Dyes and Pigments 96 (2013) 397–402

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

The synthesis and application of novel 2-chloro-4-alkylthio triazinyl reactive dyes

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ARTICLE INFO

Article history:
Received 16 July 2012
Received in revised form
13 August 2012
Accepted 15 August 2012
Available online 1 September 2012

Keywords:
Reactive dyes
Cotton
Sulphatoethylsulphone
Chloroalkylthiotriazinyl dyes
Exhaust dyeing
Fixation

ABSTRACT

Two hetero bi-functional reactive dyes (red and yellow) each containing both a sulphatoethylsulphonyl and 2-chloro-4-alkylthio-s-triazinyl reactive group have been synthesised and their dyeing properties including exhaustion, colour strength on fabric (visual colour yield), fixation and wash fastness compared with market leading products. Under the alkaline application conditions employed, both the dyes, a yellow and a red, having a novel bridging group, exhibited good build-up, fixation and wet fastness properties being essentially comparable with leading commercial products. The concept of synthesising a substituent that can be introduced into a dye as a linking group to impart increased reactivity to a chlorotriazine has been demonstrated to be viable and effective.

1. Introduction

Since the introduction of the hetero bi-functional range of Sumifix Supra reactive dyes, the thrust of much synthetic effort, both academic and industrial, on reactive dyes, has focussed on utilising existing reactive systems but in novel arrangements or combinations. The current market is dominated by two major classes of reactive systems i.e. Michael type acceptors and haloheterocyclic. Several approaches towards optimisation of the application properties of derived dyes have been adopted. Ciba disclosed a wide range of combinations of different reactive groups in a single dye molecule. These included dyes possessing a monofluorotriazine in combination with a sulphatoethylsulphone [1–4], with a thiosulphatoethyl sulphonyl group [5], an alkoxychlorotriazinyl group [6] and a difluorochloropyrimidinyl group [7]. Triazinyl derivatives containing a cyanamino group were disclosed by [8] Sandoz and [9–12] by Hoechst, although this group contributes minimally to fixation. Factors which determine the ease with which a haloheterocyclic, or related, system undergoes activated heteroaromatic substitution such as hydrolysis on fixation to cotton, include the nature (electronegativity) of the leaving group, the number and type of heterocyclic atoms in the heteroaromatic ring and other ring substituents. 2,4-Dichloro-6-methylthio-[1,3,5] triazine (Fig. 1, Structure 1) has been known and used in other chemical industries, especially agrochemicals, for many years. Its synthesis has been reported in the literature by several different routes [13] and [14].

Monochlorotriazines derived from 2,4-6-alkylthio-[1,3,5] triazine, of the type depicted in Structure 2(a) as shown in Fig. 2, having an alkylthio substituent have received little attention. Carboxymethylthiol-triazine and carboxyethylthiol-triazines studied by Lehr [15] and cysteamine crosslinked triazine systems to give tri- and tetra functional chlortriazinyl dyes [16] were also reported. Nitrogen is more electronegative than sulphur and therefore, more electron withdrawing by an inductive effect. However, both atoms possess a lone pair of electrons and so can function as electron donators by a mesomeric effect. Sulphur being a much larger atom, than nitrogen, cannot donate its lone pair of electrons as effectively as nitrogen. Hence an alkylamino or arylamino substituent is more electron donating (deactivating with respect to nucleophilic substitution), overall, than an alkylthio group when attached to a triazine ring.

In order to evaluate this concept, novel hetero bi-functional dyes incorporating both a 2-alkylthio-4-chlorotriazine and a sulphatoethylsulphonyl (masked vinyl sulphone) group were prepared.

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http://dx.doi.org/10.1016/j.dyepig.2012.08.016

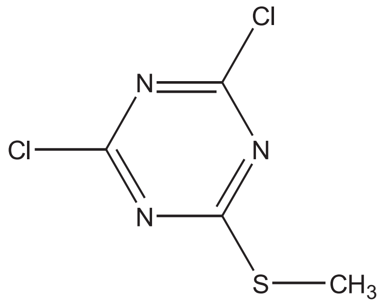

Fig. 1. Structure 1, Dichloromethylmercapto-[1,3,5] triazine.

2. Experimental

2.1. Materials

Proton NMR spectra were recorded using a Brűker DPX 300 instrument equipped with a proton/carbon, z-gradient, dual probe with an automatic sample changer. The solvent used was deuterium oxide >99.9 atom% D, with tetramethyl silane as an internal standard.

Mass spectra were obtained using two different techniques, FAB (fast atom bombardment) and MALDI (matrix assisted laser desorption ionisation). Elemental analyses for carbon, hydrogen, nitrogen and sulphur were carried out on a Carlo Erba 1108 elemental analyser. Thin layer chromatography was performed on aluminium plates coated with silica gel, 60 F_{254} (Merck). The eluent system used was iso-butanol:n-propanol:ethyl acetate:water (2:4:1:3), unless otherwise stated. The developed plates were visualised under both short and long wavelength ultraviolet light.

Procion Yellow MX-3R and Procion Red MX-8B were available commercially. Samples of 3-aminoacetanilide, 2-aminonaphthalene-3,6,8-trisulphonic acid and benzidine-2,2′-disulphonic acid were generously provided by DyStar.

The strength of any given dyestuff sample was estimated from the ratio of its actual molecular weight (MW) to its effective molecular weight (Mole In) estimated by titanous chloride titration method [17], each water-soluble dyestuff usually being contaminated with varying amounts of non-coloured (mainly inorganic) materials.

2.2. 4-(-β-[Sulphatoethyl-]sulphonyl-) chloroacetanilide

Para aminophenyl-β-sulphatoethyl sulphone (2.92 g, 0.01 mol, M.I. 292) was stirred in distilled water (20 ml), sodium carbonate solution (10% w/v) was added drop wise and the pH was raised to 5. Chloroacetyl chloride (2.82 g, 0.025 mol) was added drop wise, at 4–6 °C, and the pH was maintained at 4–5 with sodium carbonate (10% w/v) solution, with control by t.l.c. Completion of the reaction was also indicated by a negative test with Ehrlich's reagent. The reaction mixture (250 ml) was filtered to remove any insoluble impurities and the product (structure shown in Fig. 3) was precipitated by the portion wise addition of potassium chloride (25 g, 10% w/v) to the stirred solution. Solid was collected and dried under reduced pressure. R_f 0.73, PABSES 0.60, h.p.l.c. retention time 0.79 min, $(M\text{-}H^+)$ 356.7, molecular weight 357, ^{1}H-NMR, δ_H (300 MHz, D_2O): 7.85 ppm (2H, doublet, aromatic, ortho to SO_2), 7.7 ppm (2H, doublet, aromatic, ortho to NH), 4.2 ppm (4H, triplet and singlet, $-SO_2-CH_2-$, and $-CH_2-Cl$), 3.65 ppm (2H, triplet, $-CH_2-OSO_3H$), Found: C, 25.25%; H, 1.95%; N, 3.10%; S, 13.55%. $C_{10}H_{11}NO_7ClS_2\cdot K$ (84%) requires C 25.50%, H 2.3%, N 3.0%, S 13.60%, yield 3.4 g, 76%, Mole In (M.I.) 470. Effective agent (ea) strength 84%.

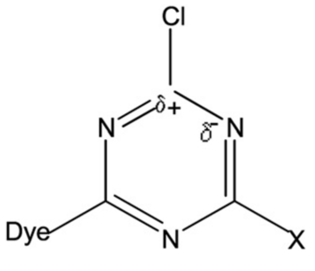

Fig. 2. Structure 2, (a) X = $-SCH_3$ (b) X = $-NHR(Ar)$.

2.3. Yellow dye

2-Aminonaphthalene-3,6,8-trisulphonic acid (55.9 g, 0.1 mol, Moles In 559, strength 68.50%) was dissolved in sodium carbonate in water (100 ml) at 3–5 °C together with sodium nitrite (6.9 g, 0.1 mol). The solution was added to hydrochloric acid (0.25 mol, 36%) at 0–5 °C and the mixture stirred for 1 h. The resulting diazonium salt suspension was added to a stirred solution of (3-aminophenyl) urea (22.9 g. 0.1 mol, M.I. 229) in water (250 ml) at 4–6 °C. The pH was raised to 6–6.5 with aqueous sodium carbonate solution (10% w/v) and maintained at this value for 2 h. The mixture was filtered to remove a small quantity of insoluble material and the resulting solution added to a freshly prepared, stirred suspension of cyanuric chloride (18.5 g, 0.1 mol), 0–5 °C and pH 6–6.5. After 1.5 h reaction was essentially complete and the temperature was raised to 30–35 °C, for 1.5 h to destroy any excess cyanuric chloride. The solution was filtered to remove any insoluble impurity and sodium chloride was added slowly to the stirred filtrate. The precipitated dichlorotriazine was collected and dried. R_f 0.39, Yield 74 g, 82%. M.I. 903. E.a. 77%.

Sodium hydrogen sulphide (1.56 g, 0.02 mol) was added portion wise to a solution of the freshly prepared dichlorotriazine dye (9.03 g, 0.01 mol), at 8–10 °C; temperature was allowed to rise to 16–18 °C, at pH 8–9.5. After completion of the reaction, as judged by t.l.c. and h.p.l.c. (2 h), the mixture was filtered to remove insoluble impurities and a solution of N-chloroacetyl para aminophenyl-β-sulphatoethyl sulphone was added (7.05 g, M.I. 470, 1.5:1 M ratio) at 16–18 °C to the stirred filtrate at 20 °C and at pH 6–6.5. After 4 h the mixture was filtered, the filtrate collected and the product was precipitated with potassium chloride (26 g, 8% w/v). The resulting solid, yellow dye (structure shown in Fig. 4) was collected and dried under vacuum. R_f 0.18. $(M\text{-}OSO_3H)^+$ 915.43, $(M\text{-}SO_3)^+$ 932.43, mol. Wt. 1012.45 R.T (h.p.l.c.) 3.50 min. Yield 3.67 g, 24%, M.I. 1512. E.a. strength 72.7%, ε_{max} 22,368 mol^{-1} cm^{-1} l.

2.4. Red dye

A solution of 1-hydroxy-8-aminonaphthalene-3,6-disulphonic acid, H-acid (38.8 g, 0.1 mol M.I. 388), in water at pH 6.5, was added to a stirred, freshly prepared, suspension of cyanuric chloride (18.45 g, 0.1 mol) in aqueous acetone 0–5 °C and the cold mixture stirred for 3 h, after which reaction was essentially complete. The resulting solution of N-dichlorotriazinyl H-acid was filtered to remove a small amount of insoluble material. Concurrently, diazotisation of 2-aminonaphthalene-1,5-disulphonic acid

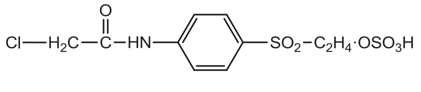

Fig. 3. Structure 3, N-chloroacetyl para aminophenyl-β-sulphatoethyl sulphone.

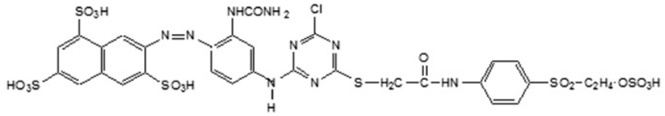

Fig. 4. Syn. yellow dye.

(52 g, 0.1 mol, M.I. 520) was accomplished with sodium nitrite (6.9 g, 0.1 mol) and hydrochloric acid (0.25 mol, strength 35%) at 3–4 °C. The resulting suspension of diazonium salt was added to the freshly prepared solution of N-dichlorotriazinyl H-acid at pH 6–6.5 and at 8–10 °C. After 60 min the reaction was essentially completed and product was salted out by slowly adding sodium chloride (15% w/v) to the stirred solution and dried under reduced pressure. R_f 0.53. R.T. (h.p.l.c.) 1.89 min. Yield 108 g, 65%. M.I. 1808. E.a. strength 45%.

This red dichlorotriazinyl dye (18.08 g, 0.01 mol, M.I. 1808) was dissolved in water at 8–10 °C, the pH of the solution was raised to 8 to 9 with sodium carbonate solution (10% w/v). Sodium hydrogen sulphide (1.95 g, 0.025 mol) was added directly portion wise to this solution at 8–10 °C and the temperature slowly raised to about 18 °C at pH 8–9, with control by t.l.c. and h.p.l.c. After 1.5 h, the solution was filtered, the filtrate was collected and excess N-chloroacetyl para aminophenyl-β-sulphatoethyl sulphone (7.05 g, 0.015 mol, M.I. 470) was added. The reaction was stirred at room temperature at pH 6–6.5 (sodium carbonate solution). After 3 h, the solution was filtered, the filtrate collected and the product was precipitated by slow portion wise addition of potassium chloride (55 g, 13.75% w/v). The resulting precipitated red dye (structure shown in Fig. 5) was collected and dried under vacuum. R_f 0.20, $(M\text{-}OSO_3H)^+$ 1003.51, $(M\text{-}SO_3)^+$ 1020.51, molecular weight 1100.51, h.p.l.c. retention time 2.14 min, yield 18 g, 63%, M.I. 2833, E.a. 42.72%, $\varepsilon_{max.}$ 31,250 mol^{-1} cm^{-1} l.

2.5. *Exhaust dyeing method*

Each dye was applied to bleached unmercerised woven cotton at five depths, viz. 1%, 2%, 4%, 6% and 9% dye o.m.f. at 60 °C and liquor ratio 10:1, using the quantities of Glauber's salt (exhaustion for 30 min) and soda ash (fixation for 60 min) shown in Table 1. After dyeing, the fabric was rinsed well with cold and hot water before soaping at the boil for 10 min. Finally the fabric was rinsed with cold water and air dried at room temperature.

Table 1
Quantities of salt and alkali applied.

(% Dye o.m.f.)	Glaubers salt (g/l)	Soda ash (g/l)
1	35	20
2–9	50	20

2.6. *SER$_5$F profiles of dyes*

The SER$_5$F profile (substantivity, exhaustion, reactivity and fixation) of each dye was measured at 3% dye o.m.f., under similar dyeing conditions to those used for the assessment of build-up, except that in this case time spent by dyes in the dyebath, in presence of fabric and salt before addition of alkali, was 60 min to ensure almost complete primary exhaustion [18] and [19]. A set of eighteen dyeing tubes was needed to measure the substantivity, exhaustion and fixation of each dye. The liquor ratio used for 2.5 g fabric was 10:1. Each dyeing tube was prepared as follows:

2.6.1. *Dyebath 1 (control)*

The required weight of dye solution, Glaubers salt solution and water were added to the dyeing tube and placed in the dyeing machine at 60 °C. After 60 min the tube was removed from the dyeing machine and immediately dipped into tap water for a couple of minutes to cool to room temperature. Later the optical density of the solution was measured and used as the control to calculate the substantivity and exhaustion.

2.6.2. *Dyebath 2–5*

The same weights of dye, salt and water were added to make each of dyebaths 2–5 as were used in making dyebath 1. The only difference was that a 2.5 g piece of cotton was added to each dyebath. The tubes were then placed in a dyeing machine at 60 °C for 10, 20, 30 and 60 min. After the required period, each tube was removed from the dyeing machine and cooled to room temperature by dipping in cold water. Excess liquor was squeezed back into the tube by applying the same pressure to each fabric from tubes 2–5. To ensure consistency in squeezing out excess liquor each piece of fabric was weighed after squeezing until the same weight was achieved. The dye solutions (excess liquor) from tubes 2–5 were kept at room temperature and later their optical densities were measured to allow calculations of the substantivity and exhaustion of the dyes.

2.6.3. *Dyebath 6 (control B)*

The same weight of dye, salt and water were added as in control A without fabric and placed in dyeing machine for 60 min at 60 °C. Then a measured amount of alkali (sodium carbonate solution) was added and the tube was replaced in the dyeing machine at 60 °C. After 60 min the tube was removed, cooled to room temperature and the optical density of the solution was measured to calculate the value of fixation.

2.6.4. *Dyebaths 7–12*

Dyebaths 7, 8, 9, 10, 11 and 12 were made up as for dyebath 6 (control B). The exception was that in dyebath 6 there was no fabric, whereas a piece of fabric weighing 2.5 g was added in each of dyebaths 7–12. After the completion of the exhaustion period (60 min) the measured amount of alkali was added to each tube and

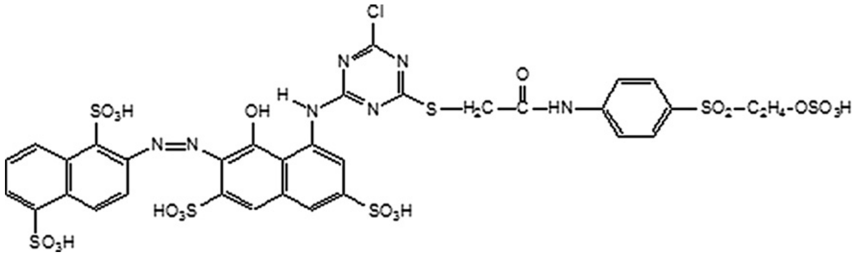

Fig. 5. Syn. red dye.

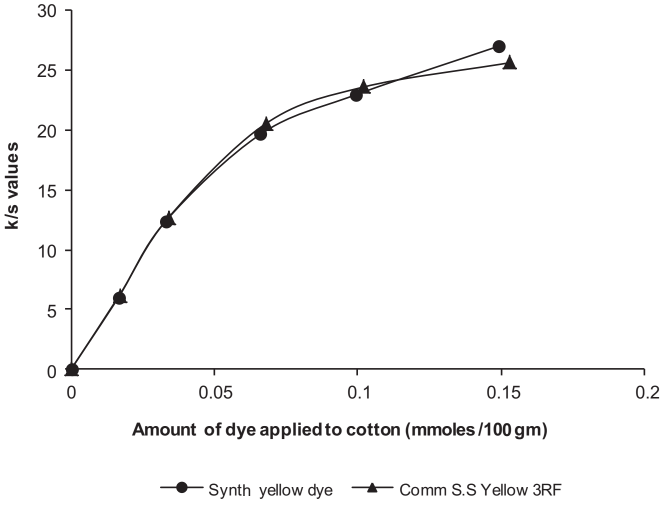

Fig. 6. Colour yield (k/s) versus dye applied (Sumifix Supra yellow 3RF and synthesised yellow dye).

then the tubes were returned to the dyeing machine for 5, 10, 20, 30, 45 and 60 min for tubes 7, 8, 9, 10, 11 and 12 respectively. At the end of the designated time each tube was removed from the dyeing machine and cooled to room temperature by dipping in cold water; excess liquor was removed by squeezing the fabric. Again the amount of excess liquor remaining on the fabric was controlled by weighing and squeezing each fabric to constant weight i.e., 5.5 ± 0.1 g. The solutions were used to measure optical densities to determine the exhaustion and fixation.

2.6.5. *Dyebaths 13–18*

Distilled water (47.5 ml) was measured and added to the dyeing tubes 13–18 and placed in the rotadyer at 95 °C. When the temperature reached the desired value, squeezed fabric from dyebaths 7–12 were placed in tubes 13–18 respectively, then the tubes were placed again in the rotadyer at 95 °C for 30 min. After that tubes were removed from the dyeing machine, cooled to room temperature and excess liquor was squeezed back into the tube and later optical densities of these solutions were measured along with other solutions collected during the whole exercise. These values were used to determine the amount of unfixed dye removed during washing off and therefore, gave the true fixation.

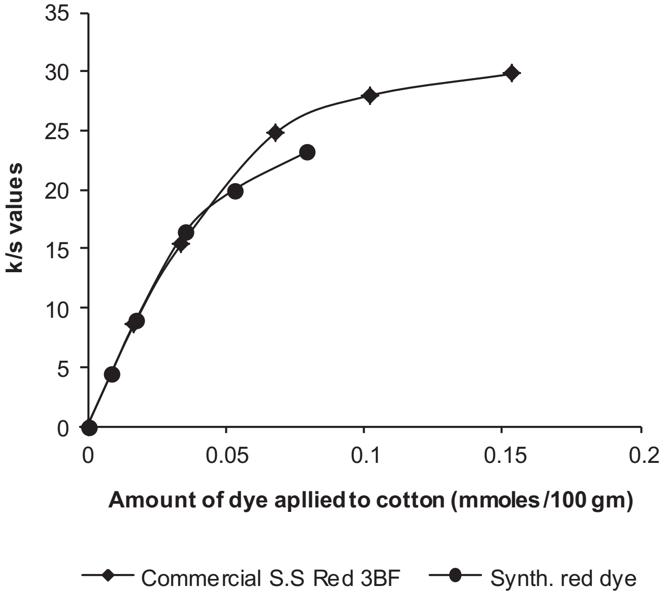

Fig. 7. Colour yield (k/s) versus dye applied (Sumifix Supra red 3BF and synthesised red dye).

2.7. *Optical density measurements*

Optical densities were measured using a Pye Unicam PU 8700 spectrophotometer. All readings were taken at room temperature in the presence of aqueous buffer (pH 7).

2.8. *Substantivity, exhaustion and fixation*

These were calculated as follows.
Tube 1 = OD1 = Control A.
Tubes 2–5 = OD_{2-5} = 10, 20, 30 and 60 min in salt only.
Tube 6 = OD6 = Control B.
Tubes 7–8 = OD_{7-12} = 60 min salt and 5, 10, 20, 30, 45 and 60 min in alkali.
Tubes 13–18 = OD_{13-18} = wash off of tube 7–12 respectively.

- Percent substantivity = $(OD_1{-}OD_n)/OD_1$

n = from tube 2 to tube 5.

- Percent exhaustion = $(OD_6{-}OD_n)/OD_6$

n = from tube 7 to tube 12.

- Percent fixation after n minutes = $((OD_6{-}OD_{7-12}{-}OD_{13-18})/OD_6) \times 100$

2.9. *Wash fastness I.S.O. 105: CO6/C2S test*

This test assesses both the change (or loss) of colour and staining of adjacent fabrics that occurs during washing. Samples were dried in air at room temperature and assessed for any change of colour and staining of the adjacent multi-fibre strip.

2.10. *Dye – fibre bond stability in aqueous alkali*

For each dye, a given weight of cotton fabric was dyed at 3% dye (o.m.f.). A measured amount of buffer solution (pH 12) was placed

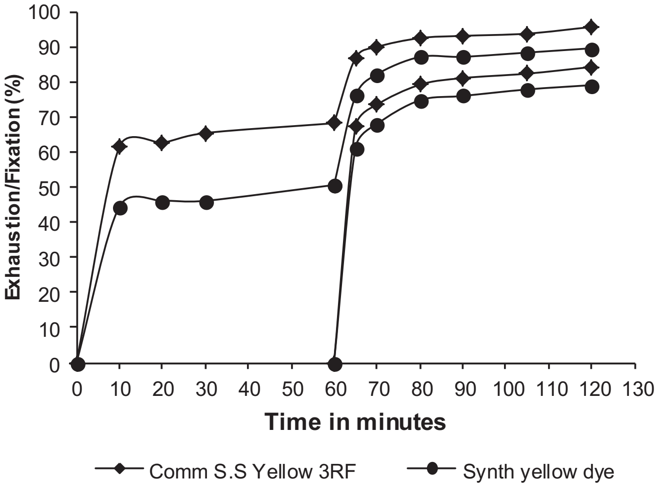

Fig. 8. SER_5F profile of yellow dyes.

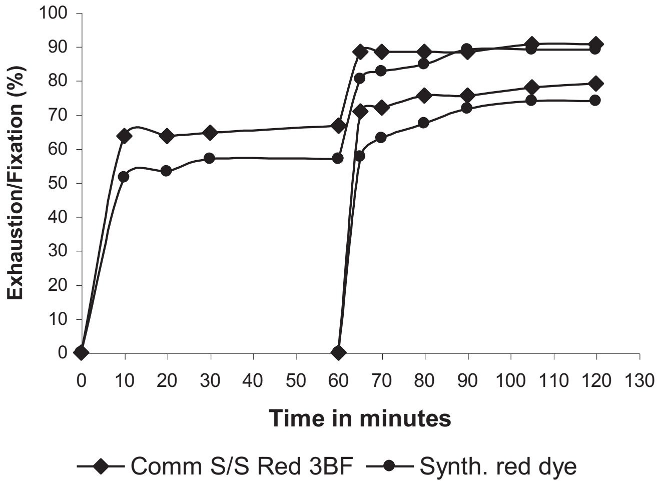

Fig. 9. SER$_5$F profile of red dyes.

in each dyeing tube so as to ensure the liquor to fabric ratio is 20:1 [20] and [21]. When the temperature of the rotadyer and buffer solutions had reached 80 °C, dyed samples of fabric were placed in separate tubes and left for 60 min with continuous rotation at 80 °C. After 60 min the samples were washed with distilled water (5 min cold wash, 10 min boiling water then 5 min cold wash) and dried at room temperature. K/S values of each fabric were measured using a Datacolor International Spectraflash 600 spectrophotometer and any reduction in the colour strength occurring during the test was assessed.

2.11. Variation in colour yield with changes in dyeing temperature

Each dye was applied at 3% o.m.f at 50 °C, 60 °C, 70 °C and 80 °C at 10:1 liquor ratio using 2.5 g pieces of knitted cotton fabric, presence of Glauber's salt (60 g/l) and soda ash (20 g/l). After dyeing, fabrics were washed and dried at room temperature and the colour strength of each dyed fabric was assessed (k/s values).

3. Results and discussion

3.1. Build-up properties of yellow and red dyes

The visual colour yields of the dyed fabrics were expressed as k/s values. In order to facilitate the comparison of the build-up properties of the these dyes, k/s values versus dye concentrations in millimoles per 100 g of fabric were plotted, as depicted graphically in Fig. 6 and Fig. 7.

At pale and medium depths of shade of yellow dyes, commercial Sumifix Supra Yellow 3RF was marginally superior but at heavy depths of shade the novel synthesised yellow dye built up better. While commercial Sumifix Supra Red 3BF built up better than synthesised red dye overall.

Table 2
I.S.O. 105: CO6/C2S test results.

Dye	Staining					
	Secondary cellulose acetate	Bleached un-mercerised cotton	Nylon 6.6	Polyester	Acrylic	Wool
S.S. yellow 3RF	5	5	5	5	5	5
Syn. yellow	5	5	5	5	5	5
S.S. red 3BF	5	5	5	5	5	5
Syn. red	5	5	5	5	5	5

Table 3
Results showing dye–fibre bond stability.

Dye	K/S values		Dye loss (%)
	Before test	After test	
Sumifix Supra yellow 3RF	17.05	14.21	16.66
Syn. yellow	14.97	12.76	14.77
Sumifix Supra red 3BF	15.87	14.69	7.44
Syn. red	16.03	15.23	5.00

3.2. SER$_5$F profiles

The SER$_5$F profiles were measured at 3% depth of shade on the fibre. The values of optical density measurements were converted into respective percentages and are depicted graphically in Fig. 8 and Fig. 9. From SER$_5$F profiles of both the synthesised yellow and red dyes it can be seen that both exhibit marginally lower fixation in medium shades (3% o.w.f.) than the commercial Sumifix Supra analogues. For both the synthesised dyes the maximum level of substantivity achieved after 60 min was less than that of the corresponding Sumifix Supra dyes.

The lower substantivity values of synthesised yellow and red dyes relative to commercial products, Sumifix Supra Yellow 3RF and Sumifix Supra Red 3BF, is attributed to the carboxamidomethylthio linking group used to attach vinyl sulphone reactive group to the chlorotriazine residue. This appears to contribute less to substantivity, hence exhaustion and fixation than the more usual triazine–NH–aryl linkage of commercial dyes.

3.3. Staining properties

Staining properties of both the synthesised yellow and red dyes were assessed using multifibre strip in CO6/C2S test. Both dyes showed no staining on any of the fibres of multifibre strip as shown in Table 2. Similar results were observed for commercial Sumifix Supra Yellow 3RF and Sumifix Supra Red 3BF.

3.4. Dye-fibre bond stability in aqueous alkali

The dye fibre bond stability of synthesised yellow and red dyes under alkaline conditions appeared superior to that of commercial Sumifix Supra dyes as less dye loss being observed on treatment with hot aqueous alkali as shown in Table 3. The established observation [22] that dye fibre bond formed by the reaction of vinyl sulphone with the cellulose cleaves more under alkaline conditions than to the dye fibre bond formed by halo triazinyl dyes, might suggest that in case of synthesised yellow and red dyes more covalent bonding to cotton occurred via triazinyl linkage as compared to commercial Sumifix Supra Yellow 3RF and Sumifix Supra Red 3BF. This is in accordance with our expectations that the presence of alkylthio group enhanced the reactivity of chloro group of triazine ring.

4. Conclusion

The concept of synthesising a substituent which can be introduced into a dye as a linking group to impart increased reactivity to a chlorotriazine has been demonstrated to be viable and effective. The improved dye-fibre bond stability, under alkaline dyeing conditions, of the synthesised yellow and red dyes, compared to their Sumifix Supra analogues, was in agreement with the concept.

Both the synthesised yellow and red dyes having a novel bridging group broadly performed similar to their commercial Sumifix Supra analogues. Use of mixed reactive system, as tried in synthesised novel yellow and red dyes, might display even better build up and fixation in conjunction with more substantive chromophores.

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