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Dyes and Pigments 69 (2006) 233–238

www.elsevier.com/locate/dyepig

Alkali-clearable disperse dyeing of poly(ethyleneterephthalate) with azohydroxypyridone dyes containing a fluorosulfonyl group

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Received 30 June 2004; received in revised form 12 November 2004; accepted 3 March 2005
Available online 25 May 2005

Abstract

Dyeing properties of a series of alkali-clearable azohydroxypyridone disperse dyes containing a fluorosulfonyl group on poly(ethyleneterephthalate) have been investigated. The dyes showed reasonably good build-up properties and had a yellow shade on PET. The dyes exhibited excellent fastness properties on PET fabric, irrespective of the clearing method. Specially, the azohydroxypyridone dyes containing a nitro group in place of the fluorosulfonyl group in the *para* position to azo group were synthesised in order to compare their dyeing and fastness properties on poly(ethyleneterephthalate) with those of fluorosulfonyl-substituted analogues.

Keywords: Azohydroxypyridone disperse dyes; Poly(ethyleneterephthalate); Build-up properties; Fastness properties; Fluorosulfonyl group

1. Introduction

In the disperse dyeing of poly(ethylene terephthalate) (PET), the usual after-treatment carried out is reduction-clearing, where the dyed fabric is treated in a strong reduction bath, usually made up of sodium hydrosulfite and caustic soda. However, when reduction-clearing is carried out with azo disperse dyes, the azo linkage itself may be reduced, giving loss of colour strength. In this case toxic amines are released into the effluent, which already has a high biological oxygen demand (BOD) due to the presence of sodium dithionite [1,2].

Alkali-clearable disperse dyes offer a means of tackling these challenges simultaneously. This type of dye does not require the use of sodium dithionite and the cost of effluent treatment is significantly reduced [3–5]. Furthermore, by avoiding the need for reduction-clearing, substantial productivity improvements are possible. These savings, including a reduction on the effluent load, are a key objective in implementing the 'rapid dyeing' approach for polyester [2].

In our previous work, novel alkali-clearable azo disperse dyes containing the fluorosulfonyl group have been discussed [6–15]. This grouping was selected for study after it was recognised that, since it could be hydrolysed by alkali, it was promising as a component of alkali-clearable disperse dyes. Azo disperse dyes containing this grouping can be hydrolysed under alkaline conditions by an SN2 mechanism (Scheme 1). Pseudo first-order kinetics have been confirmed by studying the hydrolysis using high-pressure liquid chromatography [7,8]. It would therefore be reasonable to assume that disperse dyes based on 4-amino-4′-fluorosulfonylazobenzene would be similarly alkali-clearable without reducing agent. Their spectral properties were also examined with respect to the effects of substituents in absorption spectra, halochromism and solvatochromism [9]. 4-(*N*,*N*-Diethylamino)-4′-fluorosulfonylazobenzene

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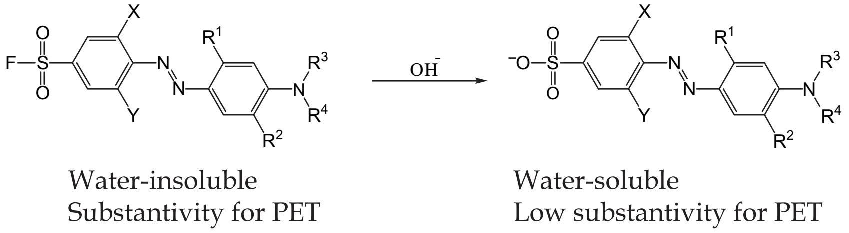
doi:10.1016/j.dyepig.2005.03.003



Scheme 1. Alkali-hydrolysis of 4-amino-4′-fluorosulfonylazobenzene disperse dyes (X, Y = H, Cl, Br, NO_2, CN, R^1, R^2 = H, CH_3, OCH_3, $NHCOCH_3$, R^3, R^4 = substituted alkyls).

dyes which have been synthesised in previous study cover a whole gamut of colours (red to greenish blue, 469–620 nm in ethanol) except the yellow shade area [9]. Recently, we have attempted to synthesise yellow disperse dyes which have good spectral properties and dyeing properties [15]. Thus, for the yellow shades, hydroxypyridone derivatives were used as coupling components since they provide greenish yellow to orange shades and have significantly high tinctorial strength [16]. However, since the introduction of new alkali-clearable disperse dyes based on azohydroxypyridone containing a fluorosulfonyl group [6], only very little information is available on the dyeing properties on PET. Therefore, it would be worth comparing their dyeing properties on PET with the conventional azo disperse dyes.

In the present study, the dyeing and fatness properties of azohydroxypyridone disperse dyes containing a fluorosulfonyl group and their nitro analogues, have been investigated and compared.

2. Experimental

2.1. Materials

Poly(ethyleneterephthalate) (PET) fabrics (KS K 0905, 70 ± 5 g/m^2; plain weave, warp and weft each 75 denier) were used throughout the study. All chemicals used in the syntheses and dyeings were of laboratory reagent grade. Diwatex (Borregaard Lignotech, anionic) was used as the dispersing agent for milling, along with Sandozin NIE (Clariant, nonionic) as the wetting agent. Lyocol RDN liquid (Clariant, anionic) was employed in the dyeing experiments.

2.2. Dye synthesis

The synthesis of disperse dyes **1** and **2** based on azohdroxypyridone disperse dyes containing a fluorosulfonyl group was carried out as described in a previous study (Table 1) [15].

2.3. Preparation of dye dispersions

Dispersions of the dyes were prepared in water. Dispersing agent (Diwatex, 40% on weight of dye), wetting agent (Sandozin NIE Liquid, 1 drop) and dye (1.0% concentration) were milled with glass beads for one week in 100 ml water buffered at pH 4.0–4.5. This gave a mean particle size in the region of 1 μm, determined using a Mastersizer (Malvern Instruments Ltd.), which employs a light-scattering technique.

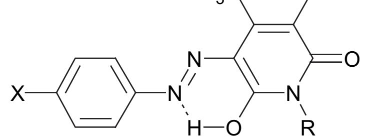
2.4. Dyeing

PET fabrics were dyed in a laboratory dyeing machine (Ahiba, Datacolor International) at a liquor ratio of 30:1. The dyebath comprised 60 ml of the above dye preparation and a dispersing agent (Lyocol RDN liquid, 1.0 ml/l). After adjusting to pH 4.5, PET fabric (2.0 g) was immersed in the dyebath and the temperature was increased to 130 °C at a rate of 1 °C/min. Dyeing was carried out at this temperature for 60 min.

2.5. Colour measurement

The colour properties (CIE L^*, a^*, b^*, C^* and h_{ab}) of the PET samples dyed with the synthesised dyes (**1**–**2**) were measured using a spectrophotometer (Spectra flash

Table 1
Azohydroxypyridone disperse dyes **1** and **2** used in the present study



Dye	X	R	Mol. weight	λ_{max} (EtOH) (nm)	Appearance
1a	NO_2	H	299.24	436	Yellow solid
1b	NO_2	CH_3	313.27	436	Orange solid
1c	NO_2	C_2H_5	327.30	438	Orange solid
2a	FO_2	H	336.30	420	Yellow solid
2b	FO_2	CH_3	350.33	422	Yellow solid
2c	FO_2	C_2H_5	364.35	422	Yellow solid

500, Datacolor, standard light D65, 10° standard observer, SPIN) interfaced with a personal computer.

The build-up property of dye was also investigated by measuring f_k values of dyed fabrics at various dye concentrations. The f_k is colour strength value which is the sum of the weighted K/S values in the visible region of the spectrum; it is calculated using Eq. (1) [17].

$$f_k=\sum_{\lambda=400}^{700}(K/S)_{\lambda}\left(\bar{x}_{10,\lambda}+\bar{y}_{10,\lambda}+\bar{z}_{10,\lambda}\right) \tag{1}$$

where, $x_{10,\lambda}$, $y_{10,\lambda}$, and $z_{10,\lambda}$ are colour matching functions for the 10° standard observer at each wavelength (ISO 7724/1-1984).

2.6. Colour fastness test

In order to evaluate the alkali-clearability of the dyes mentioned, the dyed PET fabric was after-treated in three ways, respectively, as follows: reduction-cleared (sodium dithionite, 2.0 g/l; sodium hydroxide, 2.0 g/l; soaping agent 2.0 g/l; 80 °C, 20 min); alkali-cleared (sodium hydroxide, 1.0 g/l; soaping agent, 1.0 g/l; 90 °C, 20 min); and without after-treatment. Samples of the reduction- and alkali-cleared fabrics were stentered at 180 °C for 30 s.

The dye concentration of 4.0% was chosen for the fastness tests since dyeings on PET, especially in medium and heavy depth, must normally be reduction-cleared in order to give satisfactory resistance to rubbing, washing, light and heatsetting. Colour fastness was determined according to the respective international standards: fastness to washing (ISO 105-C06/B1M), fastness to perspiration (ISO 105-E04), fastness to rubbing (ISO 105-X12), fastness to sublimation (ISO 105-P01) and fastness to light (ISO 105-B02). Change in shade and staining of adjacent multifibre (Multifibre DW, adjacent fabric, BS EN ISO 105-F10) were assessed using grey scales.

3. Results and discussion

3.1. Colour properties on PET

The colorimetric properties of the dyeings, as expressed in terms of the CIELab system, are listed in Table 2; CIE L^*, a^*, b^*, chroma (C^*) and hue angle (h) values are tabulated. The colour of the synthesised dyes **1** and **2** on PET falls into the range of yellow and nitro-substitutued dyes (**1a**–**1c**) shows relatively higher chromaticity than fluorosulfonyl-substituted dyes (**2a**–**2c**) (Fig. 1(b)). As expected, the nitro-substituted dye was slightly bathochromic on PET relative to its fluorosulfonyl analogues, owing to greater electron withdrawing power of nitro group (h_{ab} in Table 2) [18]. These trends in the colorimetric properties are consistent with their spectral properties in solvent (λ_{max} in Table 1).

Table 2
Colorimetric data and visual appearance of the dyed polyester fabrics with dyes **1** and **2** at 1.0% owf dye concentration

Dye	L^*	a^*	b^*	C^*	h_{ab}	Colour on PET
1a	82.64	−4.70	86.59	86.72	93.11	Vivid Yellow
1b	82.62	−5.16	85.70	85.86	93.45	Vivid Yellow
1c	83.59	−4.84	88.14	88.27	93.14	Vivid Yellow
2a	84.03	−5.84	51.96	52.29	96.42	Light Yellow
2b	85.84	−11.18	77.55	78.35	98.20	Brilliant Greenish Yellow
2c	85.07	−9.88	77.22	77.85	97.29	Brilliant Greenish Yellow

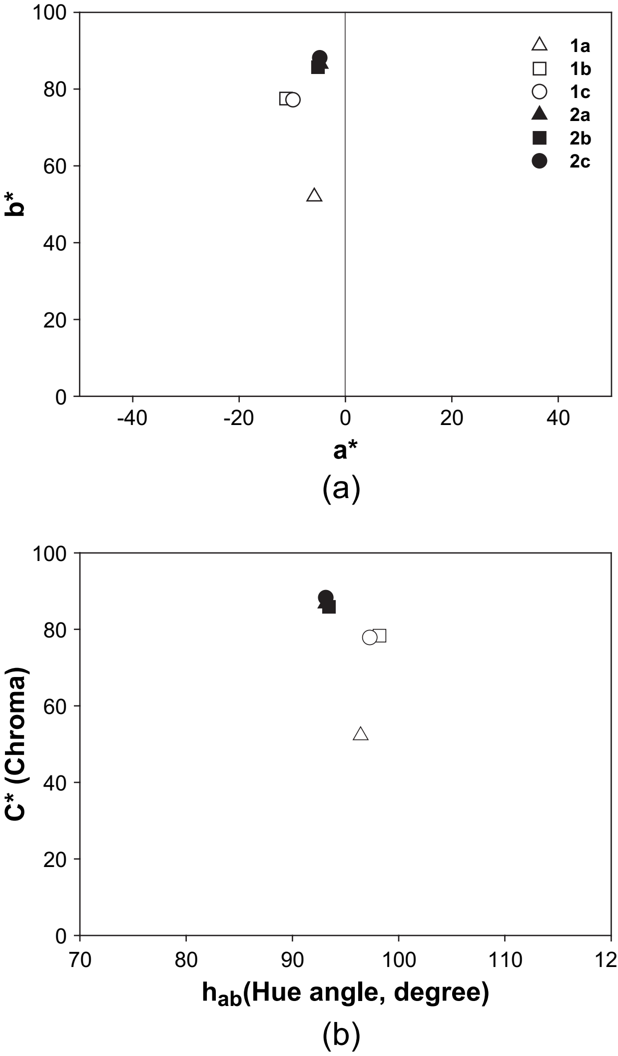


Fig. 1. Colour properties of dyes **1** and **2** on PET (a) a^* vs b^* (b) hue angle vs chromaticity.

3.2. Build-up properties on PET

Fig. 2 illustrates the relative colour strength (f_k) of dyed PET fabrics depending on the amounts of dye applied (%owf). The f_k value is a visually-weighted function of K/S, which indicates the strength of the dyeing. Most synthesised dyes showed reasonable build-up properties on PET and saturation was reached at application levels of 0.5–2.0% owf. The colour yield of the synthesised dyes on PET increased with the increase in the length of *N*-substituted alkyl chain in coupling component, presumably because the alkyl chain gives more hydrophobicity and resulting substantivity to hydrophobic PET fabric [19].

Azohydroxypyridone dyes containing a nitro group exhibited more rapid build-up and higher colour yield at saturation points compared with fluorosulfonyl analogues (Fig. 2). Thus, in the dyeing of PET fibre, the substantivity of nitro derivatives which contain a *p*-nitro group in the diazo component was shown to be higher than that of fluorosulfonyl derivatives which contain a *p*-fluorosulfonyl group. For example, dye **2a** produced a greater depth at 1.0% owf (f_k 65.53) than its fluorosulfonyl analogue (dye **2a**, f_k 15.28). Similarly, dyes **1b** and **1c** yielded marginally higher values of 63.30 and 65.83, respectively, compared with the fluorosulfonyl derivatives (**2b**, f_k 53.24; **2c**, f_k 55.24): indeed, many commercial azo disperse dyes for PET fibre contain the *p*-nitro group in the diazo component to enhance build-up.

3.3. Colour fastness properties

3.3.1. Fastness to washing

The diacetate, nylon, PET and wool components of the adjacent multifibre fabric are particularly prone to staining during washing of disperse-dyed PET. Figures for the staining of these fibres are shown in Table 3.

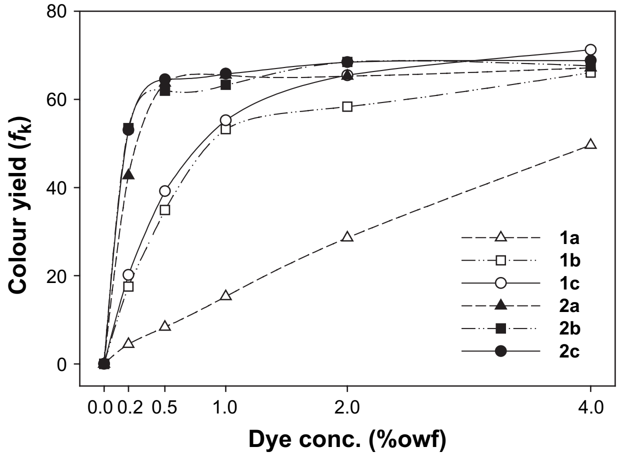


Fig. 2. Build-up properties of dyes **1** and **2** on PET.

Table 3
Fastness to washing of dyes **1** and **2** (ISO 105 C06 B1M)

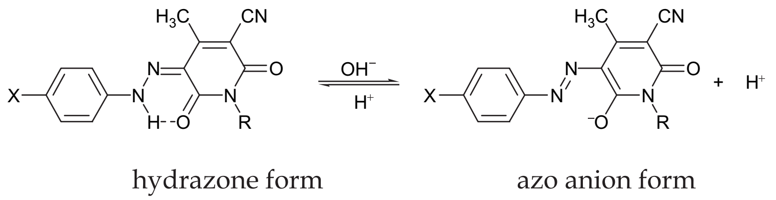
Dye	NC			AC			RC		
	D	N	W	D	N	W	D	N	W
1a	4/5	4/5	5	5	4/5	5	5	5	5
1b	4	3/4	4/5	5	4/5	5	5	5	5
1c	3/4	3	4/5	5	5	5	5	5	5
2a	5	5	5	5	5	5	5	5	5
2b	5	5	5	5	5	5	5	5	5
2c	5	5	5	5	5	5	5	5	5

D: Diacetate, N: nylon, W: wool.

In the case of azohydroxypyridone dyes containing a nitro group (**1a**–**1c**), the reduction-cleared and alkali-cleared fabric exhibited similar high fastness although these dyes were not expected to be alkali-clearable since their nitro functions cannot give water-soluble dyes on hydrolysis. The results can be accounted for by the ionisation of the dye under alkaline conditions where the hydrazone form of the hydroxypyridone dye is converted to the azo anion form (Scheme 2) [20]. The hydrazone–azo anion equilibrium of pyridone azo dyes can be represented as shown in Scheme 2. Therefore, it is obvious that the ionisation of these dyes could be advantageous in after-treatment processes as indicated previously [21].

Also, in the case of the synthesised dyes containing a fluorosulfonyl group (**2a**, **2b**), they showed excellent levels of fastness regardless of whether reduction- or alkali-clearing had been used, presumably because of the alkali-clearable property of the fluorosulfonyl group and that of azohydroxypyridone structure (Table 3). Especially, the fluorosulfonyl group of the synthesised dyes is hydrolysed by the alkali to a solubilising sulfonate group as indicated previously (Scheme 1) [6,7]. The azohydroxypyridone dyes containing a fluorosulfonyl group are therefore more readily removed by wash-off, and exhibit lower staining in wash tests, than nitro-substituted analogues (**1a**–**1c**) even without any clearing treatment; the fluorosulfonyl-analogues exhibited higher fastness by as much as 2 units in terms of staining in the case of the non-cleared samples. Appreciable staining of diacetate, nylon and wool occurred with dyes **1a**–**1c** while ratings of 5 were observed for dyes **2a**–**2c** for each component of the adjacent multifibre.

An analogous comparison between the fluorosulfonyl-substituted derivatives and nitro analogues revealed a gap in alkali-clearability as exemplified by staining of nylon (Fig. 3). Reduction-clearing and alkali-clearing produced a marked improvement in levels of staining in the case of dyes **1a**–**1c** ; while non-cleared samples gave some staining (3–5), the reduction-cleared dyeings were excellent (5). Alkali-clearing also improved fastness but to a smaller extent than reduction-clearing (4/5–5). On the other hand, in the case of fluorosulfonyl derivatives, both alkali-cleared samples and



Scheme 2. Ionisation of the hydroxypyridone dyes under alkaline condition (X = FO_2S, NO_2, R = substituted alkyls).

reduction-cleared samples did not stain nylon at all (5). These results indicate that, with these synthesised disperse dyes containing a fluorosulfonyl group and/or azohydroxypyridone structure, alkali-clearing can be used instead of reduction-clearing just as effectively.

3.3.2. Fastness to perspiration

The diacetate and nylon components of multifibre adjacent fabric are particularly prone to staining of disperse dyes during perspiration fastness test of disperse-dyed PET. Figures for the staining of these fibres are shown in Table 4. An analogous comparison between the fluorosulfonyl-substituted derivatives and nitro analogues revealed a gap in alkali-clearability as exemplified by staining of diacetate and nylon. The azohydroxypyridone dyes containing a fluorosulfonyl group exhibit lower staining in perspiration tests, than conventional disperse dyes such as nitro-substituted analogues (**1a**–**1c**) even without any clearing treatment; the fluorosulfonyl-analogues exhibited higher fastness by as much as 2 units in terms of staining in the case of the non-cleared samples.

In the case of azohydroxypyridone dyes containing a nitro group (**1a**–**1c**), the reduction-cleared and alkali-cleared fabric exhibited similar high fastness. Reduction-clearing and alkali-clearing produced a marked improvement in levels of staining; while non-cleared samples gave some staining (2–5), the reduction-cleared dyeings were excellent (5). Alkali-clearing also raised fastness levels but to a lesser extent compared with the reduction-cleared (4/5–5).

On the other hand, in the case of fluorosulfonyl derivatives, both alkali-cleared samples and reduction-cleared samples did not stain nylon at all (5). From these results, it is clear that fluorosulfonyl derivatives have excellent perspiration fastness characteristics on PET.

3.3.3. Fastness to rubbing

In the case of azohydroxypyridone dyes containing a nitro group (**1a**–**1c**), the reduction-cleared and alkali-cleared fabric exhibited similar high fastness (Table 5). Reduction-clearing and alkali-clearing produced a marked improvement in levels of staining; while non-cleared samples gave some staining (3/4–4/5), the reduction-cleared dyeings were excellent (5). Alkali-clearing also raised fastness levels but to a smaller extent compared to the reduction-cleared (4/5–5).

In the case of azohydroxypyridone dyes containing a fluorosulfonyl group (**2a**, **2b**), both alkali-cleared samples and reduction-cleared samples did not stain cotton at all (5) while non-cleared fabric gave some staining on cotton (i.e. NC: 4/5 for dye **2c**, Table 5), which also supports the alkali-clearability of the synthesised dyes containing a fluorosulfonyl group as indicated previously [6,7,10].

3.3.4. Fastness to dry heat

Ratings for fastness to dry heat of the synthesised dyes on PET are listed in Table 6. Staining was on average higher on PET than cotton at the same heat

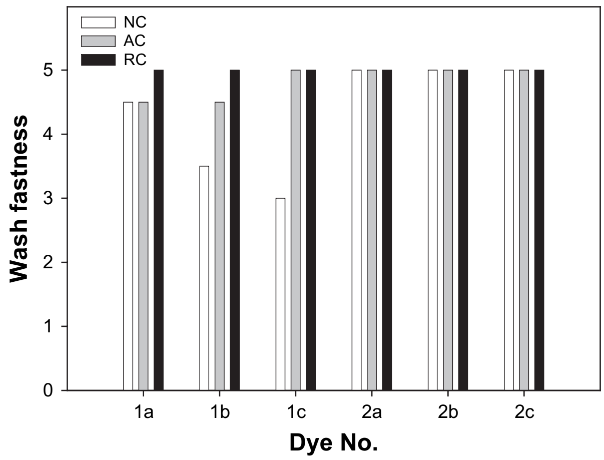


Fig. 3. Wash fastness of dyed PET with dyes **1** and **2** (staining on nylon).

Table 4
Fastness to perspiration of dyes **1** and **2** (ISO 105 E04)

Dye	Alkali						Acid					
	NC		AC		RC		NC		AC		RC	
	D	N	D	N	D	N	D	N	D	N	D	N
1a	2	2	4/5	5	5	5	2/3	2/3	5	4/5	5	5
1b	3/4	3/4	4/5	5	5	5	3/4	4	5	5	5	5
1c	4	4	4/5	5	5	5	4	4/5	5	5	5	5
2a	4	4	5	5	5	5	4	4	5	5	5	5
2b	5	5	5	5	5	5	4	4	5	5	5	5
2c	5	5	5	5	5	5	4	4/5	5	5	5	5

Table 5
Fastness to rubbing of dyes **1** and **2** (ISO 105 X12)

Dye	NC		AC		RC	
	Dry	Wet	Dry	Wet	Dry	Wet
1a	4	3/4	5	4/5	5	5
1b	4/5	3/4	5	4/5	5	5
1c	3/4	3/4	5	5	5	5
2a	5	5	5	5	5	5
2b	5	4/5	5	5	5	5
2c	4/5	4/5	5	5	5	5

treatment temperature, presumably because of the dye's higher substantivities for the former fibre; dyes are preferentially absorbed onto the more hydrophobic fibre.

The synthesised dyes possessed a wide range of fastness to dry heat, varying from 3 to 5 on cotton and 2 to 4/5 on PET. The nitro-substituted dyes showed slightly better sublimation fastness than fluorosulfonyl-substituted dyes; for example, the staining of dyes **1b** and **1c** was less than that of dyes **2b** and **2c**. The effect may be considered in terms of polarity factors. However, the effects of substitution in the diazo component and the clearing condition were not clear.

4. Conclusions

The dyeing and fastness properties of azohydroxypyridone dyes containing a fluorosulfonyl group and their nitro analogues on PET have been investigated and compared. The azohydroxypyridone dyes containing a fluorosulfonyl group showed relatively hypsochromic colour and lower chromaticity on PET relative to its nitro analogues, owing to weaker electron withdrawing power of fluorosulfonyl group. Also, in the dyeing of PET fibre, azohydroxypyridone dyes which contain the nitro group in the diazo component showed higher build-up properties than that of fluorosulfonyl analogues, probably due to their higher hydrophobicity.

The fastness properties of azohydroxypyridone disperse dyes on PET fabrics were excellent. Especially, in the case of fluorosulfonyl-substituted derivatives, not only the reduction- or alkali-cleared fabrics, but also even the non-cleared fabrics gave excellent wash fastness. This result is attributed to the excellent wash-off properties resulting from the alkali-clearability imparted by the hydrolysis of fluorosulfonyl residues and ionisation of azohydroxypyridone structure under alkaline condition. Also, in the case of nitro analogues, reduction- or alkali-cleared fabrics showed excellent fastness although the non-cleared samples gave some staining on the adjacent fabrics. These results indicate that dyes containing a fluorosulfonyl group and/or azohydroxypyridone structure dyes offer better wash fastness than conventional disperse dyes on PET and, therefore, alkali-clearing can be used instead of reduction-clearing just as effectively.

Table 6
Fastness to dry heat of dyes **1** and **2** (ISO 105 P01, 180 °C, 30 s)

Dye	Cotton			PET		
	NC	AC	RC	NC	AC	RC
1a	4/5	5	5	4/5	4/5	4/5
1b	4/5	4/5	4/5	3	3	3
1c	4/5	4/5	4/5	2/3	3	3
2a	4/5	5	5	4/5	4/5	4/5
2b	3	3/4	4	2/3	3	3
2c	3	3/4	3/4	2	2	2

Acknowledgements

This work was supported by the faculty research fund of Konkuk University in 2005.

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