Available online at www.sciencedirect.com

Dyes and Pigments 75 (2007) 747–752

www.elsevier.com/locate/dyepig

# Synthesis and application of a polyfunctional bis(monochlorotriazine/sulphatoethylsulphone) reactive dye

A.A. Mousa

*National Research Center, Textile Research Division, Tahrir Street,*
*Dokki, Cairo, Egypt*

Received 17 February 2006; received in revised form 2 April 2006; accepted 9 August 2006
Available online 9 October 2006

## Abstract

The behavior of a polyfunctional reactive dye containing bis(monochlorotriazine/sulphatoethylsulphone) reactive system on silk has been investigated. The twinned monochlorotriazine/sulphatoethylsulphone reactive system confers a relatively high fixation efficiency of this type of polyfunctional reactive dye even at low salt and/or temperature conditions when compared with that of the conventional bifunctional reactive dye containing one monochlorotriazine/sulphatoethylsulphone reactive system. The results also indicate that the fastness properties are approximately the same for both the reactive dyes under investigation.

*Keywords:* Polyfunctional reactive dye; Bifunctional reactive dye; Dyeing of silk; Low salt dyeing

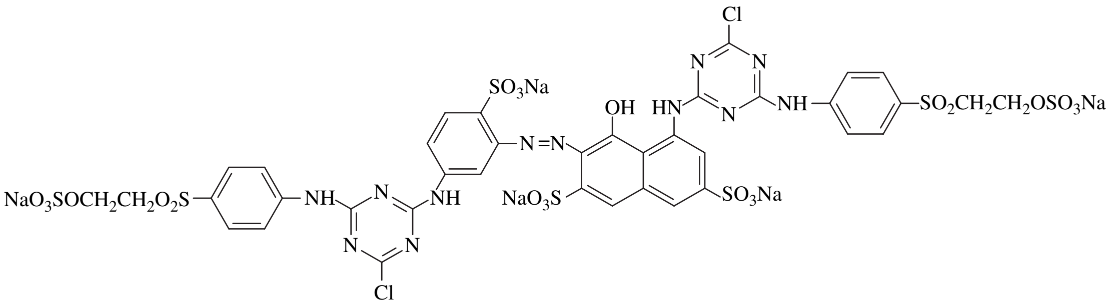
## 1. Introduction

At the beginning of the 1980s the term bifunctional dye became widespread and has been used to describe dyes of Sumifix Supra range [1]. These dyes are based on monochlorotriazine (MCT) and sulphatoethylsulphone (SES) reactive groups, which give higher fixation efficiency than the corresponding dyes containing only one reactive group [2]. The fixation efficiency of heterobifunctional MCT/SES reactive dye Sumifix Supra Brilliant Red 2BF (CI Reactive Red 194) was found to be higher on silk in neutral medium than that in alkaline medium [3,4]. In our pervious work [4] it was reported that in neutral medium the exhaustion and fixation values of the polyfunctional disulphide bis(ES-MCT/SES) reactive dye and CI Reactive Red 194 on silk were approximately the same. In alkaline medium, which was necessary for disulphide bisethylsulphone DSB(ES) β-elimination, the polyfunctional disulphide bis(ES-MCT/SES) reactive dye revealed rather high values of exhaustion and fixation than CI Reactive Red 194. This may be attributed to the formation of the polyfunctional system as a result of β-elimination of both DSB(ES) and SES groups. Therefore, a large amount of salt was required in alkaline medium to neutralise the charge on the silk fibre much more than those required in a neutral medium. With a desire to introduce a novel polyfunctional reactive dye for dyeing silk at low salt concentration with high total dye fixation yield in a neutral medium, it was thought that a dye containing only SES and MCT reactive groups similar to CI Reactive Red 194 in a polyfunctional manner would be suitable. Thus, the present work reports the synthesis of a polyfunctional reactive dye with MCT/SES H-acid coupling component as a first bifunctional reactive system and MCT/SES aminobenzenesulphonic acid diazo component as a second bifunctional reactive system. The dyeing behavior of the polyfunctional bis(MCT/SES) reactive dye (**1**) compared with CI Reactive Red 194 (**2**) on silk is also reported.

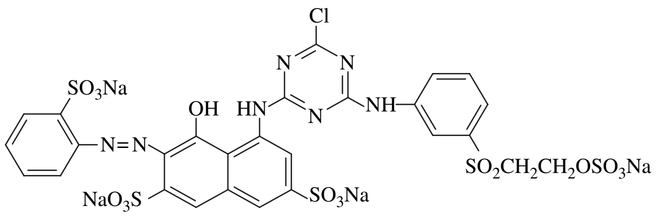
---

*E-mail address:* mousanrc@hotmail.com

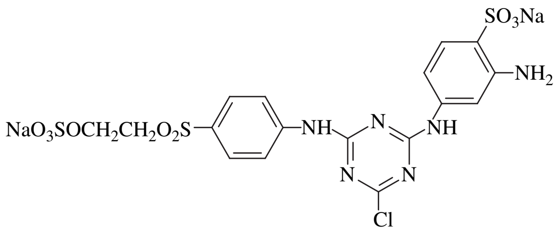
0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.08.002



**1**



**2**



**3**

## 2. Experimental

### 2.1. Materials

Degummed and bleached silk fabric (El-Khateib Co., Egypt) weighing 90 g/m$^2$ was used through this work. Before dyeing, the fabric was treated in aqueous solution containing 2 g/l non-ionic detergent (Hostapal CV, Hoechst) for 1 h at 90 °C and at a liquor ratio 50:1, then washed thoroughly in water and dried at room temperature.

CI Reactive Red 194, **2** was supplied by Sumitomo Chemical Co. Ltd, H-acid was obtained from Fluka Chemie AG, cyanuric chloride was obtained from Merck–Schuchardt, *p*-aminophenylsulphatoethylsulphone was obtained from Isma Dyestuff and Chemical Co., Egypt and 2,4-diaminobenzenesulphonic acid was obtained from DyStar. All other chemicals used in this study were of laboratory reagent grade.

### 2.2. Dye synthesis

The synthesis of the polyfunctional bis(MCT/SES) reactive dye **1** was carried out by initial preparation of the MCT/SES H-acid coupling component according to the usual procedure for the cyanuric chloride condensation reaction with H-acid and for the subsequent reaction with *p*-aminophenylsulphatoethylsulphone [5]. The condensation product was then coupled with the diazonium salt solution of MCT/SES aminobenzenesulphonic acid intermediate **3**, which was prepared and diazotised by a similar method previously described [6]. The coupling reaction was completed within 2 h at pH 6.5 with the formation of the desired polyfunctional bis(MCT/SES) reactive dye **1**. This dye was isolated by adding 15% sodium chloride, then filtered and dried in a vacuum oven at 40 °C.

### 2.3. Dye purification

For convenient dyeings and chemical investigations it was necessary to purify both the synthesised dye **1** and commercial dye **2**. The purification was carried out by dissolving the dye in dimethylsulphoxide at 50 °C. The inorganic impurities were eliminated by filtration, and the dye solution was re-precipitated in *n*-butanol at room temperature. The dye was filtered and washed with ethanol, then washed with small portions of diethylether to extract the organic impurities. The purified dye was dried in a vacuum oven at 40 °C [7].

The synthesised bis(MCT/SES) dye **1** had a maximum absorption $\lambda_{max}(H_2O) = 518.5$ nm, its purity was determined by elemental analysis, and gave the following results:

Found (%) C, 32.26; H, 2.01; N, 11.92; S, 15.76; Cl, 4.49.
Calculated (%) C, 32.28; H, 1.92; N, 11.89; S, 15.87; Cl, 5.01.

The $^1$H NMR spectra were also recorded on a Varian Mercury 300 MHz spectrometer and the chemical shift values (ppm) of the investigated polyfunctional dye **1** ($C_{38}H_{27}N_{12}S_7O_{22}Cl_2Na_5$) were found to be as follows: $\delta_H([^2H_6]DMSO)$/ppm 3.64 (4H, t, *J* 6.6, $2 \times 2\alpha\text{-CH}_{2\ (SES)}$), 4.00 (4H, t, *J* 6.6, $2 \times 2\beta\text{-CH}_{2\ (SES)}$), 7.60 (1H, s, $1H_{H\text{-}acid}$), 7.66 (1H, s, $1H_{H\text{-}acid}$), 7.72 (1H, d, *J* 8.1, $1H_{PhDiazo}$), 7.85 (4H, d, *J* 8.4, $2 \times 2H_{PhSES}$), 8.07 (5H, br s, $2 \times 2H_{PhSES}$ hidden by s, of $1H_{PhDiazo}$), 8.28 (1H, d, *J* 8.1, $1H_{PhDiazo}$), 9.01, 9.21, 10.47, 11.57 (1H each, 4 × NH).

### 2.4. Dyeing procedure

All reactive dyeings with the polyfunctional bis(MCT/SES) **1** and heterobifunctional MCT/SES **2** reactive dyes were carried out in an Ahiba dyeing machine in distilled water at a liquor ratio of 40:1 with various dye concentrations (1–5% owf). The initial dyebath was set at 30 °C in the presence of sodium sulphate (1/3 of the total specified amount) for 10 min at neutral pH. The temperature was raised to 60, 70, 80 and 90 °C over 30 min. During this period the required amount of sodium sulphate (0, 20, 40, 60, 80 and 100 g/l) was added in two portions at an interval of 15 min. Dyeing was continued at these conditions for various dyeing times (45, 60, 90 and 120 min). After dyeing, all the dyed samples were rinsed with water and air dried.

### *2.5. Measurements of dye exhaustion*

For all dyeings, the percentage of dyebath exhaustion was measured on a Shimadzu UV-2401PC UV/vis spectrophotometer at $\lambda_{\max}$. The percentage of dyebath exhaustion ($\%E$) was calculated using Eq. (1):

$$\%E = \left[1 - \left(\frac{C_2}{C_1}\right)\right] \times 100 \tag{1}$$

where $C_1$ and $C_2$ are the concentrations of the dyebath before and after the dyeing, respectively.

### *2.6. Measurements of dye fixation ratio and total dye fixation*

The dye fixation ratio, which refers to the percentage of the chemically bound dye relative to the exhausted dye, was measured by extracting the dyed samples in refluxing 50% aqueous urea solution (w/v) [8]. The colour strength ($K/S$) values of the extracted and dyed samples were then measured spectrophotometrically at $\lambda_{\max}$ [9]. Assuming $K/S$ was proportional to dye concentration in the fibre, the extent of dye fixation ratio ($\%F$) could be calculated using Eq. (2) [10,11]:

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

where $(K/S)_1$ and $(K/S)_2$ are the colour strengths of the dyed samples before and after stripping, respectively.

From the results of the dyebath exhaustion and fixation ratio, the total dye fixation ($\%T$), which refers to the percentage of dye which was chemically bound to the sample relative to the amount of the dye applied to the sample, was calculated for all dyeings using Eq. (3) [10,11]:

$$\%T = \left(\frac{\%E \times \%F}{100}\right) \tag{3}$$

The total amount of the dye that was fixed ($\%R$) was calculated using Eq. (4) [12]:

$$\%R = \frac{(\%E \times \%F)}{100} \times \%\ \text{owf dye applied} \tag{4}$$

### *2.7. Fastness testing*

The dyed samples were tested, after washing-off using 2 g/l non-ionic detergent (Hostapal CV) at 80 °C for 15 min, according to ISO standard methods [13]. The tests were as follows: colour fastness to washing, ISO 105-C02 (1989); fastness to rubbing, ISO 105-X12 (1987); fastness to perspiration, ISO 105-E04 (1989); fastness to light (carbon arc), ISO 105-B02 (1988).

## 3. Results and discussion

### *3.1. Characterisation of the polyfunctional bis(MCT/SES) reactive dye*

The $^1$H NMR spectrum of the polyfunctional dye **1** was characterized by two triplet peaks at 3.64 and 4.00 ppm, corresponding to the α- and β-methylene protons of the SES groups, respectively. The spectrum showed two singlet peaks at 7.60 and 7.66 ppm, corresponding to the aromatic protons of H-acid coupling component. The two doublets at 7.72 and 8.28 with *J*-value of 8.1 were assigned to the two *ortho* protons of the diazo component. Additionally the $^1$H NMR spectrum of dye **1** showed also four broad singlets, each describes one exchangeable NH-proton.

### *3.2. Effect of dyeing temperature*

Figs. 1 and 2 show the effect of dyeing temperature on the dyeing of silk with the polyfunctional bis(MCT/SES) reactive dye **1** and heterobifunctional MCT/SES reactive dye **2** (3% owf) under the same neutral dyeing conditions of 40 g/l $Na_2SO_4$ from which it can be seen that dye **1** has higher exhaustion values over the range of temperatures studied if compared with dye **2**. It is anticipated from the dye structures of **1** and **2** that both dyes after β-elimination reaction of SES groups under the dyeing condition [3,4], although their resultant structure will be trisulphonated, the hydrophobic/hydrophilic

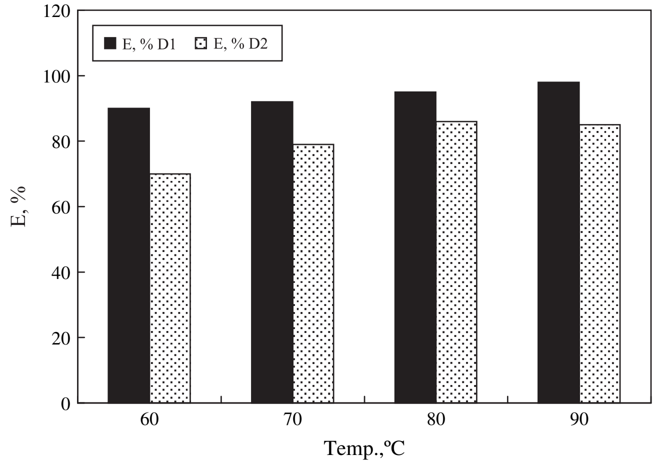


Fig. 1. Exhaustion ($E$) of bis(MCT/SES) dye **1** and MCT/SES dye **2** (3% owf) at different dyeing temperatures.

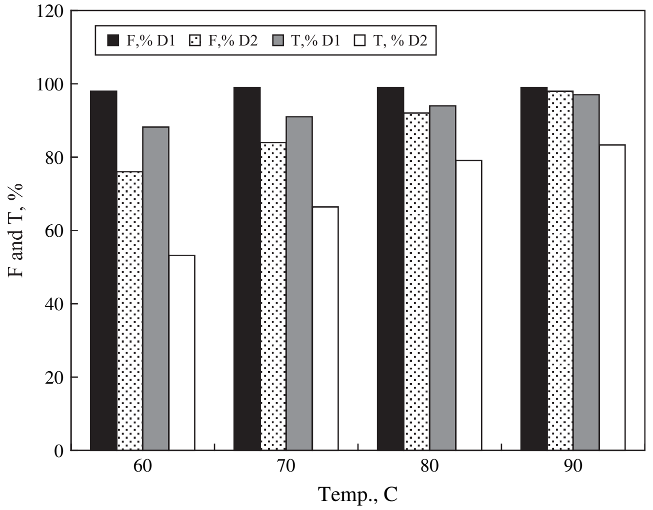


Fig. 2. Fixation (*F*) and total fixation (*T*) of bis(MCT/SES) **1** and MCT/SES **2** (3% owf) at different dyeing temperatures.

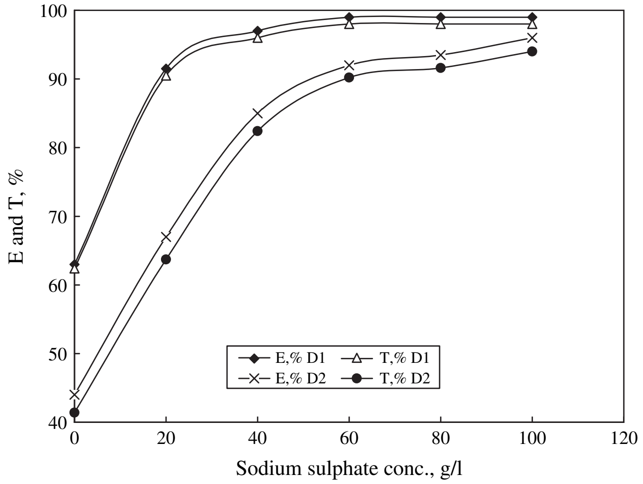


Fig. 3. Exhaustion (*E*) and total fixation (*T*) of bis(MCT/SES) **1** and MCT/SES **2** (3% owf) at different sulphate concentrations.

ratio of dye **1** will be higher than that of dye **2**. This, in turn, would contribute to the increase in the substantivity of the polyfunctional reactive dye **1** on silk, resulting in higher exhaustion values than that of the bifunctional MCT/VS reactive system of dye **2**.

Following the fixation percentage of dye **1** secured in Fig. 2, it seems that dye **1** is almost completely fixed on silk over the range of dyeing temperatures studied and its fixation is significantly higher than that of dye **2**. This is because, dye **1** containing two MCT/VS reactive systems at both ends, behaves as homobifunctional bis(VS) and bis(MCT) reactive dye at the same time. This, in turn, would maximise the probability of dye–fibre interaction through both the more reactive VS groups at low temperature and the less reactive MCT groups at high temperature. Thus, it would be expected that the twinned MCT/VS reactive system in dye **1** molecule may result in higher fixation efficiency than dye **2** containing only one MCT/VS reactive system in close proximity. This is in agreement with previous studies which reported that the reactive dyes containing two VS reactive groups residing at both ends of the dye molecule exhibit high fixation efficiency when applied to silk [4,14].

In other words, VS reactive group acts as a nucleophile at lower temperature than MCT reactive group. This reactivity difference is reflected in Figs. 1 and 2, where dye fixation for dye **1** is significantly higher than dye **2** at 60, 70 and 80 °C. At 90 °C although the fixation for both the dyes is similar, the total dye fixation for dye **1** is higher than that for dye **2** over all temperatures.

### 3.3. *Effect of salt concentration*

At neutral dyeing conditions, the study was extended to investigate the effect of salt concentration on the dyeing behavior of both bis(MCT/SES) dye **1** and MCT/SES dye **2** (3% owf) and at 90 °C. The results shown in Fig. 3 indicate that, in case of dye **1**, the low salt concentration had a pronounced effect on its exhaustion and fixation even at 20 g/l sodium sulphate. Whilst the exhaustion and total fixation yield of dye **2** increased considerably with the increase of salt concentration from 20 to 60 g/l and then level off somewhat at greater salt concentrations.

The salt effect can be rationalized by the fact that its presence in the dyebath enhances dye substantivity toward the fibre and also neutralises the negative charge that may exist on the surface of fibre. As mentioned above, the higher hydrophobicity of dye **1** in the dyebath relative to dye **2** makes dye **1** more sensitive toward salt addition than dye **2**. Therefore, it is reasonable that a little salt concentration in the dyebath will be effective for a higher dye exhaustion and fixation for dye **1** on silk fibre.

In other words, the twinned MCT/VS reactive system of dye **1** could result in two overlap effects, i.e. contribute to increase both the reactivity and the hydrophobicity character of this type of polyfunctional reactive dye. The formation of bis(VS) reactive system in dye **1** under neutral condition increases not only the hydrophobic interaction between the dye and the fibre, but also maximise the probability of the nucleophilic interactions between the two separate VS reactive groups and the amino group of silk. This would also result in higher total fixation yield of dye **1** than that of dye **2**.

On the other hand, the enhancement of dye exhaustion may also be attributed to the self-sustainment of dye fixation–exhaustion processes by two MCT reactive groups as a result of liberation of HCl that partially protonates some of the amino groups on silk fibre. Under neutral condition, this protonation will increase further dye uptake by ion–ion interaction between the protonised amino group on silk and the sulphonic groups present on the dye molecule, resulting in higher exhaustion and fixation values of dye **1** even at low salt concentrations. Consequently, the amount of salt required would be reduced in case of dye **1** if compared with dye **2**. For example, the exhaustion value of ca. 92% for dye **2** when applied at 60 g/l salt concentration was achieved using dye **1** at a low salt concentration of 20 g/l. Thus, it can be concluded that the use of this type of polyfunctional reactive dye for dyeing silk under neutral conditions could contribute to reduce the amounts of electrolyte required.

### 3.4. *Effect of dyeing time*

The extent of exhaustion and fixation of both dyes **1** and **2** (3% owf) on silk at different dyeing time was investigated under the same neutral dyeing conditions of 40 g/l $Na_2SO_4$ and at 90 °C. The results shown in Fig. 4 reveal that the highest total fixation of ca. 84% for dye **2** when applied for 120 min was achieved using dye **1** for 60 min.

On the other hand, dye **1** has higher exhaustion and total fixation yield if compared with dye **2** over the range of dyeing time studied. This is due to the fact that the polyfunctional bis(MCT/VS) reactive system of dye **1** is able to react more effectively (more substantivity and more probability of dye—fiber interaction) with the nucleophilic amino group in silk fibre than the bifunctional MCT/VS reactive system of dye **2**, resulting in high fixation efficiency of dye **1** even at shorter dyeing time.

The results also indicate that the values of fixation significantly affect the absorption of polyfunctional reactive dye **1**. It is believed that during dyeing process, equilibrium is established between the dye in the fibre and the dye in solution. This equilibrium is disturbed when the two VS and two MCT dye reactive groups react with fibre leading to a further dye uptake. Thus, increasing the rate of dye fixation for dye **1** would lead to an increase of dye exhaustion values during the fixation stage of dyeing.

### 3.5. *Effect of dye concentration*

Exhaustion and total fixation of dyeing silk with different concentrations of both dyes **1** and **2** (1–5% owf) under the same neutral dyeing conditions of 40 g/l $Na_2SO_4$ and at 90 °C were investigated and the results are shown in Fig. 5.

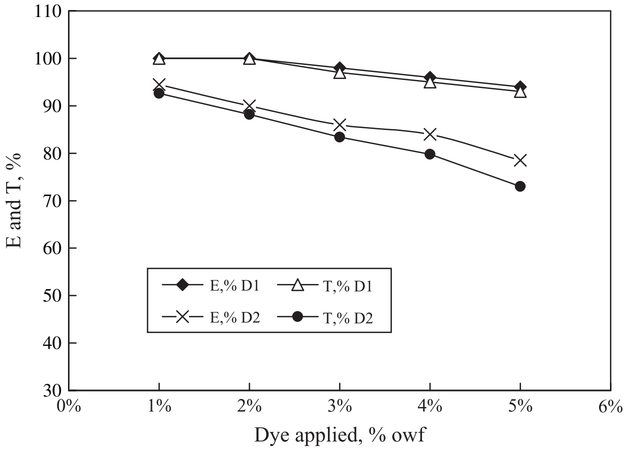


Fig. 5. Exhaustion (*E*) and total fixation (*T*) at different concentrations of bis(MCT/SES) **1** and MCT/SES **2**.

The important feature of the polyfunctional dye **1** as shown from Fig. 5 is that it can reach a complete dye exhaustion and total fixation yield (100%) on silk especially at low dye concentrations, but at a concentration of 5% owf, the dye exhibits 94% exhaustion and 93% total fixation yield.

It is also clear that the extent of exhaustion and total fixation values secured using the polyfunctional bis(MCT/SES) dye **1** was higher than that of the conventional bifunctional MCT/SES dye **2**. These results also indicate that the extent of exhaustion and total fixation values appears to decrease with increasing dye concentrations. This is believed to be due to the fact that increasing dye concentration would lead to an increase in dye aggregation, which in turn lowers dye penetration in the fibre and thus lower exhaustion and fixation are obtained.

The total dye fixation yield (% owf) at various dye concentrations is shown in Fig. 6. This results show that the polyfunctional dye **1** has the higher values, i.e. greater efficiency of

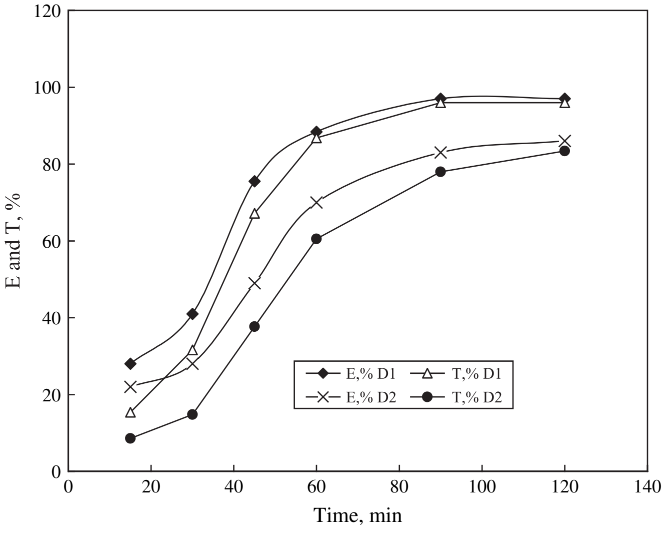


Fig. 4. Exhaustion (*E*) and total fixation (*T*) of bis(MCT/SES) **1** and MCT/SES **2** (3% owf) at different dyeing times.

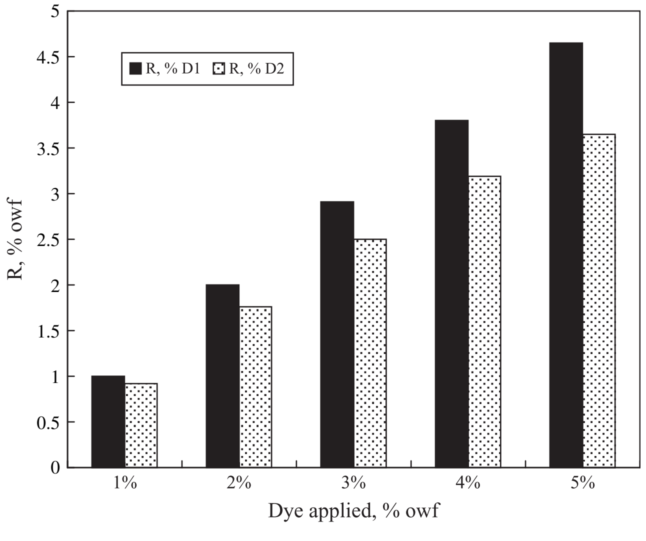


Fig. 6. Extent of the total fixation (% owf) at different dye applications of bis(MCT/SES) **1** and MCT/SES **2**.

dye–fibre fixation than the conventional bifunctional dye **2** over the range of dye concentrations studied. This seems reasonable as dye **1** is able to react polyfunctionally with silk through its bis(MCT/VS) reactive system if compared with the bifunctionality reaction of MCT/VS reactive system in dye **2**.

In view of these results obtained on dyeing silk with this type of polyfunctional reactive dye, it is convenient to conclude that the dye under investigation exhibited higher exhaustion and total fixation values if compared with our previously reported results using polyfunctional disulphide bis(ES-MCT/SES) reactive dye [4] at all dye concentrations. It is worth to mention that the present dye could be applied in neutral medium with excellent dyeability, whereas the previously reported dye exhibited high exhaustion and total fixation only in alkaline medium. The merit of the present dye may be relied on its applicability in neutral medium, which would lower the need of excess salt. Therefore, the present polyfunctional dye would have a better environmental impact.

## 4. Fastness properties

The fastness properties of both dyes **1** and **2** on silk fibre, dyed at 3% owf, pH 7, liquor ratio 40:1, 40 g/l $Na_2SO_4$ and at 90 °C were investigated and are given in Table 1. The results show that colour fastness to washing and perspiration of both dyes examined were approximately the same, depending on the proportion of the dye fixed. The dry and wet rubbing fastness of all dyeings seems to be high. The high fastness is probably due to the fact that both dyes are reactive and well penetrated inside the silk fibre. Also the light fastness for both the dyes was found to be the same. This seems reasonable as the polyfunctional dye **1** under investigation has approximately the same chromophoric system as the bifunctional dye **2**.

## 5. Conclusion

The main purpose of this investigation was to compare the results of dyeing silk fabrics with a polyfunctional bis(MCT/SES) dye **1** and a commercial bifunctional MCT/SES dye **2**. As a result of the β-elimination reactions of the two separate SES groups in dye **1**, the formation of the polyfunctional bis(MCT/VS) reactive system under neutral dyeing conditions promotes higher exhaustion and fixation if compared with the bifunctional MCT/VS reactive system of dye **2** even at low salt concentrations. All the reactive dyeings in this study exhibited high fastness properties. In comparison with our previous polyfunctional disulphide bis(ES-MCT/SES) reactive dye, the present polyfunctional dye exhibited a higher exhaustion and total fixation values on silk.

Table 1
Fastness properties of reactive dyes bis(MCT/SES) **1** and MCT/SES **2** on silk

| Dye | Fastness to rubbing | | Wash fastness | | | Fastness to perspiration | | | | | | Light |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Alkaline | | | Acidic | | | |
| | Dry | Wet | Alt | SC | SW | Alt | SC | SW | Alt | SC | SW | |
| **1** | 4–5 | 4–5 | 5 | 5 | 5 | 4–5 | 5 | 5 | 5 | 5 | 5 | 4–5 |
| **2** | 4 | 4–5 | 5 | 5 | 5 | 4–5 | 5 | 5 | 4–5 | 5 | 5 | 4–5 |

Alt = alteration; SC = staining on cotton; SW = staining on wool.

## References

[1] Renfrew AH, Taylor JA. Rev Prog Color 1990;20:1–9.
[2] Matsui M, Meyer U, Zollinger H. J Soc Dyers Colour 1988;104:425–31.
[3] Agarwal D, Sen K, Gulrajani ML. J Soc Dyers Colour 1995;112:10–6.
[4] Youssef YA, Mousa AA. Color Technol 2002;118:325–9.
[5] Lewis DM, Ho YC. Dyes Pigments 1995;28:171–92.
[6] Omura T, Yokogawa K, Kayane Y, Tezuka Y. Dyes Pigments 1995;29:1–21.
[7] Guo LN, Petit-Ramel M, Gauthier R, Chabert B, Jacquet A. J Soc Dyers Colour 1993;109:213–9.
[8] Gulrajani ML, Jain A, Agarwal D. Indian J Fibre Text Res 1995;20:150–5.
[9] Kuehni RG, Bunge HH. In: Mark H, Kroschwitz JI, editors. Encyclopedia of polymer science and engineering. 2nd ed., vol. 5. New York: John Wiley & Sons; 1986. p. 214.
[10] Lewis DM, Renfrew AH, Siddique AA. Dyes Pigments 2000;47:151–67.
[11] Lewis DM, Shao JZ. J Soc Dyers Colour 1995;111:146–50.
[12] Bahrini Z, Burkinshaw SM. Dyes Pigments 1995;27:169–82.
[13] Methods of test for colour fastness of textiles and leather. 5th ed. Bradford: SDC; 1990.
[14] Meyer U, Yang J-Z, Zollinger H. Textilveredlung 1985;20:354–6.