour yield was achieved using saturated steam as fixation medium and pH 4–5. The colour yield obtained on Coloursafe fabric was higher than that achieved on conventional nylon 6,6. A simple wash-off process was used to remove unfixed dye and print paste from the printed fabrics. The prints displayed excellent fastness to repeated wash testing and to cold water contact fastness. The print paste was stable after up to 3 months storage. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Currently, nylon 6,6 is printed mainly using non-metallised acid and pre-metallised acid dyes [1], the latter type of dye being preferred when high wet fastness prints are required. Nevertheless, despite the generally very good wet fastness properties of pre-metallised acid dyes on nylon 6,6, recourse is often necessary to an aftertreatment with a commercial synthetic tanning agent (syntan) to secure highest levels of wash fastness, especially in moderate to deep depths of shade [2]. However, aftertreatment poses several problems in terms of printed nylon 6,6, insofar as aftertreatment:

- can impart a change in shade of the ground colour which may be objectionable especially when the ground is white [1];
- makes the printing process longer [1];
- is temporary in nature and loses its effectiveness after a few washes [3].

Recently, the dyeing of nylon 6,6 with reactive dyes has attracted interest [4–10] through the launch of the patented 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. 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 without recourse to an aftertreatment with a syntan.

This paper describes the printing of nylon 6,6 with the *Stanalan* and other commercial ranges of reactive dye; a comparison is also made of the printing of conventional nylon 6,6 and *Tactel*

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Coloursafe with regards to build-up and fastness of prints to multiple wash-off.

2. Experimental

2.1. Fabric

Samples of scoured, knitted, nylon 6,6 and *Tactel Coloursafe* (modified nylon 6,6) fabrics, each of 78f68 (1.1dtexpf) grade, were kindly supplied by Du Pont (UK) Ltd.

2.2. Chemicals

The reactive dyes used are listed in Table 1; all dyes were commercial samples that were not purified prior to use.

Lanapex R (a non-ionic surfactant) was generously provided by ICI Surfactants and *Alcoprint RT-BC* (an acrylic acid based thickener) was kindly supplied by Allied Colloids. The composition of the McIlvaine buffers used are shown in Table 2 [11].

2.3. Colour measurement

This was carried out using an *X-Rite* spectrophotometer coupled to a PC using D_{65} illuminant, 10° observer, with spectral component excluded and UV component included. The fabric was folded once to give two thickness and an average of four readings was taken for each sample.

2.4. Fastness

The fastness of prints to five, successive ISO 105 C06/C2 [12] wash tests was determined without intermediate drying but changing the multifibre strip after each wash-off. The result of the staining of the multifibre strip was reported as a corresponding grey scale rating and the extent of shade change was reported in ΔE CMC (2,1) units. The cold water contact test (ISO 105 E01 [12]) was carried out using multifibre strip as adjacent fabric and the extent of any staining was reported in terms of the corresponding staining grey scale rating.

Table 2
Composition of McIlvaine buffers

pH	0.2 M Na_2HPO_4	0.1 M Citric acid
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

Table 1
Dyes used

Commercial name	C.I. generic name	Maker
Remazol Red BS	Reactive Red 198	DyStar
Remazol Yellow 3RS	Reactive Yellow 176	
Remazol Black B	Reactive Black 5	
Basilen Brilliant. Red P-B	Reactive Red 24	BASF
Basilen Brilliant Yellow P-3GN	Reactive Yellow 151	
Basilen Navy Blue P-G	Reactive Blue 233	
Cibacron Red C-2G	Reactive Red 228	Ciba-Geigy
Cibacron Yellow C-2R	Reactive Yellow 168	
Cibacron Blue P-6B	None ascribed	
Stanalan Navy Blue MFF-B	None ascribed	DyStar
Stanalan Scarlet MFF-N	None ascribed	
Stanalan Brilliant Red MFF-B	None ascribed	
Stanalan Dark Red MFF-N	None ascribed	
Stanalan Yellow MFF-R	None ascribed	
Stanalan Yellow MFF-6GL	None ascribed	

2.5. Printing

Stock print pastes were prepared using the following recipe, all percentages being based on w/w.

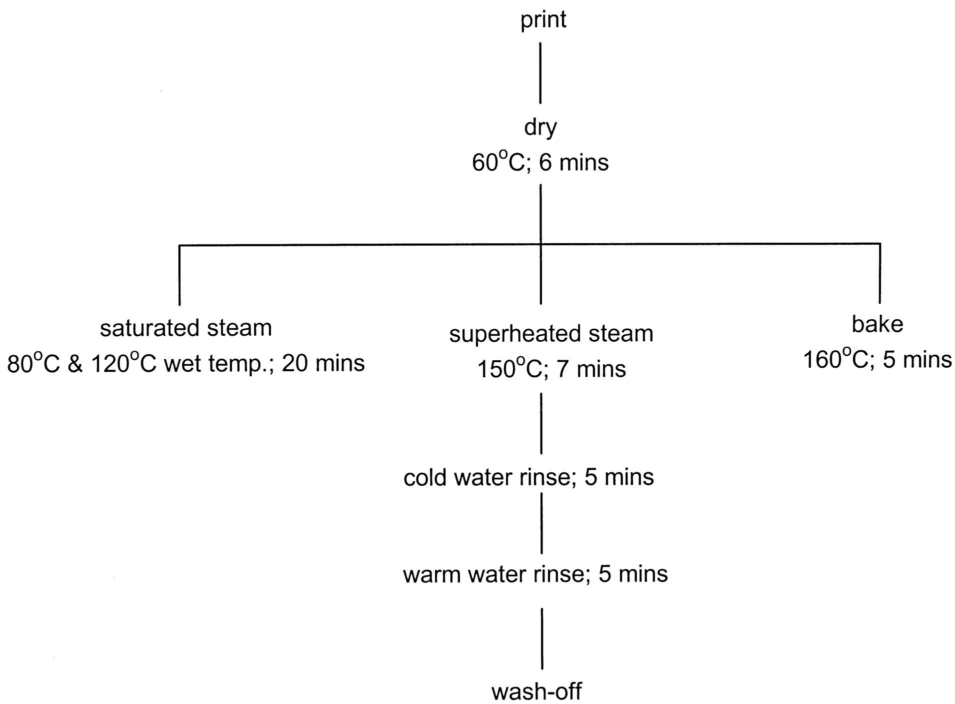
Urea	10% (unless stated)
Alcoprint 7860	6–7.5%
Mcllvaine Buffer	x%

To the above stock print paste was added 3% w/w dye (unless otherwise stated). The viscosity of the print paste was measured using a *Brookefield* viscometer, spindle number 6 and 10 rpm; the viscosity of the paste was adjusted to 10,000 cps by adding either the thickener or the McIlvaine buffer solution. The pH of the print paste was buffered at values of 4.5, 5, 6, 7 and 8. Hand screen printing was carried out using a screen of mesh 60×60 threads inch^{-1}; the printing process is shown in Scheme 1.

The prints were washed-off in a fresh bath, employing a liquor ratio of 25:1, using 2 g l^{-1} *Lanapex R* and 1 g l^{-1} Na_2CO_3 at 60°C for 15 min in sealed, stainless steel containers of 300 cm^3 capacity, housed in laboratory scale Zeltex *Polycolor* dyeing machine. The wash-off process was carried out twice, after which, the prints were rinsed in cold tap water and allowed to dry in the open air.

3. Result and discussion

During the past 44 years, since the commercial introduction of reactive dyes (for cellulosic fibres), research in the chemistry and application of reactive dyes has overwhelmingly focussed on cellulosic fibres. In contrast, much less attention has centred on the natural polyamide fibres such as wool and silk and, in addition, nylon fibres have enjoyed only meagre consideration. Consequently, while several different commercial ranges of reactive dye are currently marketed for cellulosic fibres, comparatively fewer dye ranges are available for natural polyamide fibres and only one



Scheme 1. Printing process.

commercial reactive dye range (*Stanalan*) which has been devised and marketed specifically for application to nylon 6,6 fibre, is at the present time available. This situation is reflected in the facts that:

- the amount of published information on the dyeing of nylon with reactive dyes is very small;
- the use of reactive dyes on nylon 6,6 has on the whole been confined to cellulosic fibre-type reactive dyes which, in general, were considered to display a mix of good/bad dyeing characteristics on nylon 6,6 [10];
- such publications generally project the image that reactive dyes are not suitable for nylon 6,6 [10];
- very little research has attended the printing of nylon 6,6 with reactive dyes [13,14].

The research project, from which work presented in this paper is taken, comprises a fundamental study of the dyeing and printing of nylon 6,6 with reactive dyes.

Fig. 1 shows the colour yield obtained for three *Stanalan* dyes on *Coloursafe* nylon 6,6 fabric using the three methods of fixation examined in this study. It is evident that saturated steam gave by far the best colour yield for each of the dyes used. The difference in colour yield obtained for the three fixation methods used may be due to the different water content of the three fixation media. It is well known that the water content of the three media used decrease in the order saturated steam > superheated steam > baking, it can be anticipated that a corresponding difference would result in the extents of fibre swelling and dye diffusion under the three fixation media used. In view of the findings presented in Fig. 1, all subsequent prints were fixed using saturated steam.

Table 3 shows the colorimetric data and wash fastness data obtained for conventional nylon 6,6 and also *Coloursafe* nylon 6,6 fabric which had been printed with reactive dyes from various commercial ranges. Table 3 shows that prints on both types of nylon 6,6 showed excellent fastness to the repeated washing tests as evidenced by the low ΔE values obtained between an unwashed

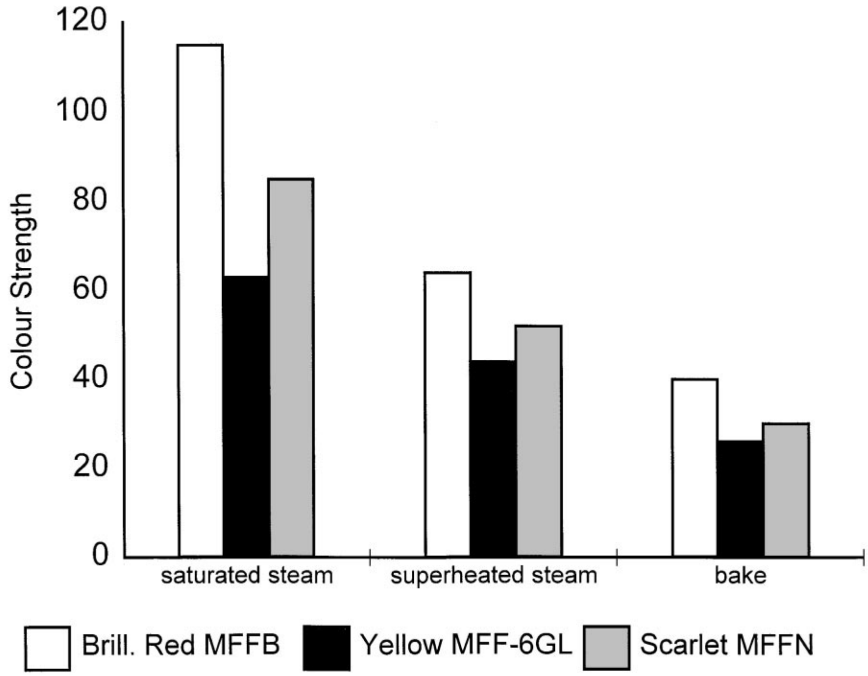


Fig. 1. Relationship between colour yield and fixation method used.

Table 3
Colorimetric and wash fastness data for conventional and *Coloursafe* fabrics

Dye	Washes	L^*	a^*	b^*	f_k	ΔE
Cibacron Blue P 6B	0	48.3	5.1	−49.0	43.6	2.6
	5	52.4	2.7	−46.6	31.6	
Cibacron Yellow C 2R	0	76.8	19.9	62.6	28.3	0.2
	5	77.0	19.6	62.3	27.7	
Cibacron Red C 2G	0	43.4	57.9	2.9	86.4	1.9
	5	42.5	54.9	0.2	82.6	
Basilen Brill Red P 4BN	0	45.8	64.7	13.3	125.5	3.1
	5	47.1	63.0	9.8	90.8	
Basilen Yellow P 3R	0	82.3	−6.4	80.5	52.2	3.0
	5	83.8	−6.6	71.4	31.3	
Remazol Yellow 3RS	0	74.8	22.2	75.6	56.9	1.0
	5	74.6	23.8	76.5	59.0	
Remazol Black B	0	35.9	−1.7	−17.9	79.5	1.8
	5	37.2	−3.3	−18.3	73.7	
Navy Blue MFFB	0	32.7	0.1	−23.6	100.0	3.3
	5	35.5	−0.1	−23.6	81.1	
Brill. Red MFFB	0	41.2	61.2	2.4	120.4	0.7
	5	41.6	60.6	1.3	113.2	
Yellow MFF6GL	0	86.9	−5.4	90.7	64.1	0.8
	5	86.2	−4.2	89.6	63.6	
Blue MFFB	0	38.4	−9.1	−28.8	86.4	2.7
	5	41.1	−9.0	−29.5	73.8	
Yellow MFFR	0	80.0	14.1	89.8	83.6	1.0
	5	80.0	14.6	86.8	65.7	

print and a corresponding print which had been subjected to five, repeated wash tests. The high fastness of the prints to the repeated wash fastness protocol employed can be attributed to the covalent nature of the dye–fibre interaction.

Table 4 shows the extent of staining of multi-fibre strip achieved for prints on *Coloursafe* nylon 6,6 fabric in the cold water contact test. Clearly, the dyes used had little tendency to migrate from the printed fabric. This finding was expected in view of the very good/excellent fastness of the prints to repeated washing and can be attributed to the covalent fixation of the dye to the substrate.

Fig. 2 shows a comparison of the build-up of some *Stanalan* dyes on conventional and *Coloursafe* fabrics. For this part of the work, printing was carried out according to Scheme 1 but a more stringent wash-off process (90 min using 3 g l^{-1} *Lanapex R* and 1 g l^{-1} sodium carbonate) was used to remove unfixed dye. Fig. 2 shows that higher colour yields were achieved using the *Coloursafe* substrate. In addition, the two curves obtained for the conventional nylon 6,6 flattens after 3% applied dye indicating that the fibre has reached saturation. In contrast, the corresponding two curves obtained for the *Coloursafe* fabric shows that saturation occurs at higher levels of applied dye. As previously mentioned, Du Pont *Tactel Coloursafe* is a modified nylon 6,6 fibre and, while no details of the chemical and physical differences between conventional and *Coloursafe* nylon fabrics can be given because of commercial confidentiality, the higher colour yields secured on *Coloursafe* fabric are a characteristic property of the modified nylon 6,6 fibre.

Fig. 3 shows the effect of pH of the print paste on the colour yield achieved for three *Stanalan* dyes on *Coloursafe* fabric. Evidently, colour yield decreased with increasing pH from pH 4 to 8. These findings suggest that the *Stanalan* reactive dyes behaved in a manner similar to other anionic dyes, such as non-metallised acid dyes, in terms of their adsorption behaviour insofar as, the extent of dye adsorption mirrored the extent of

Table 4
Cold water contact test

Dye	Wool	Acrylic	Polyester	Nylon 6,6	Cotton	Acetate
Cibacron Blue P 6B	5	5	5	5	5	5
Cibacron Yellow C 3R	5	5	5	5	5	5
Cibacron Red C 2G	5	5	5	5	5	5
Remazol Black B	5	5	5	5	4/5	5
Basilen Brilliant Red P 4BN	5	5	5	5	4/5	5
Stanalan Navy Blue MFFB	5	5	5	4/5	5	5
Stanalan Brill. Red MFFB	4/5	5	5	4/5	4–4/5	5
Stanalan Yellow MFFR	5	5	5	5	5	5
Stanalan Blue MFFB	5	5	5	5	5	5

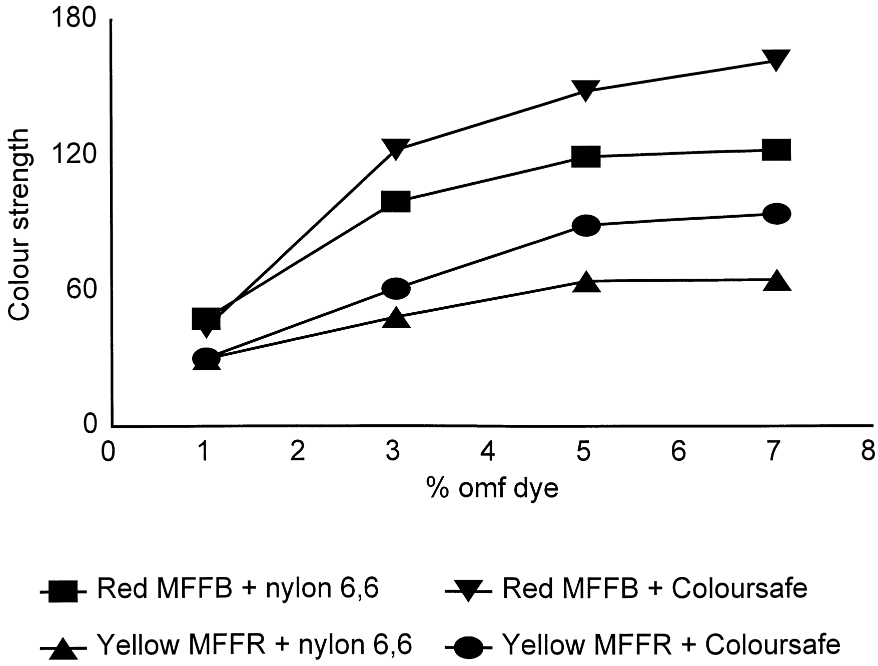


Fig. 2. Build-up characteristics of Stanalan dyes on conventional and *Coloursafe* fabrics.

protonation of the terminal amino groups in the substrate. As protonation of the terminal amino groups is an equilibrium situation (I) in which the position of the equilibrium is pH dependent, it follows that the equilibrium depicted in (I) will move to the right with decreasing pH. Thus, as the extent of protonation of the amino groups will increase with decreasing pH, the extent of dye adsorption should increase with decreasing pH, as was indeed observed (Fig. 3).

$$-NH_2 + H^+ \rightleftharpoons {}^+ - NH_3 \quad (1)$$

The observed pH-dependence of colour yield is in keeping with findings that the dyeing of nylon 6,6 with reactive dyes is pH-dependent [10]. Fig. 3 reveals that optimum colour yield was secured in the region of pH 4–5.

Table 5 shows the stability of the print paste used over a period of six months. Printing was carried out using two *Stanalan* dyes, according to

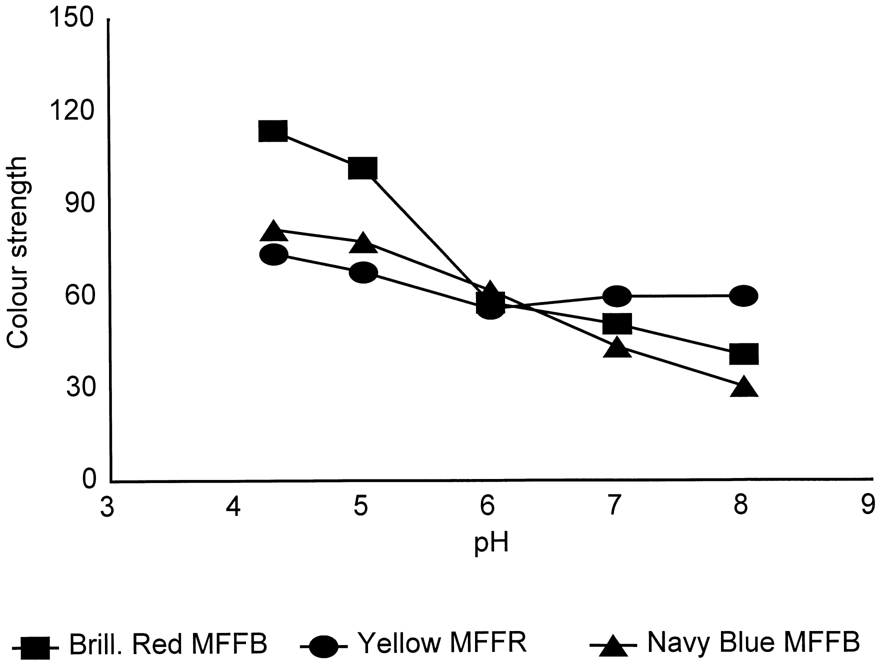


Fig. 3. Effect of print paste pH on colour yield for *Coloursafe* fabric.

Table 5
Print paste stability

Parameter	1 day	15 days	30 days	60 days	90 days
Stanalan Brilliant Red MFFR					
Viscosity/cps	10,000	10,000	9900	10,000	10,000
pH	4.5	4.5	4.5	4.5	4.5
Colour yield/f_k	120.5	123.4	128.1	124.3	125.5
Stanalan Yellow MFFR					
viscosity/cps	9800	9800	9800	9800	9800
pH	4.5	4.5	4.5	4.5	4.5
colour yield/f_k	8.3.	78.4	80.8	85.4	78.9

Scheme 1 (saturated steam) and using the previously described, stringent wash-off process (90 min using 3 g l^{-1} *Lanapex R* and 1 g l^{-1} sodium carbonate) to remove unfixed dye. Clearly, over the six month period involved, the print paste showed no change in viscosity and pH. The colour yield obtained using the print pastes over the time period used, was also unaffected.

4. Conclusions

Both conventional and *Coloursafe* nylon 6,6 fabrics can be printed with reactive dyes from various commercial ranges. The print paste recipe is simple and the printing process is short. The colour yield obtained on *Coloursafe* fabric is higher than that achieved on conventional nylon 6,6. The optimum pH for printing is in the range pH 4–5 as determined by colour yield. A simple wash-off process is needed to remove unfixed dye and print paste from the printed fabrics. The prints displayed excellent fastness to repeated wash testing and to cold water contact fastness. The print paste displays excellent stability.

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