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Short Communication

An Investigation into the *In situ* Preparation of Hetero Bifunctional Monochlorotriazinyl-Vinyl Sulphone Reactive Dyes for Cotton

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Abstract. An attempt has been made in *in-situ* preparation and application of two isomers (para and meta) of aminophenyl-β-sulphatoethyl sulphone reagents (PABSES and MABSES) with three dichlorotriazinyl dyes i.e. CI Reactive Orange 86, CI Reactive Red 11 and CI Reactive Blue 168 to generate mixed hetero bifunctional dyes in dye bath. Dyeing results when compared with similar targeted type of commercially available Sumifix Supra dyes were found not up to the mark. Build up properties of all *in situ* prepared dyes were lower except for few light depth of shades as compared to preformed commercial Sumifix Supra dyes. This could be because of inefficient condensation of dichlorotriazinyl dyes with the aminophenyl-β-sulphatoethyl sulphone. However, meta isomer of aminophenyl-β-sulphatoethyl sulphone appeared to be more effective than the para isomer.

Keywords: colouration, reactive dyes, cotton, hetero bifunctional dyes, fixation

Sumifix Supra dyes developed by Sumitomo showed minimal sensitivity to changes in electrolyte, alkali, liquor and exhibit high fixation over a range of processing conditions as compared with homobifunctional dyes (Aspland, 1993; Abeta *et al*., 1984; Fujioka and Abeta, 1982). These hetero bifunctional reactive dyes are also robust to changes in processing conditions such as application temperature (Hunter and Renfrew, 1999). Earlier it was assumed that under strict neutral conditions and at constant temperature the major reaction would be the condensation reaction of dichlorotriazinyl dyes with aminophenyl-β-sulphatoethyl sulphone not the hydrolysis of dichlorotriazinyl dyes or of vinyl sulphone group with water (Lewis and Loan, 2007; Weber and Vicki, 1993). An attempt was made in this research work to condense dichlorotriazine dyes with aminophenyl-β-sulphatoethyl sulphone in the dye bath under neutral conditions prior to addition of salt and alkali required for the (neutral) exhaustion and (alkaline) fixation stages.

Dichlorotriazinyl dyes CI Reactive Orange 86, CI Reactive Red 11, CI Reactive Blue 168 and dyes of Sumifix Supra type CI Reactive Yellow 145, CI Reactive Red 195, CI Reactive Blue 221 were available commercially. All other chemicals used in this study were of general laboratory grade purchased from Aldrich or Merck. Samples of para and meta aminophenyl-β-sulphatoethyl sulphone were generously provided by BASF. The strength of dyestuff samples were estimated from the ratio of its actual molecular weight (MW) to its effective molecular weight (Mole In) estimated by titanous chloride titration method (Murtagh, 2004) and is given in Table 1.

Table 1. Effective dye strength

Dyes	Moles In
CI Reactive Orange 86	1792
CI Reactive Red 11	1482
CI Reactive Blue 168	2919
CI Reactive Yellow 145	1472
CI Reactive Red 195	1705
CI Reactive Blue 221	3310

Experimental results suggested that for *in situ* application of dichlorotriazine dye and sulphatoethyl sulphones agents, temperature of dye bath should be at 70 °C, and pH should be 6.0–6.5 using phosphate buffer with reaction time of 1 h, however, reaction period of 2 and 4 h were also measured. Each dye was applied to bleach 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) as shown in

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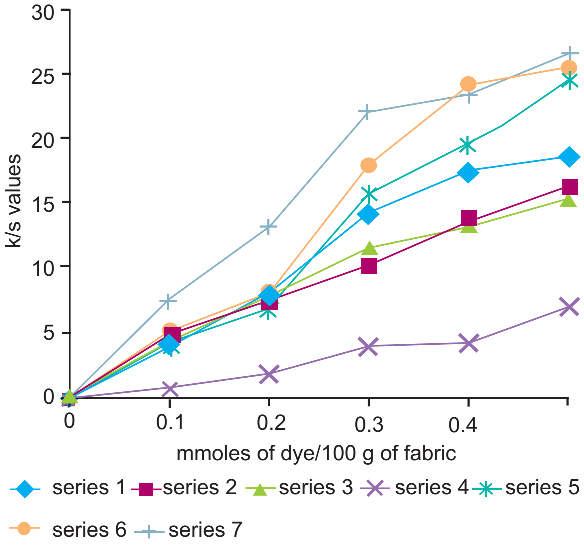


Legends: Series 1: CI Reactive Orange 86 with para aminophenyl-β-sulphatoethyl sulphone (PABSES), reaction time one hour at 70 °C before dyeing, **Series 2:** CI Reactive Orange 86 with PABSES, reaction time two hour at 70 °C before dyeing, **Series 3:** CI Reactive Orange 86 with PABSES, reaction time four hour at 70 °C before dyeing, **Series 4:** CI Reactive Orange 86 kept in dye bath under same conditions as for series 1, 2 and 3 but without PABSES before dyeing, **Series 5:** CI Reactive Orange 86 dyed to cotton without any modification at standard Sumifix Supra dyeing conditions, **Series 6:** CI Reactive Orange 86 dyed to cotton without any modification at standard MX dyeing conditions, **Series 7:** Commercial CI Reactive Yellow 145 dyed to cotton without any modification at standard Sumifix Supra dyeing conditions.

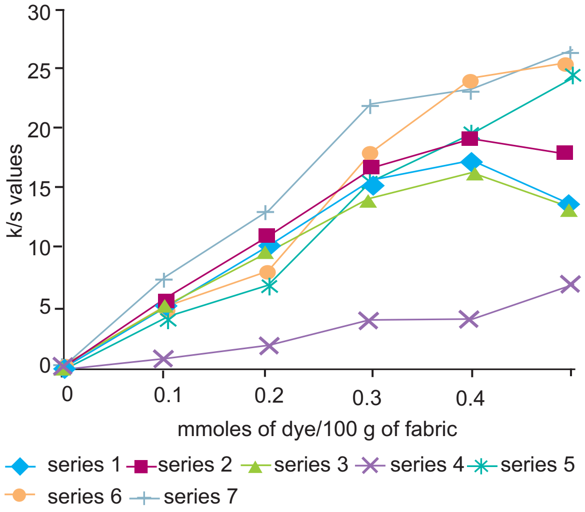
Fig. 1. CI Reactive Orange 86 with PABSES.

Table 2. After dyeing, the fabric was rinsed with cold and hot water before soaping at boil for 10 min and finally rinsed with cold water and air dried at room temperature. Colorimetric properties of dyeing were determined using a Spectraflash 600 spectrophotometre (D65 illumination, 10° observer). To facilitate the comparison of the build-up properties of these dyes, k/s values versus dye concentrations in millimoles per 100 g of fabric were plotted.

Table 2. Amount of salt and alkali used

Shades	Sodium sulphate (g/L)		Sodium carbonate(g/L)	
% dye (o.m.f)	Procion MX	Sumifix supra	Procion MX	Sumifix supra
1 & 2	35	35	10	20
4	45	50	15	20
6 & 9	55	50	20	20

Dyeing results of CI Reactive Orange 86 with PABSES (Fig. 1) showed that the depths of shade under these conditions are far inferior to when PABSES is present, supporting the premise that a Sumifix Supra type of heterobifunctional dye is indeed formed in the dye bath. Dyeing results appeared to indicate partial conversions of dichlorotriazine to a monochlorotriazine-vinyl sulphone mixed reactive system. Results for meta isomer (MABSES) are given in Fig. 2 and shows that significant conversion to mixed bifunctional dye had occurred within two hours but again build up was inferior on an equimolar basis to CI Reactive Yellow 11.

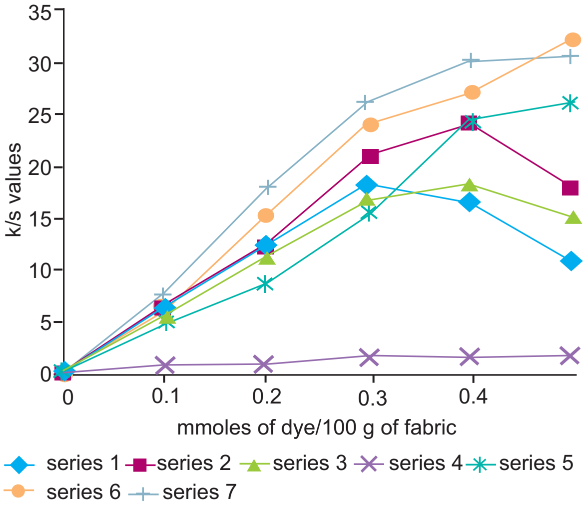


Legends: Series 1: CI Reactive Orange 86 with meta amino-phenyl-β-sulphatoethyl sulphone (MABSES), reaction time one hour at 70 °C before dyeing, **Series 2:** CI Reactive Orange 86 with MABSES, reaction time two hour at 70 °C before dyeing, **Series 3:** CI Reactive Orange 86 with MABSES, reaction time four hour at 70 °C before dyeing, **Series 4:** CI Reactive Orange 86 kept in dye bath under same conditions as for series 1, 2 and 3 but without MABSES before dyeing, **Series 5:** CI Reactive Orange 86 dyed to cotton without any modification at standard Sumifix Supra dyeing conditions, **Series 6:** CI Reactive Orange 86 dyed to cotton without any modification at standard MX dyeing conditions, **Series 7:** Commercial CI Reactive Yellow 145 dyed to cotton without any modification at standard Sumifix Supra dyeing conditions.

Fig. 2. CI Reactive Orange 86 with MABSES.

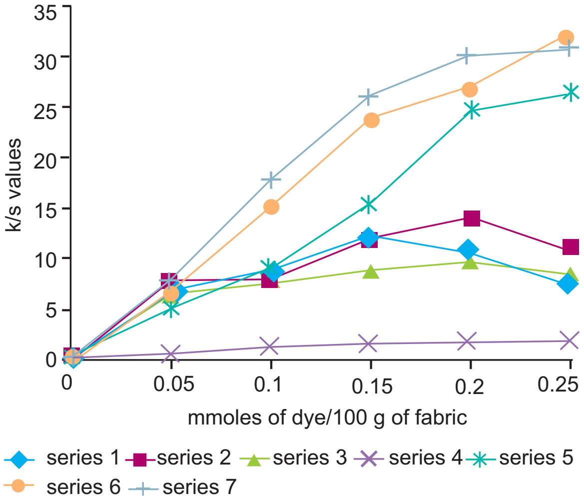
Results for both isomers (PABSES and MABSES) with CI Reactive Red 11 are depicted in Fig. 3-4 and shows that the best build up was obtained when dichlorotriazine and amine were reacted at 70 °C for 2 h prior to addition of salt and alkali. Interestingly, with CI Reactive Red 11, the para isomer performed significantly better than the meta isomer.

CI Reactive Blue 168 showed mixed results which are shown in Fig. 5-6. In some cases build-up was almost comparable to CI Reactive Blue 168 (commercial counterpart). However, in all cases build-up tailed off above 4% depth of dye shade.



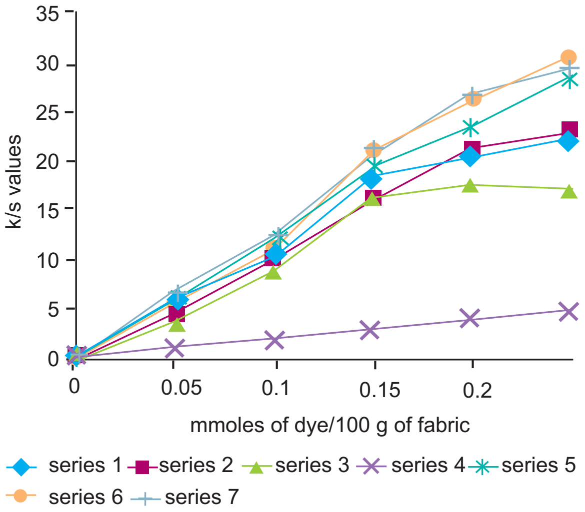
Legends: Series 1: CI Reactive Red 11 with para aminophenyl-β-sulphatoethyl sulphone (PABSES), reaction time one hour at 70 °C before dyeing, **Series 2:** CI Reactive Red 11 with PABSES, reaction time two hour at 70 °C before dyeing, **Series 3:** CI Reactive Red 11 with PABSES, reaction time four hour at 70 °C before dyeing, **Series 4:** CI Reactive Red 11 kept in dye bath under same conditions as for series 1, 2 and 3 but without PABSES before dyeing, **Series 5:** CI Reactive Red 11 dyed to cotton without any modification at standard Sumifix Supra dyeing conditions, **Series 6:** CI Reactive Red 11 dyed to cotton without any modification at standard MX dyeing conditions, **Series 7:** Commercial CI Reactive Red 195 dyed to cotton without any modification at standard Sumifix Supra dyeing conditions.

Fig. 3. CI Reactive Red 11 with PABSES.



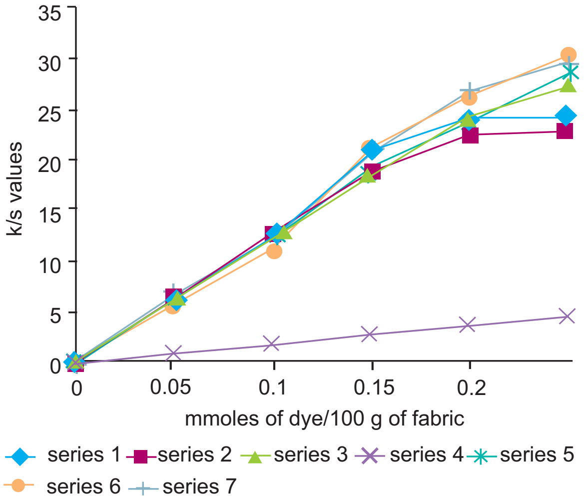
Legends: Series 1: CI Reactive Red 11 with meta amino-phenyl-β-sulphatoethyl sulphone (MABSES), reaction time one hour at 70 °C before dyeing, **Series 2:** CI Reactive Red 11 with MABSES, reaction time two hour at 70 °C before dyeing, **Series 3:** CI Reactive Red 11 with MABSES, reaction time four hour at 70 °C before dyeing, **Series 4:** CI Reactive Red 11 kept in dye bath under same conditions as for series 1, 2 and 3 but without MABSES before dyeing, **Series 5:** CI Reactive Red 11 dyed to cotton without any modification at standard Sumifix Supra dyeing conditions, **Series 6:** CI Reactive Red 11 dyed to cotton without any modification at standard MX dyeing conditions, **Series 7:** Commercial CI Reactive Red 195 dyed to cotton without any modification at standard Sumifix Supra dyeing conditions.

Fig. 4. CI Reactive Red 11 with MABSES.



Legends: Series 1: CI Reactive Blue 168 with para amino-phenyl-β-sulphatoethyl sulphone (PABSES), reaction time one hour at 70 °C before dyeing, **Series 2:** CI Reactive Blue 168 with PABSES, reaction time two hour at 70 °C before dyeing, **Series 3:** CI Reactive Blue 168 with PABSES, reaction time four hour at 70 °C before dyeing, **Series 4:** CI Reactive Blue 168 kept in dye bath under same conditions as for series 1, 2 and 3 but without PABSES before dyeing, **Series 5:** CI Reactive Blue 168 dyed to cotton without any modification at standard Sumifix Supra dyeing conditions, **Series 6:** CI Reactive Blue 168 dyed to cotton without any modification at standard MX dyeing conditions, **Series 7:** Commercial CI Reactive Blue 221 dyed to cotton without any modification at stand. Sumifix Supra dyeing conditions.

Fig. 5. CI Reactive Blue 168 with PABSES.



Legends: Series 1: CI Reactive Blue 168 with meta amino-phenyl-β-sulphatoethyl sulphone (MABSES), reaction time one hour at 70 °C before dyeing, **Series 2:** CI Reactive Blue 168 with MABSES, reaction time two hour at 70 °C before dyeing, **Series 3:** CI Reactive Blue 168 with meta MABSES, reaction time four hour at 70 °C before dyeing, **Series 4:** CI Reactive Blue 168 kept in dye bath under same conditions as for series 1, 2 and 3 but without MABSES before dyeing, **Series 5:** CI Reactive Blue 168 dyed to cotton without any modification at standard Sumifix Supra dyeing conditions, **Series 6:** Procion Blue MX-4GD dyed to cotton without any modification at standard MX dyeing conditions, **Series 7:** Commercial CI Reactive Blue 221 dyed to cotton without any modification at standard Sumifix Supra dyeing conditions.

Fig. 6. CI Reactive Blue 168 with MABSES.

Dyeing results when compared with commercial Sumifix Supra dyes of similar shades were inferior in performance. Meta isomer of aminophenyl-β-sulphatoethyl sulphone appeared to be more effective than the para isomer. This probably reflects more nucleophilic character of the former isomer (Sheng, 1998). The falling-off of the build-up properties of some of the dyes at darker shades may be due to blocking effect.

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