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Alkali-hydrolysis kinetics of 4-amino-4′-fluorosulfonylazo benzene disperse dyes and their dyeing fastness properties

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Abstract

The alkali-hydrolysis kinetics of a series of 4-amino-4′-fluorosulfonylazobenzene disperse dyes were investigated using HPLC, and their fastness properties on poly(ethyleneterephthalate) were examined. Most of the dyes showed a reasonable level of hydrolysis (%) under relatively mild alkaline conditions and the dyes having more electron-accepting groups in the diazo component exhibited a lower rate of hydrolysis. The use of fluorosulfonyl containing disperse dyes showed excellent dyeing fastness properties and offer the option of alkali clearance to achieve high wash fastness, replacing reductive clearing and sodium hydrosulfite in particular, which places a very high BOD on conventional disperse dyeing effluents and then generates aromatic amines.

Keywords: Alkali-hydrolysis kinetics; 4-amino-4′-fluorosulfonylazobenzene; Disperse dye; Poly(ethyleneterephthalate); Dyeing fastness; Alkali-clearance

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1. Introduction

Since disperse dyes have a limited solubility in water, some particulate disperse dye molecules may still be occluded onto the fibre surface after the dyeing is complete. If not removed, this surface contamination can undermine the brightness of the shade as well as the wash, sublimation, and rubbing fastness results. The usual 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 the conventional reduction clearing process is applied to azo disperse dyes, azo linkage is broken and, carcinogenic amines are possibly liberated into the effluent which has high BOD values due to the presence of sodium hydrosulfite [1–3]. Alkali-clearable disperse dyes offer a means of tackling both of these challenges simultaneously. These so-called alkali-clearable disperse dyes obviated the need for sodium hydrosulfite and significantly reduced the cost of effluent treatment [4–10]. Furthermore, it is thought that minimizing the need for reduction clearing can

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lead to substantial productivity improvements and water and chemical savings as well as a reduction on the effluent load and should be a key objective in implementation of a “Rapid Dyeing” approach for polyester [2].

In previous work, we suggested novel alkali-clearable azo disperse dyes containing a sulfonyl fluoride group. Azo disperse dyes containing a fluorosulfonyl group are hydrolysed under alkaline conditions by an S_N2 mechanism (Scheme 1), and pseudo first-order kinetics were determined by analysis of the dye hydrolysis under alkaline conditions using HPLC [7,8]. Therefore, it can be presumed that 4-amino-4′-fluorosulfonylazobenzene disperse dyes have an alkali-clearable property which enables an alkaline treatment to substitute for the reduction clearing process, thus preventing the generation of potentially carcinogenic amines.

In this study, we reported the alkali-hydrolysis kinetics of monoazo disperse dyes containing a fluorosulfonyl group, 4-(*N*,*N*-diethylamino)-4′-fluorosulfonylazobenzene derivatives (**1**–**5**) as well as the fastness properties on poly(ethyleneterephthalate).

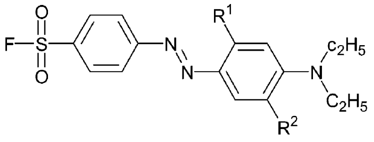
2. Experimental

2.1. Materials

Poly(ethyleneterephthalate) (PET,) fabrics (KS K 0905, 70 ± 5 g/m^2, plain weave, warp : 8.3 tex, weft: 8.3 tex) were used for dyeing throughout the study. All the chemicals used in the synthesis, HPLC analysis and dyeing were of laboratory-reagent grade. Diwatex (BASF, nonionic) was used as a dispersing agent for milling and Lyocol RDN Liquid (Clariant, anionic) was used as a dispersing agent for the dyeing of polyester fabric. Sandozin NIE (Clariant, nonionic) was used as a wetting agent.

2.2. Dye synthesis

The synthesis of 4-(*N*,*N*-diethylamino)-4′-fluorosulfonylazobenzene disperse dyes has been described in a previous paper [10]. The dyes (**1**–**5**) that were used throughout the study are given in Table 1.



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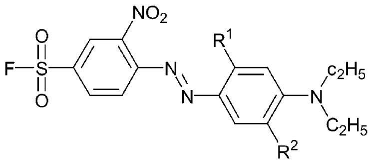

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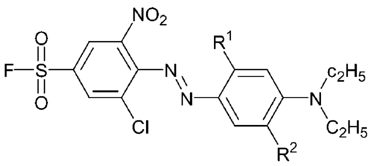

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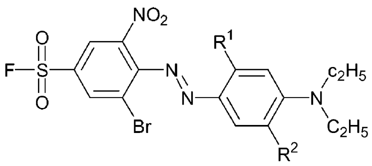

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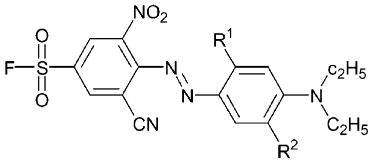

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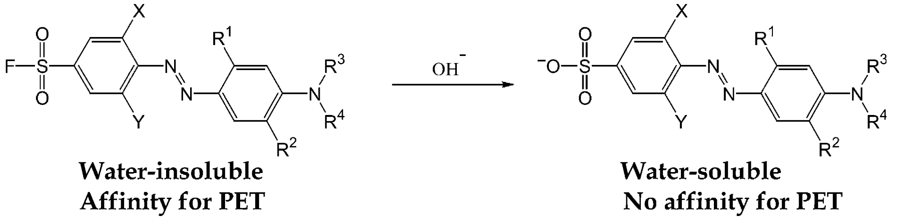
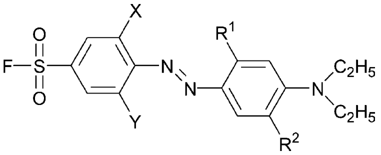
R^1 = H, NHAc, R^2 = H, OMe



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 alkayls).

Table 1
4-(*N*,*N*-Diethylamino)-4′-fluorosulfonylazobenzene dyes (**1**–**5**) used in the present study



Dye	X	Y	R^1	R^2	λ_{max} (EtOH, nm)
1a	H	H	H	H	469
1b	H	H	CH_3	H	478
1c	H	H	$NHCOCH_3$	OCH_3	519
2a	NO_2	H	H	H	513
2b	NO_2	H	CH_3	H	524
2c	NO_2	H	$NHCOCH_3$	OCH_3	573
3a	NO_2	Cl	H	H	520
3b	NO_2	Cl	CH_3	H	539
3c	NO_2	Cl	$NHCOCH_3$	OCH_3	595
4a	NO_2	Br	H	H	522
4b	NO_2	Br	CH_3	H	542
4c	NO_2	Br	$NHCOCH_3$	OCH_3	594
5a	NO_2	CN	H	H	540
5b	NO_2	CN	CH_3	H	580
5c	NO_2	CN	$NHCOCH_3$	OCH_3	620

2.3. Alkali-hydrolysis analysis

Alkaline hydrolysis kinetics was investigated at various alkali concentrations (NaOH 0.4, 1.0 and 2.0 g/l) and temperatures (80 and 90 °C) in order to determine the proper hydrolysis condition ranges for alkali clearing.

The dye liquors were prepared by dispersing 0.02 g of formulated dyes in 200 ml of buffer solution preheated to temperature in a water bath. The dye liquor was stirred at the appropriate temperature for 50 min and 2 ml aliquots were withdrawn from the dye solution at 5 min intervals and immediately neutralised to pH 4.0–4.5 with equivalent amounts of dilute HCl and then cooled to prevent further hydrolysis reactions. Acetonitrile (10 ml) was added into each of the withdrawn samples to prepare samples of proper composition (acetonitrile: water = 80 : 20) for HPLC analysis. Analysis was carried out at room temperature using a HPLC (Varian 5000 Liquid Chromatograph, USA, Varian) with a C18 reverse-phase column and a mixture of acetonitrile and deionised water was used as the mobile phase. Samples (10 μl) were injected for analysis, and were detected at the wavelength of absorption maxima (λ_{max}).

2.4. Dyeing

PET fabrics were dyed in a laboratory dyeing machine at a liquor ratio of 30:1. Dyebath (60 ml) was prepared with formulated dye and a dispersing agent (Lyocol RDN Liquid 1.0 ml/l) and adjusted to pH 4.0. Then, PET fabric (2.0 g) was immersed in the dyebath and dyed for 60 min at 130 °C.

2.5. Fastness test

In order to evaluate the alkali-clearability of the synthesised dye, these fastness tests were carried out for differently aftertreated polyester fabric; i.e. dyed polyester fabric was either reduction cleared ($Na_2S_2O_4$ 2.0 g/l, NaOH 2.0 g/l, soaping agent 2.0 g/l, 80 °C, 20 min), alkali cleared (NaOH 1.0 g/l, soaping agent 1.0 g/l, 90 °C, 20 min), or received no aftertreatment. A proportion of the reduction- and alkali-cleared samples were stentered at 180 °C for 30 s. A standard depth of 2/1 was chosen for the fastness test since dyeings on PET, especially in medium and heavy depths, are required to be reduction cleared, in order to secure optimum fastness of the dyeing to, for instance, washing, rubbing and perspiration. The colour fastness was determined according to International Standards; the specific tests used were ISO 105 C06/C2S (fastness to washing), ISO 105 X12 (fastness to rubbing), ISO 105 E04 (fastness to perspiration). Staining and change in colour were assessed using grey scales.

3. Results and discussion

3.1. Alkali-hydrolysis kinetics

Sulfonyl halide can be hydrolysed to the corresponding acid by a nucleophilic bimolecular substitution (S_N2) mechanism under alkaline conditions [11,12]. Therefore, it is presumed that azo disperse dyes containing fluorosulfonyl groups can be hydrolysed under alkaline conditions by a S_N2 mechanism as shown in Scheme 1.

Considering that addition of the hydroxide ion to the electrophilic sulfur atom is the rate-determining step of the hydrolysis reaction, and that the hydroxide ion concentration is kept constant by the use of a buffer or a large excess of alkali, the rate of the concentration decrease of the parent dye in the alkaline solution can be expressed by Eq. (1) [13]:

$$-\frac{d[P]}{dt} = k_{ps1}[P] \quad (1)$$

in which, $[P]$ is the concentration of the parent dye at hydrolysis time t, and k_{ps1} is the pseudo first-order rate constant of hydrolysis. The values of the peak areas of the components determined from the chromatograms are linearly related to their amount. Replacement of the concentrations of the parent dye with peak areas leads to Eq. (2):

$$\ln\left(\frac{A_0}{A}\right) = k_{ps1}t \quad (2)$$

where, A_0 and A are values of peak areas of the parent dye at the time $t=0$ and at a later time t. This equation shows that if $\ln(A_0/A)$ is plotted against t, then a first-order reaction will give a straight line [14].

In order to optimise the alkali-clearing condition in the polyester dyeing process, hydrolysis analysis of the disperse dyes containing fluorosulfonyl groups was carried out under various alkali concentrations and temperatures. From the results of a previous study on the hydrolysis analysis of the synthesised dyes, it was found that a hydrolysis temperature of 100 °C gave a higher hydrolysis rate, even in milder alkaline conditions, than at any other hydrolysis temperature. However, the temperature of 100 °C was not considered for determining optimum alkali-clearing conditions since the destruction of the dye molecules that have been diffused into the amorphous region could occur at a temperature above boiling point [7,8]. Hydrolysis was monitored every 5 min for 20 min since any conventional clearing process of a PET dyeing can take no longer than 20 min. Also, the feasibility of any commercial process would need to consider the energy consumption and dyeing effluent, together with wash fastness requirements.

Hydrolysis behaviour of dyes at 80 °C under the alkaline condition of 0.4 g/l NaOH is shown in Fig. 1. It shows the expected exponential decrease in the amount of parent dye with increasing hydrolysis time and the plot of $\ln(A_0/A)$ against time t yields a straight line passing through the origin with high correlation coefficients. Also, taking a closer look reveals that the dyes having more electron-accepting groups in the diazo component showed a lower rate of hydrolysis; however, no clear relationship between the electron-donating power of the substituents in the coupling components and the hydrolysis rate was found.

According to Eq. (2), the expected pseudo first-order kinetics was confirmed (Fig. 1) and the slope of the plot was calculated to determine the pseudo first-order rate constant k_{ps1}. Fig. 2 shows the determined pseudo first-order rate constants of synthesised dyes at different alkaline concentrations (NaOH 0.4, 1.0 and 2.0 g/l) and temperatures (80 and 90 °C). It is apparent that the effect of temperature between 80 and 100 °C on the hydrolysis rate between was more pronounced than ththe effect of the alkali concentrations between (0.4 and 2.0 g/l).

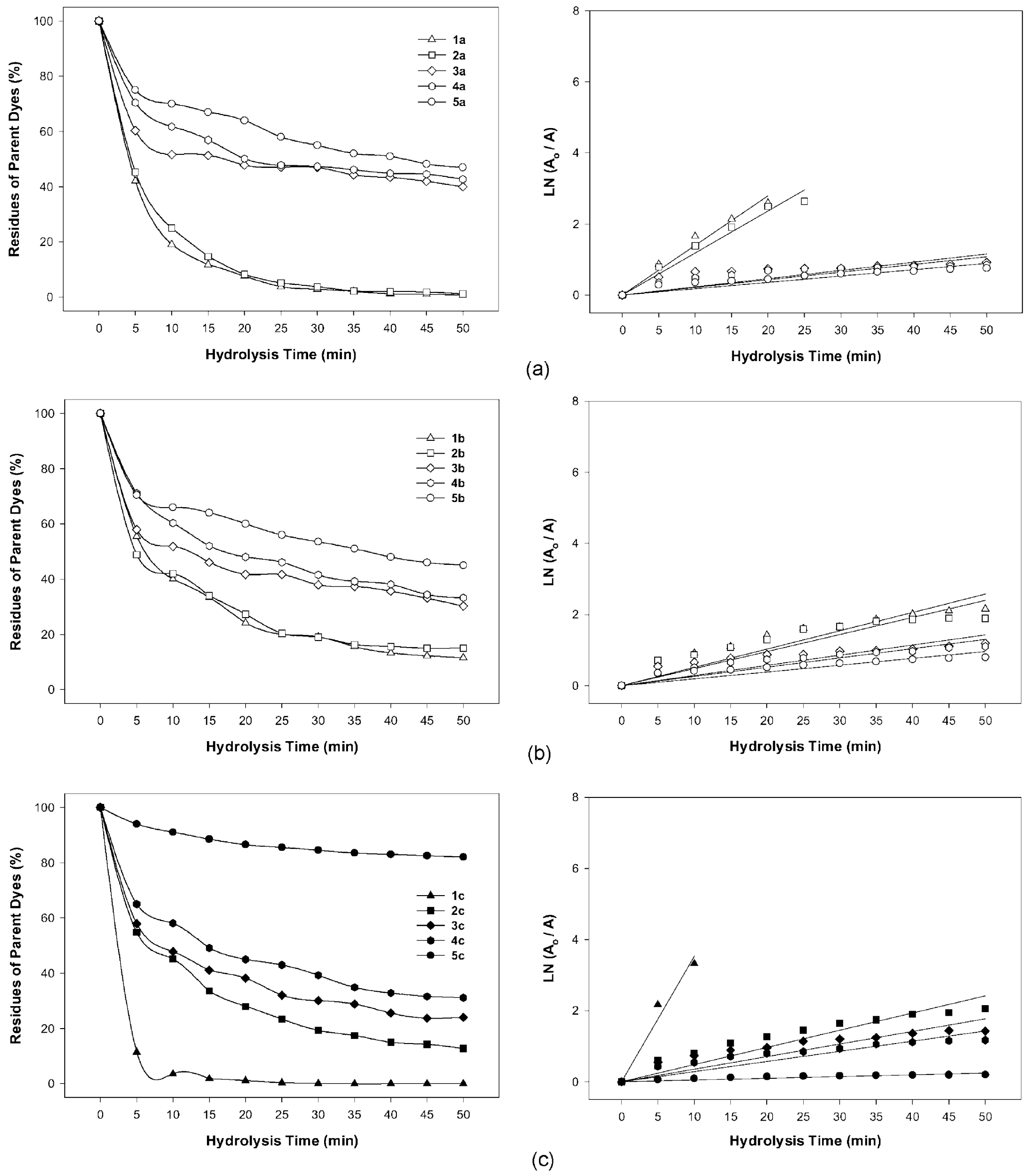


Fig. 1. Alkali-hydrolysis behaviours of **1**–**5** at 80 °C (NaOH 0.4 g/l): (a) **1a**–**5a**; (b) **1b**–**5b**; (c) **1c**–**5c**.

Assuming that any alkali clearing of polyester dyeing can take no longer than 20 min and that more than 70% hydrolysis (%) is required, then it seems that at temperatures of 80 °C, the rate of hydrolysis is slow and insufficient alkali clearance occurs even at 2.0 g/l of NaOH (Fig. 3). Therefore, in order to guarantee enough alkali clearability for the optimum wash fastness within 20 min, the optimum conditions that are 90 °C and 1.0 g/l of NaOH. However, in the case of dye **5c**, the hydrolysis was less than 70% even at the severest condition, i.e. 67% of hydrolysis at 90 °C and 2.0 g/l NaOH. From the overall results of hydrolysis, 20 min at 90 °C and 1.0 g/l NaOH was chosen for the optimum alkali-clearing condition.

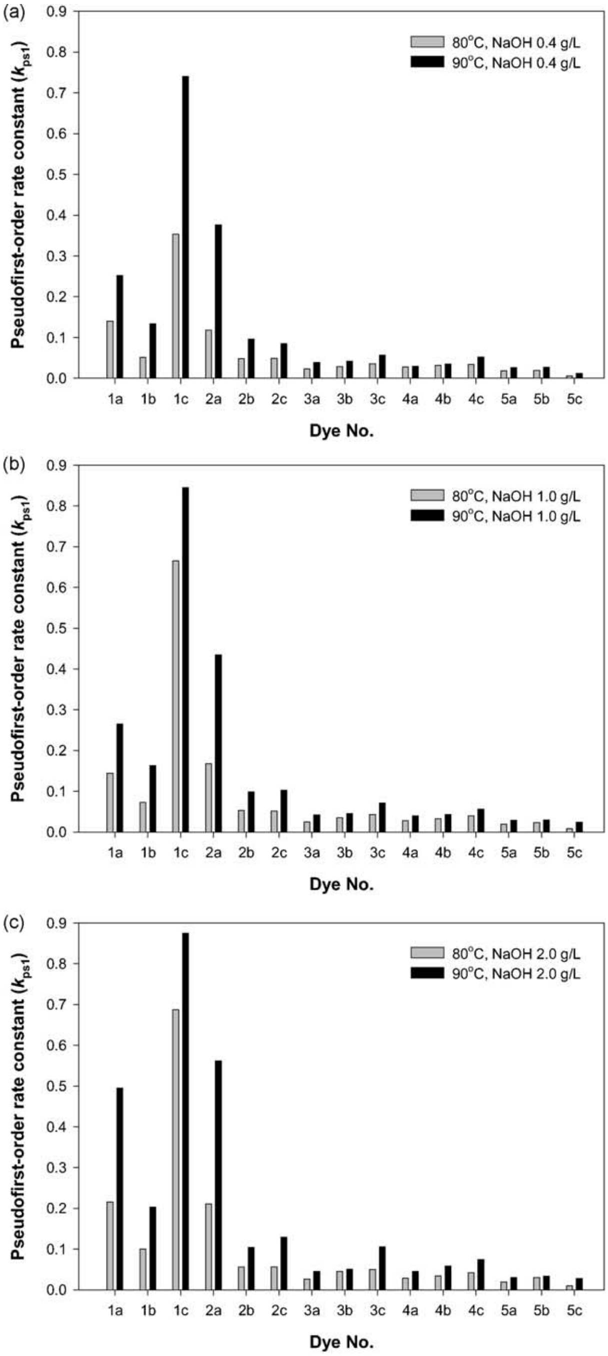


Fig. 2. Pseudo first-order rate constants of the dyes **1**–**5** at various alkali concentrations: (a) NaOH 0.4 g/l; (b) NaOH 1.0 g/l; (c) NaOH 2.0 g/l.

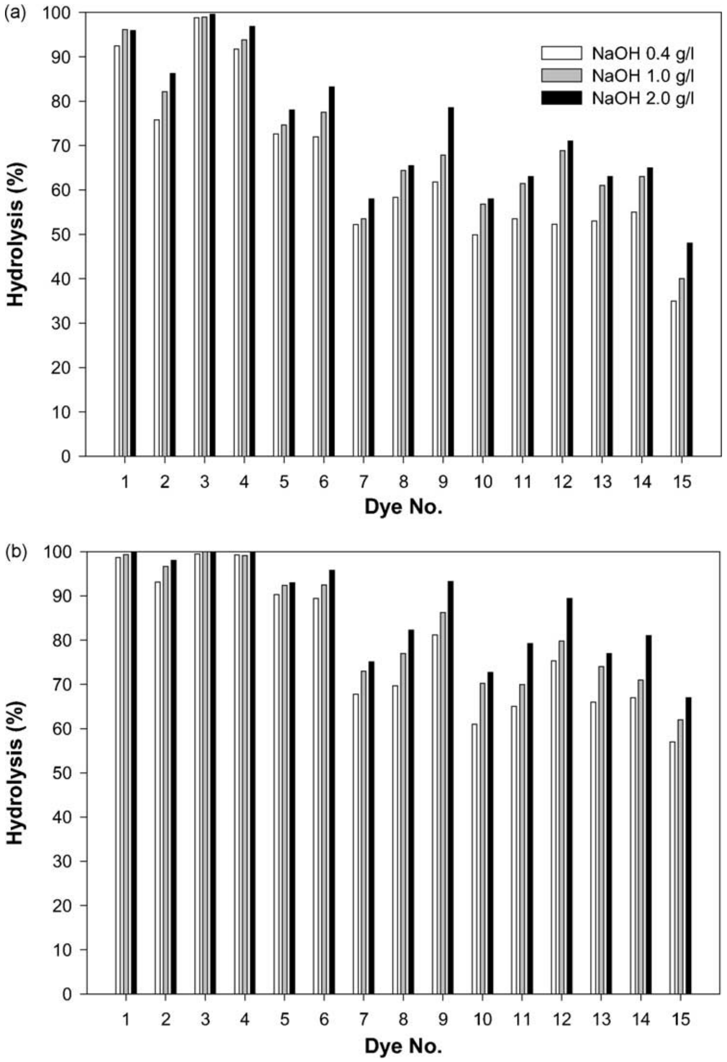


Fig. 3. Hydrolysis (%) of parent dyes **1**–**5** after 20 min at various alkali concentrations: (a) 80 °C; (b) 90 °C.

3.2. Fastness properties

The fastness of polyester dyeings of dyes **1**–**5** was examined in an attempt to assess whether the presence of the fluorosulfonyl function conferred the property of alkali-clearability. The fastness test was performed for dyeings which have been conventionally reduction cleared (RC) or received no treatment at all (NC). In addition, ratings were obtained for another set of dyeings which were treated only with 1.0 g/l of aqueous NaOH at 90 °C for 20 min (AC) in order to establish the effectiveness of attempting to clear using just alkali. Also, a proportion of the reduction- and alkali-cleared dyeings were heat set prior to washing to reveal the extent to which thermomigration undermines the effects of either type of clearing.

The synthesised dyes containing a fluorosulfonyl group showed excellent levels of wash fastness using the ISO 105 C06/C2S. The diacetate, nylon, polyester and wool components of multifibre adjacent fabrics are particularly prone to staining during washing of disperse dyed polyester and loss of sample colour did not occur perceptibly.

Figures for the staining of these fibres are shown in Table 2. Predictably, the reduction-cleared and alkali-cleared fabric exhibited similarly high fastness while non-cleared fabric gave some staining on multifibre adjacent fabric, presumably because the fluorosulfonyl group of the synthesised dyes is hydrolysed in alkali to solubilising sulfonate groups, as was investigated in a previous studies [7,8]. These alkali-clearable dyes are therefore readily removed by alkaline wash-offs, and exhibit low staining in wash fastness tests. In all cases, heat setting as anticipated lowered fastness owing to thermomigration, although, while ratings did not fall as low as those without clearing, the same values were obtained irrespective of whether reduction clearing or alkali clearing had been employed prior to the heat treatment. These results indicate that, with these synthesised disperse dyes containing a fluorosulfonyl group, alkali clearing can be used just as effectively as reduction clearing. Nylon and diacetate were consistently the most stained components of the multifibre, presumably because of the combination of the dye's substantivity for these materials and the fibres' accessibility at the test temperatures. While the dyes are substantive to polyester and acrylic, diffusion of the dyes into these materials at the test temperature is low and, consequently, staining was less pronounced than that with the nylon and diacetate. The hydrophilicity of cotton ensures that it was stained least.

Also, in the case of the rubbing fastness of the washed-off polyester dyeings, the reduction-cleared and alkali-cleared fabric exhibit similarly high fastness, while non-cleared fabric gave some staining on cotton (Table 3), which also supports the alkali-clearability of the synthesised dyes, as was indicated earlier. The ratings of colour fastness to rubbing for the alkali- or reduction-cleared samples were in the range of 4/5 to 5.

Ratings for fastness to perspiration of the synthesised dyes on polyester are listed in Tables 4 and 5. The diacetate, cotton, nylon and polyester

Table 2
Fastness to washing of dyes **1**–**5** (ISO 105 C06 C2S, 2/1 standard depth)[a]

Dye	No heat setting												Heat setting (180 °C, 30 s)							
	NC				AC				RC				AC				RC			
	D[b]	N[c]	P[d]	W[e]	D	N	P	W	D	N	P	W	D	N	P	W	D	N	P	W
1a	4/5	4	5	4/5	5	5	5	5	5	5	5	5	4/5	4/5	5	5	4/5	4/5	5	5
1b	5	4/5	5	4/5	5	5	5	5	5	5	5	5	4/5	4/5	5	5	4/5	4/5	5	5
1c	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
2a	5	4/5	5	4/5	5	5	5	5	5	5	5	5	4/5	4/5	5	5	4/5	4/5	5	5
2b	5	4/5	5	4/5	5	5	5	5	5	5	5	5	4/5	4/5	5	5	4/5	4/5	5	5
2c	5	4/5	5	5	5	5	5	5	5	5	5	5	5	4/5	5	5	5	4/5	5	5
3a	4/5	4	5	5	5	5	5	5	5	5	5	5	5	4/5	5	5	5	4/5	5	5
3b	4	3/4	5	4/5	5	5	5	5	5	5	5	5	4/5	3/4	5	4/5	4/5	3/4	5	4/5
3c	4/5	4	5	4/5	5	5	5	5	5	5	5	5	5	4	5	5	5	4	5	5
4a	4/5	4/5	5	4/5	5	5	5	5	5	5	5	5	4/5	4/5	5	4/5	4/5	4/5	5	4/5
4b	4/5	4	5	4/5	5	5	5	5	5	5	5	5	5	4	5	4/5	5	4	5	4/5
4c	4/5	4	5	4/5	5	5	5	5	5	5	5	5	5	4	5	4/5	5	4	5	4/5
5a	4/5	4/5	5	4/5	5	5	5	5	5	5	5	5	4/5	4/5	5	5	4/5	4/5	5	5
5b	4/5	4	5	4/5	5	5	5	5	5	5	5	5	5	4/5	5	5	5	4/5	5	5
5c	4/5	3/4	5	4	5	5	5	5	5	5	5	5	5	4/5	5	5	5	4/5	5	5

[a] All samples had ratings of 5 for colour change and staining of cotton and acrylic.

[b] D, diacetate.

[c] N, nylon.

[d] P, polyester.

[e] W, wool.

Table 3
Fastness to rubbing of dyes **1**–**5** (ISO 105 X12, 2/1 standard depth)

Dye	No heat setting						Heat-setting (180 °C, 30 s)			
	NC		AC		RC		AC		RC	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
1a	3/4	3	4/5	4/5	4/5	4/5	4/5	4	4/5	4
1b	4/5	5	5	5	5	5	4/5	4	4/5	4
1c	4/5	4/5	5	5	5	5	4/5	4/5	4/5	4/5
2a	5	5	5	5	5	5	5	4/5	5	4/5
2b	4/5	4	5	4/5	5	4/5	4/5	4/5	4/5	4/5
2c	5	5	5	5	5	5	5	5	5	5
3a	4/5	4/5	5	5	5	5	5	4/5	5	4/5
3b	5	5	5	5	5	5	5	5	5	5
3c	5	5	5	5	5	5	5	5	5	5
4a	4/5	4/5	5	5	5	4/5	4/5	4/5	4/5	4/5
4b	5	4/5	5	5	5	5	5	4/5	5	4/5
4c	5	4/5	5	5	5	5	4/5	4/5	4/5	4/5
5a	4/5	4/5	5	5	5	5	5	4/5	5	4/5
5b	5	5	5	5	5	5	5	5	5	5
5c	5	5	5	5	5	5	5	5	5	5

components of multifibre adjacent fabric are particularly prone to staining during the fastness test of disperse dyed polyester and loss of sample colour did not occur perceptibly. The majority of the polyester samples dyed with 4-amino-4′-fluorosulfonylazobenzene dyes, had excellent fastness (all ratings of 5), while the minority showed slight staining on adjacent fabrics. These results are not surprising because the polyester structure is still close-packed at body temperature (the level at which the test samples are maintained). Both the reduction-cleared and alkali-cleared fabric exhibited high fastness while non-cleared fabric gave a slight staining on cotton, which also supports the alkali-clearability of the synthesised dyes. The ratings of colour fastness to perspiration for alkali- or reduction-cleared, followed by the heat-setting, were in the range of 4/5–5 (Tables 4 and 5). The order of staining of the multifibre components was similar to that of the wash fastness tests: diacetate and nylon were stained most, presumably for the reasons mentioned earlier.

Table 4
Fastness to alkaline perspiration of dyes **1**–**5** (ISO 105 E04, 2/1 standard depth)

Dye	No heat setting												Heat setting (180 °C, 30 s)							
	NC				AC				RC				AC				RC			
	D[a]	C[b]	N[c]	P[d]	D	C	N	P	D	C	N	P	D	C	N	P	D	C	N	P
1a	4	4	4	4/5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
1b	4/5	4/5	4/5	4/5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
1c	4	4	4	4/5	5	5	5	5	5	5	5	5	4	4	4	4/5	4	4	4	4/5
2a	4/5	4/5	4/5	4/5	5	5	5	5	5	5	5	5	4/5	4/5	4/5	5	4/5	4/5	4/5	5
2b	4/5	5	4/5	5	5	5	5	5	5	5	5	5	4/5	4/5	4/5	5	4/5	4/5	4/5	5
2c	5	4/5	4/5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
3a	4/5	4/5	4/5	4/5	5	5	5	5	5	5	5	5	4/5	5	4/5	5	4/5	5	4/5	5
3b	4/5	4	4	4/5	5	5	5	5	5	5	5	5	5	5	5	5	4/5	5	4/5	5
3c	4/5	4/5	4/5	5	5	5	5	5	5	5	5	5	5	5	4/5	5	5	5	4/5	5
4a	4/5	4/5	4/5	4/5	5	5	5	5	5	5	5	5	5	5	4/5	5	5	5	4/5	5
4b	5	4/5	4/5	4/5	5	5	5	5	5	5	5	5	4/5	5	4/5	5	4/5	5	4/5	5
4c	5	4/5	4/5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
5a	4/5	4/5	4/5	4/5	5	5	5	5	5	5	5	5	4/5	5	4/5	5	4/5	5	4/5	5
5b	3/4	3/4	3/4	4/5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
5c	4/5	4/5	4/5	4/5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5

[a] D, diacetate.
[b] C, cotton.
[c] N, nylon.
[d] P, polyester.

Table 5
Fastness to acid perspiration of dyes 1–5 (ISO 105 E04, 2/1 standard depth)

Dye	No heat setting												Heat setting (180 °C, 30 s)							
	NC				AC				RC				AC				RC			
	D	C	N	P	D	C	N	P	D	C	N	P	D	C	N	P	D	C	N	P
1a	4	4	4	4/5	5	5	5	5	5	5	5	5	4/5	5	4/5	5	4/5	5	5	5
1b	4/5	5	5	5	5	5	5	5	5	5	5	5	4	4/5	4	4/5	4	5	4/5	4/5
1c	4	4/5	4/5	5	5	5	5	5	5	5	5	5	3/4	4	4	4	3/4	4	4	4
2a	4/5	4/5	4/5	5	5	5	5	5	5	5	5	5	4/5	4/5	4/5	4/5	4/5	5	5	4/5
2b	4/5	4/5	5	5	5	5	5	5	5	5	5	5	4/5	4/5	4/5	5	4/5	5	4/5	5
2c	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
3a	4/5	4/5	4	5	5	5	5	5	5	5	5	5	4/5	4/5	4/5	5	4/5	5	5	5
3b	4/5	4	4	4/5	5	5	5	5	5	5	5	5	4/5	5	4/5	5	4/5	5	4/5	5
3c	4/5	4/5	4/5	4/5	5	5	5	5	5	5	5	5	5	5	4/5	5	5	5	4/5	5
4a	4/5	5	4/5	4/5	5	5	5	5	5	5	5	5	4/5	5	4/5	5	4/5	5	4/5	5
4b	4/5	4/5	4/5	4/5	5	5	5	5	5	5	5	5	5	5	4/5	5	5	5	5	5
4c	4/5	5	5	5	5	5	5	5	5	5	5	5	5	5	4/5	5	5	5	4/5	5
5a	4/5	4/5	4/5	4/5	5	5	5	5	5	5	5	5	4/5	5	4/5	5	4/5	5	5	5
5b	3/4	3/4	3/4	4/5	5	5	5	5	5	5	5	5	5	5	4/5	5	5	5	4/5	5
5c	5	4	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5

4. Conclusions

Azo disperse dyes incorporating a fluorosulfonyl group hydrolysed under relatively mild alkaline conditions and temperatures. The hydrolysis of the fluorosulfonyl dyes in alkaline solutions at constant temperatures followed pseudo first-order kinetics. The dyes having more electron-accepting groups in the diazo component showed a lower rate of hydrolysis; however, no clear relationship between the electron-donating power of substituents in the coupling components and the hydrolysis rate was found. The effect of temperature on hydrolysis rate (between 80 and 100 °C) was more pronounced than that of alkali concentrations between 0.4 and 2.0 g/l. From the hydrolysis analysis results, in order to guarantee enough alkali clearance ($>70\%$) for the high fastness within 20 min, the optimum conditions were 90 °C and 1.0 g/l NaOH.

The use of fluorosulfonyl containing disperse dyes showed excellent dyeing fastness properties and offer the option of alkali clearance to achieve high wash fastness, replacing reductive clearing and particularly sodium hydrosulfite, which places a very high BOD on conventional disperse dyeing effluent and also generates aromatic amines. The results can be attributed to their excellent wash-off properties due to the alkali-clearability of fluorosulfonyl residues.

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