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Dyes and Pigments 68 (2006) 119–127

DYES and PIGMENTS

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Dyeing of nylon with reactive dyes. Part 2. The effect of changes in level of dye sulphonation on the dyeing of nylon with reactive dyes

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Received 13 January 2005; accepted 25 January 2005

Abstract

Four mono-functional reactive monochlorotriazinyl (MCT) dyes, each derived from the same chromophore and possessing a single monochlorotriazinyl reactive group, but differing only in degree of sulphonation, were synthesised and evaluated on nylon. The colour yield, degree of exhaustion, fixation, and the fastness properties of each dye were assessed. Initial exhaustion, at pH 4, was high for all dyes but percentage fixation, via covalent bond formation, increased with increasing levels of sulphonation. In all cases fixation efficiency reduced markedly with increasing concentrations of dye applied.

Keywords: Reactive dyes; Nylon; Fixation efficiency; Sulphonation

1. Introduction

The colouration of nylon is usually achieved with acid dyes [1,2]. These attach to the nylon via ion–ion linkages between the cationic, protonated, amino end groups of the nylon (NH_3^+) and the anionic sulphonate residue of the dye ($Dye-SO_3^-$). Although this mode of attachment renders the dyeing of nylon straightforward, at least in principle, the wet fastness is usually less than ideal, and there is often a delicate balance to be struck between level dyeing performance and wet fastness. Loss of colour and staining of adjacent fabrics arises from the facile partial dissociation of ion–ion links between dye and nylon.

In the case of dyes for cellulosic fibres high wet fastness has most often been achieved by the use of fibre reactive dyes: these function by reacting chemically with the cellulose, thus forming covalent links between fibre and dye [3–5]. Invariably, these dyes possess one or more electrophilic reactive groups, which are capable of reacting with de-protonated, nucleophilic [5,6], cellulosate anion. This mode of application is reliant upon a sufficiently large concentration of suitable hydroxyl groups being present in the cellulose to react with dye and thereby furnish heavy depths of shade.

The most notable commercial ranges, of reactive dyes for nylon, have probably been the Stanalan [7] and Eriofast [8] dyes. Other water soluble dyes possessing electrophilic reactive groups such as chlorodifluoropyrimidines [9], bromoacrylamides [10], chlorotriazines and vinylsulphones [11,12], as well as some disperse types [13] have also been evaluated on nylon. In order to render reactive dyes for nylon attractive to potential customers it is necessary that any such products exhibit an attractive balance of technical and commercial

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0143-7208/$ - see front matter © 2005 Published by Elsevier Ltd.
doi:10.1016/j.dyepig.2005.01.012

properties. Desirable technical features include high fixation, good build-up and fastness properties.

Additionally, dyes should not be prohibitively expensive. The thrust of most published work on reactive dyes for nylon has been a comparison of the relative efficacies, on nylon, of existing cellulose reactive dyes. However, much less has been reported on the effect of other dye parameters, such as molecular size and degree of sulphonation, on the application properties of reactive dyes on nylon. We have recently reported that molecular size and shape are important in determining final dye fixation [14]. Additionally, degree of sulphonation, and hence net negative charge, of a dye is important in determining its substantivity and exhaustion on cellulosic fibres. In this case, greater sulphonic acid group concentration leads to greater electrostatic repulsion between anionic dye and anionic cellulose. In the case of dyeing nylon, at low pH, the reverse might be expected. A greater degree of sulphonation, hence net negative charge, might be expected to lead to greater attraction with the positively charged fibre (Nylon—NH_3^+ under acidic conditions). Additionally, at higher pH the net charge of the nylon is negative, due to presence of anionic carboxylic acid groups and hence, at higher pH values, an increasing level sulphonation of dye might be expected to lead to reduced attraction between dye and nylon. Therefore, in order to determine the influence of the degree of sulphonation of dyes on the dyeing of nylon, selected dyes, based on the same chromophore, reactive group, and of similar molecular size and shape, but differing only in degree of sulphonation, were synthesised and evaluated.

2. Experimental

Visible absorption spectra were recorded using a Phillips model PU 8700 UV/visible spectrophotometer. Thin layer chromatography (TLC) was performed using aluminium plates coated with silica gel 60 F254 (Merck) as stationary phase, and a mixture of *iso*-butanol:*n*-propanol:ethyl acetate:water in the ratio 2:4:1:3 as mobile phase. The developed plates were visualised under both short and long wavelength ultraviolet light (254 nm, 365 nm). High performance liquid chromatography (HPLC) was performed using a Hewlett-Packard 1100 liquid chromatograph with a 10 cm, Purospher RP-18 (5 μm) packing and LichroCART 125-4 HPLC column cartridges. The mobile phases used were 0.25% CHAP solution (cyclohexylammonium phosphate) as solvent A and acetonitrile (HPLC grade) as solvent B. These solvents were passed through the column, maintained at 40 °C, in fixed ratio A:B (70:30) at the rate of 2 ml/min, and the samples were analysed spectroscopically using a diode array detector at a wavelength range from 250 nm to 650 nm. Elemental analyses for carbon, hydrogen, nitrogen and sulphur were carried out at the Department of Chemistry, UMIST, on a Carlo Erba 1108 element analyser. Mass spectrometry was performed using two different techniques, fast atomic bombardment and MALDI (matrix assisted laser adsorption ionisation) at the Department of Chemistry, UMIST. Scoured, modified nylon 6.6 "*Tactel Coloursafe*" fabric was supplied by Du Pont (UK).

2.1. Preparation of dyes

A series of dyeings were conducted using the four novel red reactive dyes listed in Table 1. The dyes, Dye 1 to Dye 4, were prepared as described below.

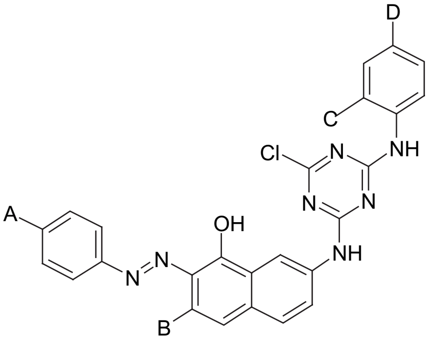
2.1.1. 1-Hydroxy-2-phenylazo-7-[2-chloro-4-(phenylamino-)triazin-6-ylamino-]naphthalene-3-sulphonic acid (Dye 1)

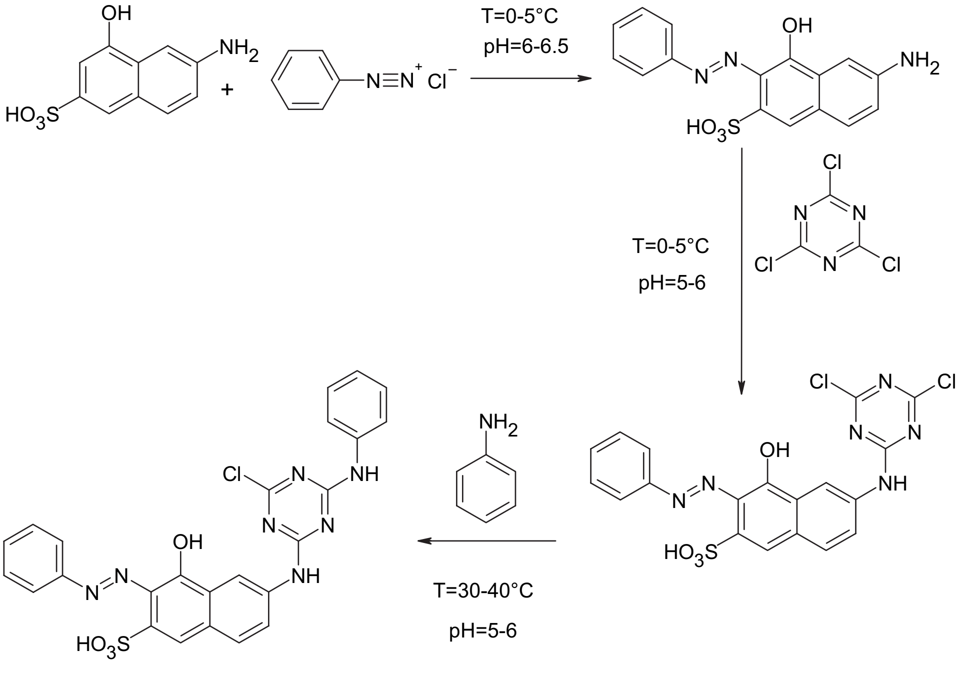
This was prepared by the route depicted in Scheme 1.

A solution of sodium nitrite (3.62 g, 0.058 mol), in water (20 ml), was added slowly to a mixture of aniline (4.66 g, 0.05), in water (20 ml) and hydrochloric acid (36%, 14.19 ml, 0.125 mol), at 0–5 °C. After 30 min at 0–5 °C and pH less than 2, excess nitrous acid was destroyed by adding sulphamic acid. The resulting solution of benzene diazonium chloride was added slowly to a solution of γ-acid (1-hydroxy-7-amino-naphthalene-3-sulphonic acid) (11.9 g, 0.05 mol), at pH 6–6.5. The mixture was stirred for 30 min at room temperature and at pH 6.5. The solid red product (1-hydroxy-2-phenylazo-7-aminonaphthalene-3-sulphonic acid) was collected and purified by dissolving in distilled water (100 ml) and re-precipitating by slow addition of potassium chloride (30% w/v) to the stirred solution.

Table 1
Novel reactive dyes synthesized and used for dyeing, *Tactel Coloursafe*

Dye	A	B	C	D
Dye 1	H	SO_3H	H	H
Dye 2	SO_3H	SO_3H	H	H
Dye 3	SO_3H	SO_3H	H	SO_3H
Dye 4	SO_3H	SO_3H	SO_3H	SO_3H





Scheme 1. Synthesis of Dye 1.

The resulting precipitated solid was collected and used direct.

2,4,6-Trichloro-*s*-triazine (9.4 g, 0.051 mol) in acetone (10 ml) and crushed ice (10–20 g), was added slowly to a solution of freshly purified 1-hydroxy-2-phenylazo-7-aminonaphthalene-3-sulphonic acid, prepared above, in distilled water (100 ml), at below 5 °C, and at pH 5–6. The mixture was stirred for 30 min at pH 6.5 with control by TLC and HPLC and the resulting red product, 1-hydroxy-2-phenylazo-7-(2,4-dichlorotriazin-6-ylamino-)naphthalene-3-sulphonic acid, collected by filtration. The product was purified by dissolving in distilled water (100 ml) and re-isolated by slow addition of potassium chloride (20% w/v). Because of the known instability of dichlorotriazines, the product was used direct without further characterisation.

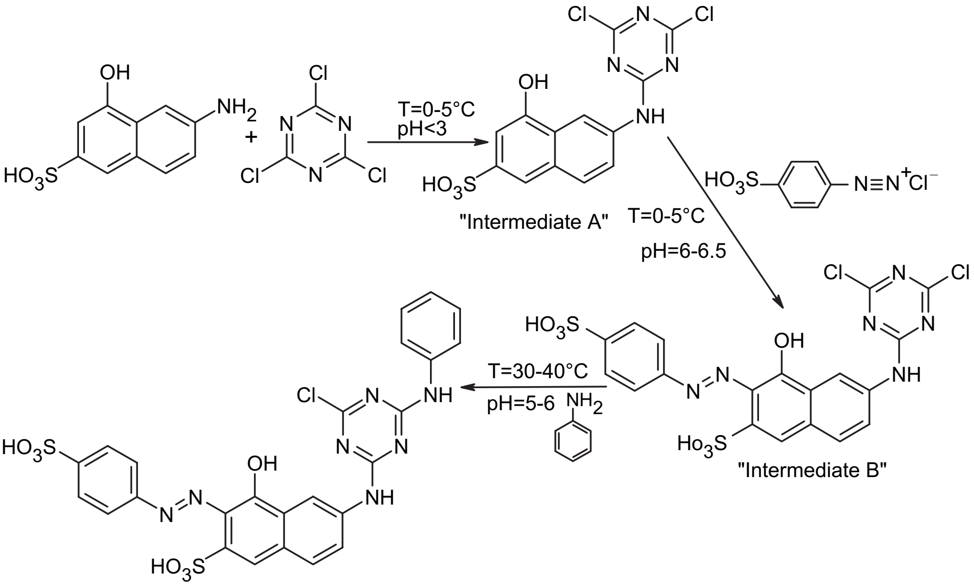
Aniline (4.66 g, 0.05 mol) was added slowly to the 1-hydroxy-2-phenylazo-7-(2,4-dichlorotriazin-6-ylamino) naphthalene-3-sulphonic acid thus prepared, in distilled water (100 ml), and the temperature was raised to 30–40 °C with stirring, at pH 5–6, for 2 h, with control by TLC and HPLC. When the reaction was complete, the solution was allowed to stand for 30 min, and the resulting precipitated product, 1-hydroxy-2-phenylazo-7-[2-chloro-4-(phenylamino-)triazin-6-ylamino]naphthalene-3-sulphonic acid, was collected by filtration and purified by dissolving in distilled water (100 ml) and re-precipitating by the slow addition of ethanol (200 ml). The product was essentially homogeneous as judged by TLC (Rf = 0.8), and HPLC (RT = 5.45 min).

The Mol. In of the product, that is the weight in gram of product which contains 1 mol of "pure" dye, was determined by titration against titanium III chloride and microanalysis. Mol. In and purity by titanous titration = 695, (79% e.a). Elemental analysis: Calc. for $C_{25}H_{18}N_7O_4SCl$: C, 54.79%; N, 17.9%. Found: C, 42.2%; N, 13.8%, corresponds to an effective agent (e.a) content of, 77%. Mass spectrometry *m*/*e*: 530 (M–OH), 548 (M), 549 (M + 1).

2.1.2. 1-Hydroxy-2-(4-sulphophenylazo)-7-[2-chloro-4-(phenylamino)triazin-6-ylamino] naphthalene-3-sulphonic acid (Dye 2)

This was prepared by the route depicted in Scheme 2.

Hydrochloric acid was added to a solution of γ-acid (1-hydroxy-7-aminonaphthalene-3-sulphonic acid) (11.38 g, 95.3% e.a, 0.05 mol) at 5 °C to produce a suspension at pH less than 4. 2,4,6-Trichloro-*s*-triazine (9.5 g, 0.05 mol) in acetone (30 ml) and crushed ice (10–20 g) was added very slowly to the γ-acid suspension at below 5 °C and at pH 2–3 with control by TLC and HPLC to give Intermediate A, 1-hydroxy-7-(2,4-dichlorotriazin-6-ylamino)naphthalene-3-sulphonic acid. A solution of sodium nitrite (3.62 g, 0.058 mol), in water (20 ml) was added slowly, at 0–5 °C, to a solution of sulphanilic acid (8.65 g, 0.05 mol) in water (20 ml) and hydrochloric acid (36%, 14.19 ml, 0.125 mol). After 30 min at 0–5 °C and pH less than 2, excess nitrous acid was destroyed by adding sulphamic acid. The solution of the resulting diazonium salt was added slowly to the solution of Intermediate A,



Scheme 2. Synthesis of Dye 2.

1-hydroxy-7-(2,4-dichlorotriazin-6-ylamino-)naphthalene-3-sulphonic acid, at pH 6–6.5. The mixture was stirred for 30 min at pH 6.5 and the resulting dye, Intermediate B, was precipitated by salting, and purified using a procedure similar to that used for Dye 1.

Aniline (4.66 g, 0.05) was added slowly to the solution of Intermediate B, in distilled water (100 ml). The temperature was raised to 30–40 °C, and the pH maintained at 5–6 for 2 h, with control by TLC and HPLC. When the reaction was complete, the solution was allowed to stand for 30 min, and the product, 1-hydroxy-2-(4-sulphophenylazo)-7-[2-chloro-4-(phenylamino)triazin-6-ylamino-]naphthalene-3-sulphonic acid, was precipitated by the slow addition of potassium chloride (KCl, 15% w/v), isolated by filtration and dried under vacuum. The resulting solid was purified by the dissolving in distilled water (100 ml) and re-precipitating by the slow addition of industrial methylated spirits (200 ml). The product was essentially homogeneous as judged by TLC and HPLC.

Mol. In by titanous titration = 800, (78% e.a). Elemental analysis: Calc. for $C_{25}H_{18}N_7O_7S_2Cl$, C, 47.8%; N, 15.6%. Found: C, 37.9%; N, 12.4%. Mol. In = 790 (79% e.a). Mass spectrometry *m/e*: 628 (M).

2.1.3. 1-Hydroxy-2-(4-sulphophenylazo)-7-[2-chloro-4-(4-sulphophenylamino)triazin-6-ylamino]naphthalene-3-sulphonic acid (Dye 3)

This was prepared by the route depicted in Scheme 3.

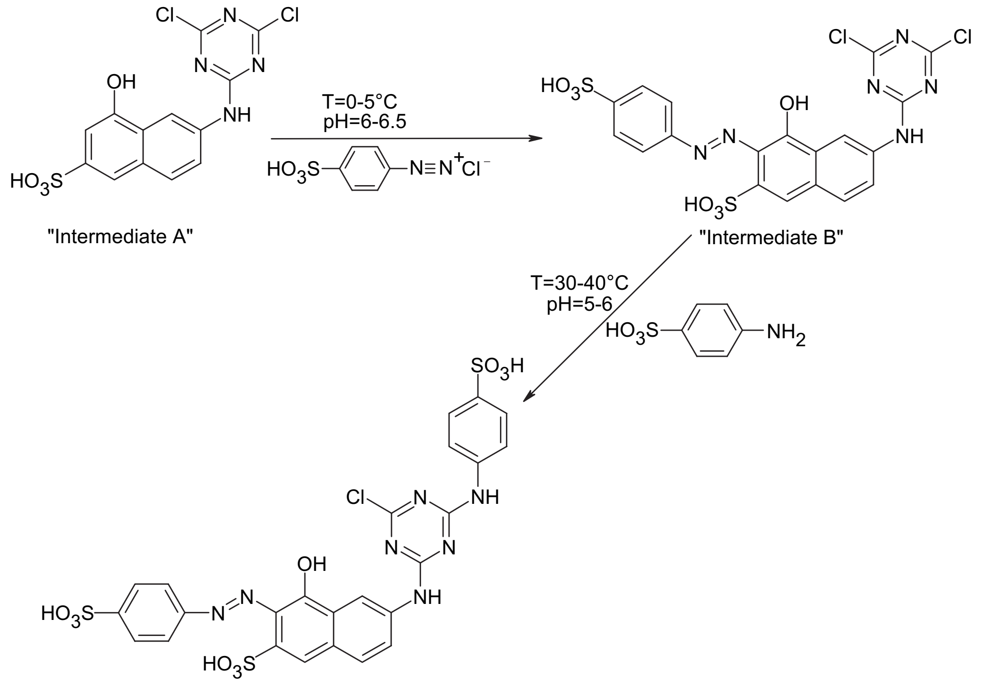
Dichlorotriazinyl reactive dye, 1-hydroxy-2-(4-sulphophenylazo)-7-(2,4-dichlorotriazin-6-ylamino)naphthalene-3-sulphonic acids, was prepared as described above and used direct. Sulphanilic acid (8.65 g, 0.05 mol) was added slowly to the solution of Intermediate B, 1-hydroxy-2-(4-sulphophenylazo)-7-(2,4-dichlorotriazin-6-ylamino)naphthalene-3-sulphonic acid, in distilled water (100 ml). The temperature was raised to 30–40 °C, at pH 5–6 for 2 h with control by TLC and HPLC. When the reaction was complete, the mixture was allowed to stand for 30 min, the red product, 1-hydroxy-2-(4-sulphophenylazo)-7-[2-chloro-4-(4-sulphophenylamino)triazin-6-ylamino]naphthalene-3-sulphonic acid, was precipitated by slow addition of potassium chloride (KCl, 30% w/v). The resulting solid was re-dissolved in distilled water (100 ml) and precipitated with industrial methylated spirits. The product was essentially homogeneous as judged by TLC (Rf = 0.6) and HPLC (RT = 4.2 min).

Mol. In by titanous titration = 833, (85% e.a). Elemental analysis: Calc. for $C_{25}H_{18}N_7O_{10}S_3Cl$: C, 42.4%; N, 13.85%. Found: C, 32.7%; N, 10.3% corresponds to Mol In = 934 (76% e.a). Mass *m/e*: 628 (M−SO_3H), 708 (M).

2.1.4. 1-Hydroxy-2-(4-sulphophenylazo)-7-[2-chloro-4-(2,4-disulphophenylamino)triazin-6-ylamino]naphthalene-3-sulphonic acid (Dye 4)

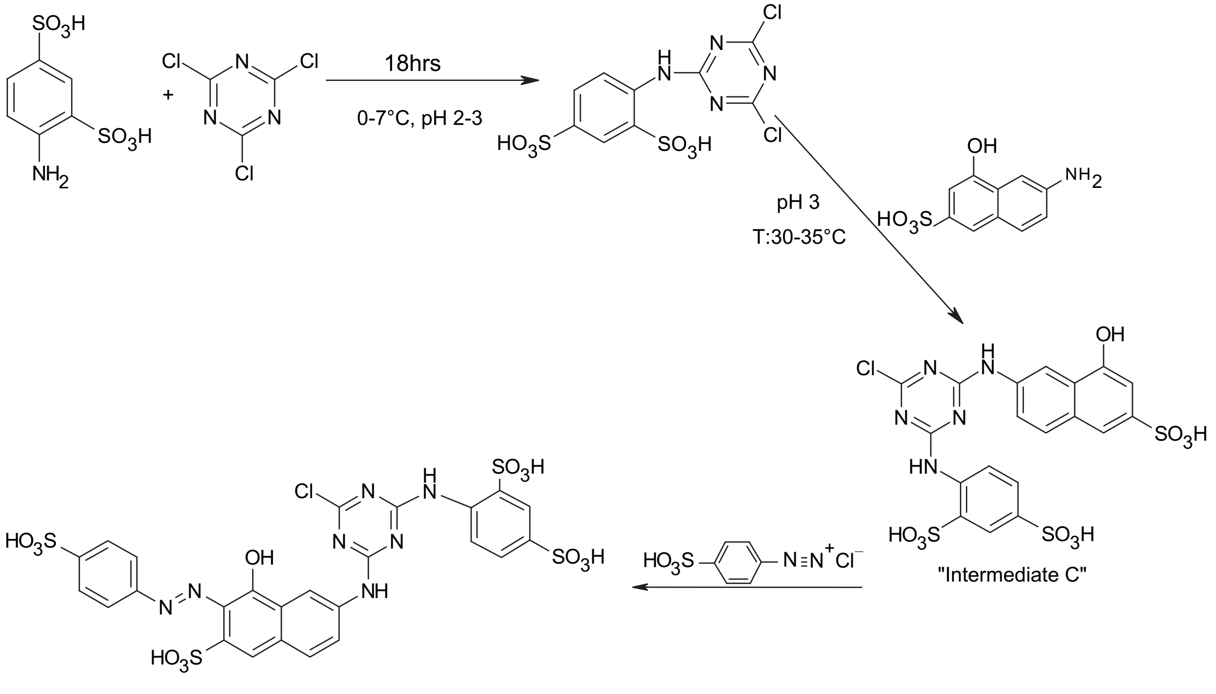
This was prepared by the route depicted in Scheme 4.

2,4,6-Trichloro-*s*-triazine (9.5 g, 0.05 mol) in acetone (30 ml) and crushed ice (10–20 g), was added very slowly to the solution of aniline-2,4-disulphonic (12.7 g, 0.05 mol) in distilled water (100 ml) at 5 °C and pH 3.5, the mixture was stood for 18 h, with stirring and control by TLC and HPLC, to produce the desired product, 2,4(dichloro)-6-(2,4-disulphophenylamino)triazine. This was added to a suspension of γ-acid (11.9 g, 0.05 mol), and the temperature raised to 30–35 °C, at pH 3–4, with control by TLC and HPLC, to produce,



Scheme 3. Synthesis of Dye 3.

1-hydroxy-7-[2-chloro-4-(2,4-disulphophenylamino)triazin-6-ylamino]naphthalene-3-sulphonic acid, Intermediate C, which was used direct without isolation. A solution of 4-sulphophenyldiazonium chloride (0.05 mol), prepared as described above, was added slowly to the stirred solution of "Intermediate C" at pH 6–6.5. After 30 min at pH 6, the product, 1-hydroxy-2-(4-sulphophenylazo)-7-[2-chloro-4-(2,4-disulphophenylamino)triazin-6-ylamino]naphthalene-3-sulphonic acid, was precipitated by slow addition of potassium chloride (KCl, 20% w/v), and was essentially homogeneous as judged by TLC (Rf = 0.58)and HPLC (RT = 4.1 min).



Scheme 4. Synthesis of Dye 4.

Mol. In by titanous titration = 995, (79%). Elemental analysis: Calc. for $C_{25}H_{18}N_7O_{13}S_4Cl$: C, 38.1%; N, 12.4%. Found: C, 28.2%; N, 8.9%. Mol. In = 1080, (73% e.a). Mass *m*/*e*: 707 ($M-SO_3H$), 788.5 (M + H).

2.1.5. 1-Hydroxy-2-(4-sulphophenylazo)-7-[2-hydroxy-4-(2,4-disulphophenylamino)triazin-6-ylamino]naphthalene-3-sulphonic acid (Dye 5)

Dye 4 (2 g, 0.0013 mol) was dissolved in distilled water. Sodium hydroxide (2 N, 10 ml) was added and the solution was heated at 50 °C for 4 h with control by HPLC (RT = 3.8 min) and TLC (Rf = 0.6). The resulting hydrolysed dye was precipitated by the addition of industrial methylated spirits, isolated by filtration and dried under vacuum.

Mol. In by titanous titration = 995, (77% e.a). Mass *m*/*e*: 770 (M + H).

2.2. Dyeing

A Roaches dyeing machine (Mathis Labomat BFA 12) was used to dye 5 g pieces of fabric, at a liquor ratio of 20:1, in stainless steel dyepots of 200 cm^3 capacity. The dyeing method is depicted in Fig. 1. At the end of the dyeing, fabric was removed and rinsed in cold tap water for 5 min. Dyeings were carried out at eight depths of shade (0.05%, 0.1%, 0.2%, 0.5%, 0.8%, 1%, 1.5% and 2% o.m.f), at pH 4 using a McIlvaine buffer as shown in Table 2 [15].

2.3. Colour strength (*K*/*S*) of dyes on fabric

Reflectance measurements on the dry dyed fabrics were carried out using a Datacolor Spectraflash 600 specrophotometer under a D65 lamp. The dyed fibre was folded twice so as to provide four layers and the average of three reflectance measurements, taken at different positions, was used.

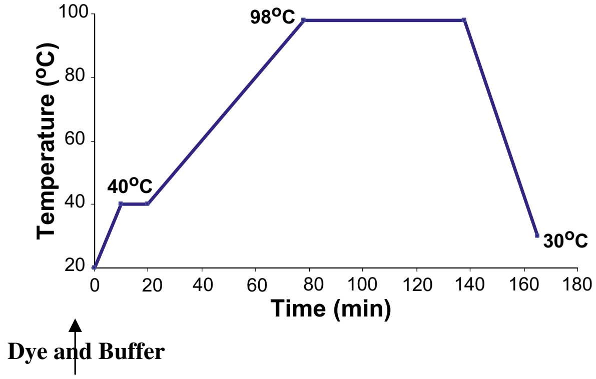


Fig. 1. Dyeing profile for the commercial reactive dyes.

Table 2
Composition of McIlvaine buffer in a total volume of 80 cm^3

pH	0.2 M Na_2HPO_4 (cm^3)	0.1 M citric acid (cm^3)
4	30.9	49.1

2.4. Dye exhaustion

The extent of dye exhaustion (%*E*) was determined spectrophotometrically. The absorbance of each dyebath solution before and after dyeing was measured, using 1 cm quartz cells housed in a Philips PU 8720 UV/visible scanning spectrophotometer, at the λ_{max} of each dye. The percentage dyebath exhaustion (%*E*) was calculated from Eq. (1), where A_0 and A_1 are the absorbance of the dyebath before and after dyeing, respectively.

$$\%E=\frac{A_0-A_1}{A_0}\times 100 \tag{1}$$

2.5. Dye fixation

Only a proportion of the total dye which exhausts on to the substrate reacts to form covalent linkages, whilst the remaining dye is attached by ionic bonds and by van der Waals forces. Therefore, in order to determine the degree of dye fixation the following procedure was used. A sample (1 g) of dyed fabric was immersed in 150 cm^3 of 20% aqueous pyridine solution, the temperature was raised rapidly to boiling and treatment continued under reflux until no further dye was removed from the fibre, this took approximately 3 h. The stripped dyeing was thoroughly rinsed in tap water and allowed to dry at room temperature. The percentage of exhausted dye which fixed was determined by a method used by several earlier workers [9–14] using Eq. (2), where $(K/S)_1$ and $(K/S)_2$ represent the colour strength of the dyeing before and after stripping, respectively. This method assumes, at least at the concentrations of dyes employed, that (*K*/*S*) values are proportional to the concentration of dye on fabric.

$$\%F=\frac{(K/S)_2}{(K/S)_1}\times 100 \tag{2}$$

The overall fixation efficiency of dye (%*T*) was then calculated using Eq. (3).

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

2.6. Determination of effective agent content of dyes

The effective agent content of each dye was determined by titration against titanium (III) chloride as

Table 3
Extinction coefficient, ε_{max}, and wavelength of maximum absorbance, λ_{max}, of novel reactive red dyes

Dye	λ_{max} (nm)	ε_{max} ($mol^{-1} cm^{-1} l$)
Dye 1	519	17,550
Dye 2	515	20,162
Dye 3	511.2	20,328
Dye 4	506.2	24,345

previously described [14,16,17]. Invariably the products as isolated contained salt and water, Mole In (MI) represents the weight in grams of dye, as isolated, which contains 1 mol of "pure" dye. To confirm the results obtained by titration against titanium (III) chloride, the percentage effective agent contents of the dyes were also determined by microanalysis. In the latter method the average of the figures for carbon and nitrogen only were used.

2.7. Visible absorption spectra of dyes

Solutions of the four novel dyes Dye 1 to Dye 4, in the concentration range of (0.01–0.12 g/l), were prepared in water buffered to pH 7, and the visible absorbance values (optical densities) were measured at the wavelength of the maximum absorption, using 1 cm cells and a Philips model PU8720 spectrophotometer. The molar extinction coefficients (ε_{max}) of the dyes were determined and are shown in Table 3.

3. Results and discussion

3.1. Visible absorption spectra of dyes

The dyes were yellowish red and the wavelengths of maximum absorption varied from 506 nm (Dye 4) to 519 nm (Dye 1). Thus the dye derived from aniline as diazo component (D1), was the most bathochromic. This is consistent with the known behaviour of hydrazo derivatives of this type in which an electron withdrawing group e.g. the sulphonate group in the diazo compound of Dye 2, Dye 3, and Dye 4, causes a hypsochromic shift. The strength of the dyes, as assessed by molar extinction coefficients, varied slightly, but were approximately 20,000 $mol^{-1} cm^{-1}$. The effect of successively introducing electron withdrawing sulphonate groups into the "second leg" component attached to the halotriazine also resulted in a hypsochromic shift. Thus Dye 4, λ_{max} 506 nm, aniline-2,4-disulphonic acid as "second leg" was hypsochromic relative to Dye 3, sulphanilic acid as "second leg", λ_{max} 511 nm, which was hypsochromic relative to Dye 2, λ_{max} 515 nm, aniline as "second leg".

Table 4
Effective agent content of novel dyes

Dye	Molecular weight (M_W)	Mole. In (MI)	Strength (%)
Dye 1	547.5	957	53.8
Dye 2	627.5	795	79
Dye 3	707.5	884	89
Dye 4	787.5	1037	76
Dye 5	769	995	77

Table 5
$(K/S)_1$, $(K/S)_2$, %E and %T of dyes at pH 4

Dye		Dye (o.m.f)			
		0.09	0.36	0.72	1.44
Dye 1	$(K/S)_1$	1.1	4.2	8.3	15.9
	$(K/S)_2$	0.45	0.52	0.79	1.1
	%E	100	100	100	100
	%F	41	12.5	9.5	6.9
	%T	41	12.5	9.5	6.9
Dye 2	$(K/S)_1$	0.8	3.1	6.2	12.7
	$(K/S)_2$	0.8	0.85	1.3	1.8
	%E	100	100	100	100
	%F	100	27.2	21	14
	%T	100	27.2	21	14
Dye 3	$(K/S)_1$	0.8	3.0	6	12
	$(K/S)_2$	0.8	1.2	2.2	2.4
	%E	100	100	96.9	95.05
	%F	100	40	36.6	20
	%T	100	40	35.5	19
Dye 4	$(K/S)_1$	0.6	2.3	4.7	8.7
	$(K/S)_2$	0.6	1.5	2.7	3.5
	%E	100	100	98.2	92.1
	%F	100	65	57.4	40
	%T	100	65	56.4	37
Dye 5	$(K/S)_1$	–	1.3	2.6	5
	$(K/S)_2$	–	0.2	0.3	0.5
	%E	–	100	100	98
	%F	–	15.3	11.5	10
	%T	–	15.3	11.5	9.8

3.2. Build-up properties of dyes on nylon

Having established from earlier work [14] that the optimum pH for application of dyes was 4, the build-up properties of the dyes were determined using the dyeing profile shown in Fig. 1. The strengths of the dyes were

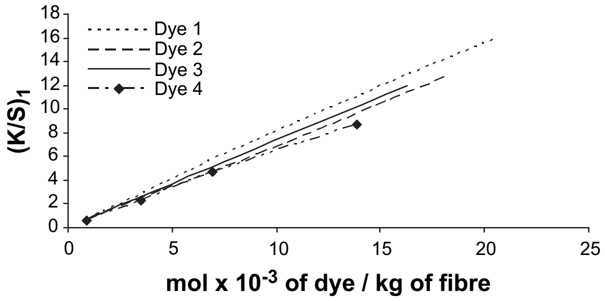


Fig. 2. Effect of degree of sulphonation on the initial exhaustion $(K/S)_1$ values of dyes.

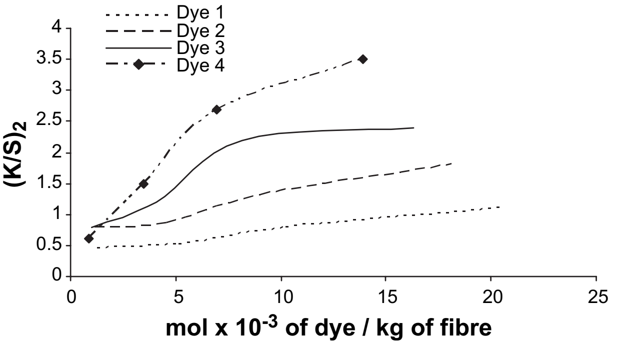


Fig. 3. Effect of degree of sulphonation on the final exhaustion $(K/S)_2$ values of dyes.

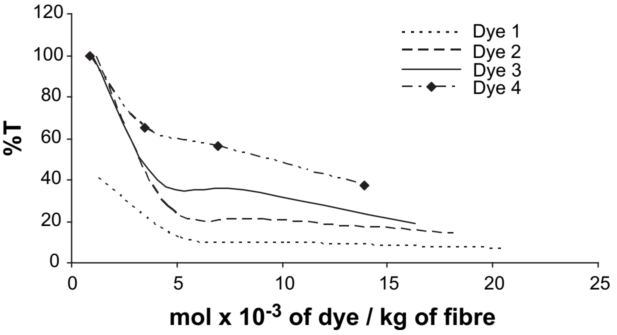


Fig. 4. Effect of degree of sulphonation on the total fixation (%T) of dyes.

determined by titration with titanium (III) chloride [17] and the results are shown in Table 4.

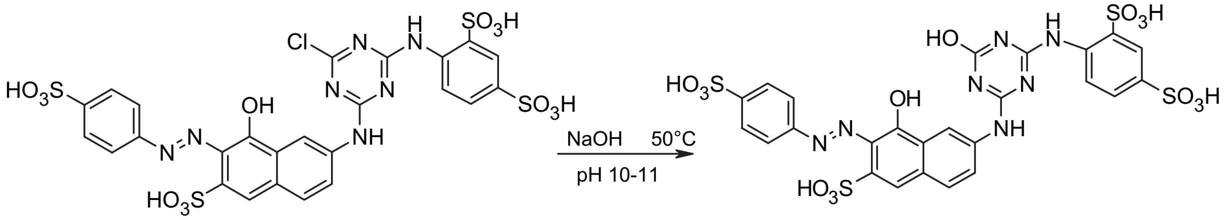
Table 5 lists the build-up data (K/S values) and percentage fixation (%T) obtained on dyeing nylon 6.6 with the novel anionic red reactive dyes at pH 4.

Results are depicted graphically below, Figs. 2–4. In order to obviate discrepancies arising from the different molecular weights and effective agent contents of the dyes, build-up data were plotted using milli-molar concentrations of dye o.m.f; therefore, the dye concentration on the x-axis has been expressed in milli-moles of dye per kilogram of fibre.

All four dyes are derived from the same chromophore and each possesses a single monochlorotriazinyl unit as reactive group. From the results displayed in Table 5 and Figs. 2–4, it can be seen that the levels of initial exhaustion $(K/S)_1$ are extremely high for all dyes, at all depths of shade. This presumably reflects almost complete attachment by ion–ion bonding between anionic dye and cationic protonated primary amino groups on fibre. However, the final exhaustion, $(K/S)_2$, appears to increase with increasing degree of sulphonation, as does the level of fixation. In terms of final exhaustion and percentage fixation, the tetra-sulphonic acid dye (Dye 4) was more fixation efficient than the tri, di and mono sulphonic acid dyes analogues (Dye 3, Dye 2 and Dye 1). This may suggest that in the case of percentage fixation, a greater degree of sulphonation, hence net negative charge leads to greater attraction with the positively charged fibre (Nylon$-NH_3^+$) under acidic conditions. Within this relatively enclosed micro-environment, any un-protonated amino end group can react with adsorbed dye molecule, resulting in dye–fibre covalent bond formation. Since the possibility of ion–ion bonding is very high it was necessary to prove that fixation occurs via covalent bond formation. Accordingly, a non-reactive dye (Dye 5), (Scheme 5) which was otherwise identical in structure to Dye 4, was synthesised. This was accomplished by simple hydrolysis in aqueous alkali; under these conditions the reactive chlorotriazine was converted to a non-reactive hydroxytriazine, capable of forming only ion–ion bonds with fibre. Thus, if the hydrolysed dye exhibits similar fixation characteristics to its chlorotriazinyl precursor, it can be concluded that dye fixes with the fibre via ionic bonds, rather than covalent bonds.

From the results displayed in Table 5 and Fig. 5, it can be seen that the initial exhaustion, as indicated by $(K/S)_1$ is similar for both dyes, but final exhaustion of hydrolysed Dye 5 is far less than that of reactive Dye 4; this would be expected if reaction between the fibre and the reactive dye was via covalent bond formation. Essentially no fixation took place with hydrolysed dye, confirming that in the case of the reactive dyes fixation occurs via covalent bond formation. Under the acidic dyeing conditions used, as the number of sulphonic groups increases, the opportunity for salt formation between anionic sulphonate groups and cationic protonated terminal amino groups in the fibre increases. Additionally, this might help in positioning the reactive groups within the proximity of a un-protonated amino groups thus facilitating covalent bond formation.

It is interesting to note (Fig. 4 and Table 5) that the highest concentration of dye fixed to fibre in any case is



Scheme 5. Synthesis of Dye 5.

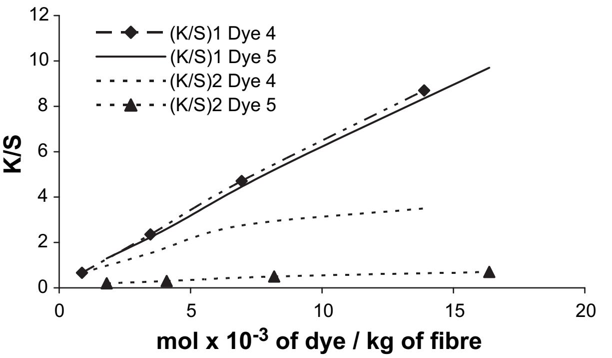


Fig. 5. Comparison of initial, $(K/S)_1$, and final, $(K/S)_2$, exhaustion of Dyes 4 and 5.

5.3 g/kg fibre (37% of 1.44% applied Dye 4). This equates to 5.14 mmol of dye/kg of fabric. That is, even in the case of the dye displaying highest fixation efficiency at 1.44% dye (Dye 4) o.m.f, only a relatively small percentage of the formally available amino groups undergo covalent bond formation with an electrophilic reactive monochlorotriazinyl group. The inability of dye to build up further is therefore likely to be restricted by steric hindrance and/or electrostatic repulsion where fixed dye impedes approach of further dye.

3.3. Wash fastness properties of dyes

The wash fastness properties of dyes were assessed using the ISO 105CO6/C2S wash fastness test at 60 °C [18]. The change in shade and the degree of cross staining were assessed visually using grey scales and the results are presented in Table 6.

Washing fastness as expected, of each dye fixed to nylon 6.6 fabrics was very good at each of the four depths of shade employed.

4. Conclusions

- All dyes displayed high initial exhaustion on nylon regardless of level of sulphonation. The degree of sulphonation played an important role in determining dye fixation. With increasing level of sulphonation, and hence net negative charge, the final exhaustion $(K/S)_2$ and fixation efficiency increased.
- Fixation via covalent bond formation increased with level of sulphonation in all cases.
- Build up and fixation tailed off before all well the formally available amino groups had reacted with dye.
- Build up is likely to be limited, not by the number of amino sites present on the fibre, but more by steric hindrance and/or electrostatic repulsion.
- The wash fastness of dyes covalently bound to nylon was good at all depths of shade.

Table 6
Wash fastness results of dyes in the ISO 105CO6/C2S

Dye	Staining					
	Secondary cellulose acetate	Bleached Un-merc. cotton	Nylon 6.6	Polyester	Acrylic	Wool
Dye 1	4/5	4/5	4/5	4/5	4/5	4/5
Dye 2	4/5	4/5	4/5	4/5	4/5	4/5
Dye 3	4/5	4/5	4/5	4/5	4/5	4/5
Dye 4	4/5	4/5	4/5	4/5	4/5	4/5

Acknowledgement

We wish to express our gratitude to UMIST and to Professor D.A.S Phillips for financial support (to A.S.-G.).

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