

## High Performance Thiophene-Based Bifunctional Sulphatoethylsulphone Disazo Reactive Disperse Dye on Silk and Nylon 6 Fabrics

Farouk R., Mohammed F. A., Youssef Y. A. and Mousa A. A

Textile Research Division, National Research Centre, 12622 Dokki, Cairo, Egypt  
[fatmaali\\_611@yahoo.com](mailto:fatmaali_611@yahoo.com)

**Abstract:** A new disazo reactive disperse dye was prepared by coupling 2-aminothiophene-3-carbonitrile with 4-sulphatoethylsulphonebenzene diazonium chloride, and the product was re-diazotized and coupled with 2-aminonaphthalene-6-sulphatoethylsulphone to produce the target bis-sulphatoethylsulphone dye. The dye was applied to nylon 6 and silk fabrics over a wide range of pH. Optimum dye exhaustion and fixation were achieved at pH 8 and 100 °C. All the dyed fabrics tested displayed high light fastness and excellent washing fastness properties. This model of dye has a merit of being combine between highly reactive system represented by the temporarily anionic bis sulphatoethylsulphone groups and bathochromic shift effect represented by using aminothiophene moiety derivative for achieving a high dyeing performance disazo reactive disperse dye. [Farouk R., Mohammed F. A., Youssef Y. A. and Mousa A. A **High Performance Thiophene-Based Bifunctional Sulphatoethylsulphone Disazo Reactive Disperse Dye on Silk and Nylon 6 Fabrics.** *J Am Sci* 2012;8(12):1101-1105]. (ISSN: 1545-1003). <http://www.jofamericanscience.org>. 148

**Keywords:** Reactive disperse dye; Thiophene; Bifunctional Sulphatoethylsulphone; Silk; Nylon 6.

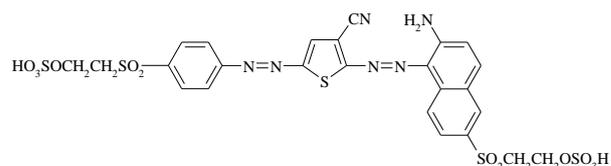
### 1. Introduction

Most heterocyclic dyes of technical interest for application to textiles are derived from diazo components consisting of five-membered rings containing one sulphur heteroatom. Systems of this kind are capable of providing red to blue disperse dyes (Hari and Vithal, 2002) The colours of nonionic monoazo dyes containing thiophene rings were investigated as long ago as 1949 by (Dann, 1949). Thiophene-containing azo dyes have many advantages including a colour deepening effect as an intrinsic property of the thiophene ring (Alaa and Tarek, 2006) moreover, the 2-aminothiophenes having electron withdrawing substituents in the three and five position exhibit deep colours with outstanding light fastness, in addition azo disperse dyes derived from 2-aminothiophene possess excellent dischargeability and sublimation fastness (Gewald *et al.*, 1966).

Other types of thiophene-based azo dyes were investigated, for example nonionic monoazo reactive disperse dyes containing substituted 3-aminobenzothiophenes as diazo component and vinylsulphonyl-ethyl-m-toluidine as coupling component have been reported (Nishida *et al.*, 1981). Also nonionic disazo reactive disperse dye containing 2-aminothiophene-3- carbonitrile and monofluorotriazine reactive group, was applied to polyester/cotton blend in one bath using supercritical carbon dioxide dyeing technique (Maeda and Kunitou, 2004).

In our previous studies, we reported the synthesis and evaluation of some novel temporarily anionic sulphatoethylsulphone reactive disperse dyes as having potentially high fixation and fastness properties (Mousa *et al.*, 2006, Youssef *et al.*, 2007, Youssef *et al.*, 2007, Mousa *et al.*, 2007, Youssef *et al.*, 2009 and Mousa *et al.*, 2011). The

affinity of these dyes was greatly enhanced by introducing a bis-sulphatoethylsulphone system into the disperse dye molecule. The colour of these dyes ranges from yellow to red. To the best of our knowledge no significant work has been done on aminothiophene reactive disperse dyes containing temporarily anionic SES group. In the interest of understanding the role of temporarily anionic SES reactive group in the disperse dye molecule having bathochromic shift for achieving deep colour shades, we now report the synthesis and evaluation of related bifunctional sulphatoethylsulphone disazo reactive disperse dye based on 2-aminothiophene-3- carbonitrile as a coupling and diazo component at the same time.



Bis(SES) reactive disperse dye

### 2. Experimental

#### General

Dye purity was assessed by thin layer chromatography (TLC) using butan-1-ol: DMF: acetic acid (24:11:2, v/v) eluent on silica gel plates. Infrared (IR) spectra were recorded on a Nexus 670 FTIR Spectrometer (KBr; Thermo Nicolet).

<sup>1</sup>H-NMR spectra were recorded on a JEOL JNM-EX 500 MHz spectrometer using tetramethylsilane (TMS) as an internal standard. The maximum absorption wavelength ( $\lambda_{max}$ ) was measured on a Shimadzu UV-2401PC UV/Vis spectrophotometer. Dyed samples were evaluated for their colour properties using an UltraScan PRO

spectrophotometer (Hunter Lab) with a D<sub>65</sub> illuminant and 10° standard observer.

### Materials

Degummed and bleached silk fabric, 80 g/m<sup>2</sup> was obtained from El-Khateib Co. Before application, the fabric was treated in an aqueous solution containing 2 g/L (Hostapal CV, Clariant, Egypt) for 1 h at 80 °C and a 50:1 liquor ratio (LR), then washed thoroughly in water and air dried at room temperature.

Scoured and bleached single jersey knitted polyamide 6 (nylon 6) fabric, 114 g/m<sup>2</sup>, 135 d/30f was obtained from El-Shourbagy Co., Egypt. Before dyeing, the fabric was treated with a solution containing 2 g/l nonionic detergent (Hostapal CV, Clariant, Egypt) at 60 °C for 30 min, thoroughly washed in water and air dried at room temperature. 2-Aminothiophene-3-carbonitrile was obtained from Aldrich, 2-aminonaphthalene-6-β-sulphatoethylsulphone, and 1-aminobenzene-4-β-sulphatoethylsulphone were obtained from Amar Impex, Mumbai, India. All other chemicals and solvents used in this study were laboratory reagent grade.

### Synthesis of bifunctional bis(SES) reactive disperse dye

1-Aminobenzene-4-β-sulphatoethylsulphone (2.96 g; 0.01 mol; 95%) was diazotized by the method previously described (Lewis *et al.*, 2000). The resulting diazonium solution was added in portions over 30 min at a temperature below 4 °C to a solution of 2-aminothiophene-3-carbonitrile (1.28 g; 0.01 mol; 97%) which was dissolved in acetone/water mixture (2:1). The reaction mixture was stirred at 0-5 °C for 4 hrs. The precipitated dye was filtered off and dried at room temperature under vacuum. The resultant dye (2.08 g; 0.005 mole) was dissolved in at least amount of DMF and the solution was cooled to 0-5 °C, then 9 ml of diluted sulphuric acid (54%) was added. The reaction mixture was stirred at these conditions for 30 min. A solution of NaNO<sub>2</sub> (0.36 g; 0.00524 mole) in water (4 ml) was added over a period of 10 minutes with stirring. Stirring was continued for an additional 1 h, maintaining the temperature below 5°C. The excess of nitrous acid (gave a positive test on starch-iodide paper) was decomposed with the required amount of sulphamic acid. A solution of 2-aminonaphthalene-6-β-sulphatoethylsulphone (1.84 g; 0.005 mol; 90% w/w), dissolved in a mixture of 25 ml distilled water/50 ml ethanol, was added to the diazo solution over 30 min. at 0-5 °C, the pH was adjusted to 4.5-5 by 2M aqueous solution of sodium carbonate solution, then the reaction was continued at these conditions for a further 2 hrs.

The resultant dye was filtered off and dried at room temperature under vacuum. The dye was characterized by TLC ( $R_f = 0.71$ ) and its wavelength of maximum absorption ( $\lambda_{max}$ ) in 50% aqueous DMF = 560 nm.

The structure of the dye (C<sub>25</sub>H<sub>22</sub>N<sub>6</sub>O<sub>12</sub>S<sub>5</sub>) is confirmed from the following results:

Elemental analysis, Calc. (%): C, 39.57; H, 2.92; N, 11.08; S, 21.13. Found (%) C, 37.9; H, 2.10; N, 11.80; S, 20.00. IR (ν/cm<sup>-1</sup>): 3406, 3328 (NH<sub>2</sub>), 1627 (-N=N-), 1133 (-SO<sub>2</sub>-), 1253, 1048, and 1000 cm<sup>-1</sup> (-OSO<sub>3</sub>H). <sup>1</sup>H-NMR: δH (ppm) in [<sub>2</sub>H<sup>6</sup>] DMSO: 3.61-3.64 (4H, *t*, J = 6.9 Hz, α-CH<sub>2</sub> (SES)), 3.90-3.95 (4H, *t*, J = 6.9 Hz, β-CH<sub>2</sub> (SES)), 7.74 (2H, *d*, J = 8.4 Hz, phenyl H), 7.77 (1H, *s*, thiophene H), 7.87 (2H, *d*, J = 8.4 Hz, phenyl H), 8.23 (3H, *m*, naphthyl H) and 8.96 (2H, *m*, naphthyl H).

### Dyeing Procedure

Dyeings of the bis (SES) reactive disperse dye were carried out in an Ahiba dyeing machine at a liquor ratio of 50:1. The dye bath was prepared at room temperature at a range of dye concentrations (1-5% owf) at pH 4, 5, 6, 7 and 8 in 0.2 M disodium hydrogen phosphate/0.1 M citric acid as buffer solutions in the presence of 1 g/L anionic dispersing agent (Eganal PSE, Clariant). Dyeing was started at 40 °C and then the temperature raised to 100 °C over 70 min. Dyeing was continued at the desired temperature for a further 60 min (130 min total dyeing time) for studying the effect of pH and dye concentration. To study the effect of dyeing time, dyeing were examined at intervals up to total dyeing time of 150 min. After dyeing, all dyed samples were rinsed with water and air dried. Dye exhaustion and total dye fixation on the dyed fabric were evaluated spectrophotometrically.

### Measurements and testing

#### Dye exhaustion

The uptake of dye by the nylon 6 and silk fabrics was measured by sampling the dyebath before and after dyeing. The dye concentration (g/l) of the dyebath, diluted 20-fold with 50 % aqueous DMF, was measured on a Shimadzu UV- 2401PC UV/VIS spectrophotometer at  $\lambda_{max}$  using a calibration curve previously obtained using known dye concentrations in 50% aqueous DMF. The percentage of dyebath exhaustion (%E) was calculated using Eqn 1 (Burkinshaw *et al.*, 2001):

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

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

### Dye fixation

The dye fixation ratio (%*F*), the percentage of exhausted dye chemically bound on the fibre, was measured by refluxing the dyed samples in 50% aqueous DMF (liquor ratio 20:1) for 10 min to extract the unfixated dye. This procedure was repeated until the extract was clear. The concentration of the extract was then measured spectrophotometrically at ( $\lambda_{\max}$ ) and the dye fixation ratio calculated using Eqn 2

$$\%F = \frac{(C_1 - C_2 - C_3)}{(C_1 - C_2)} \times 100 \quad (2)$$

Where  $C_3$  is the concentration of extracted dye.

From the dyebath exhaustion (*E*) and dye fixation ratio (*F*), the total dye fixation (*T*), which is the percentage of dye chemically bound relative to the total amount of dye used, was calculated for all dyeings using Eqn 3

$$\%T = \frac{(\%E \times \%F)}{100} \quad (3)$$

### Fastness Testing

Dyed samples, after washing-off using 2 g/L nonionic detergent at 80 °C for 15 min, were tested by standard ISO methods (Methods of tests for color fastness of textiles and leather, 1990). Wash fastness (ISO 105-C02 (1989), crock fastness (ISO 105-X12 (1987)), and fastness to perspiration (ISO 105-E04 (1989)) were evaluated using the visual ISO Gray Scale for both colour change (AATCC Evaluation Procedure (EP) 1—similar to ISO 105-A02) and colour staining (AATCC EP 2—same as ISO 105-A03) Light fastness (carbon arc) was evaluated using ISO 105-B02 (similar to AATCC test method 16-1990) and (Technical Manual of the AATCC, 1993)

## 3. Results and Discussions

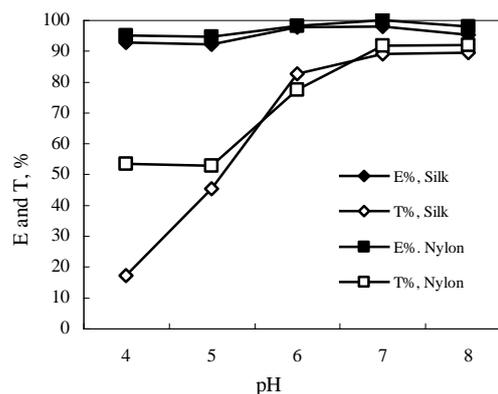
### Characterization of the disazo bis(SES) reactive disperse dye

The purity of the dye was evaluated by TLC using butan-1-ol: DMF: acetic acid as eluent system. IR spectrum of the dye showed  $\text{NH}_2$  stretching absorption bands at 3406 and 3328  $\text{cm}^{-1}$  and CN group absorption at 2210  $\text{cm}^{-1}$ . The presence of sulphated groups was revealed by the absorption bands at 1253, 1133, 1048 and 1000  $\text{cm}^{-1}$ , relative to the stretching of  $-\text{SO}_3^-$  and  $\text{SO}_2$  groups. The  $^1\text{H}$  NMR spectrum of the synthesized dye shows two triplets at 3.63 and 3.91 ppm, each integrated to four protons, assignable to the  $\alpha$ - and  $\beta$ -methylene protons of the SES groups, respectively.

### Effect of dyeing pH

In order to determine the optimum dyeing conditions for such type of reactive disperse dye on silk and nylon 6 fabrics, the dye bath pH is one of the important factors to be studied. For this purpose, a series of dyeing were carried out using 2 % owf dye concentration by varying the dyebath pH from 4 to 8 at dyeing temperature 100 °C to examine the dye exhaustion and total fixation yield on silk and nylon 6 fabrics. The results given in Figure 1 clearly show that the optimum dye exhaustion and fixation on both silk and nylon 6 fabrics were achieved at pH 8. Despite that the exhaustion values slightly vary over the pH range, this feature appeared for both fabrics, but on the other hand increasing the pH from 4 to 8 increases the total fixation yield on both fabrics, reaching a maximum value at pH 8. This would not only increase the  $\beta$ -elimination of the temporarily anionic sulphatoethylsulphone group but also maximize the concentration of the nucleophilic amino end-groups on the fiber. This may suggest that the nonionic bifunctional vinylsulphone derivative of the dye, generated from the  $\beta$ -elimination reaction of the two temporarily anionic sulphatoethylsulphone groups, can maximize the nucleophilic reaction with the amino groups on both fabrics.

The results also clearly show that the exhaustion and total fixation yield on nylon 6 was slightly higher than that on silk. This may be due to the hydrophobic character of the nonionic bifunctional vinylsulphone derivative, which would increase the dye substantivity towards nylon 6 as more hydrophobic than silk fabric.

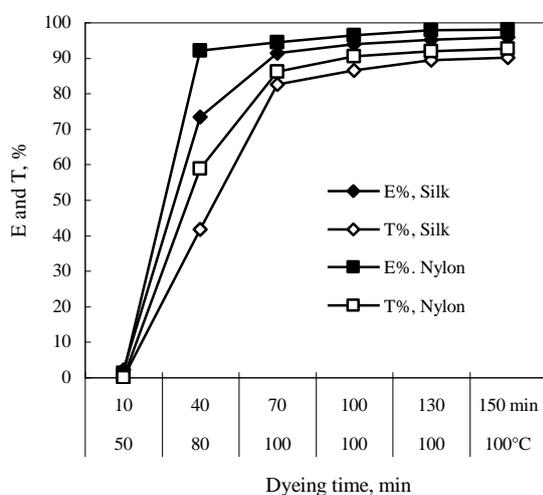


**Figure 1:** Effect of pH on the exhaustion (*E*) and total fixation (*T*) of the bis (SES) reactive disperse dye (2% owf) at 100 °C on silk and nylon 6 fabrics.

### Effect of dyeing time

The extent of exhaustion and total fixation yield of the dye was investigated on both fabrics at different dyeing times. Figure 2 shows the dyeing rate examined with 2% owf dye concentration at

100 °C and at the optimum pH 8 for both fabrics. At the early stage of dyeing, the percentage of dye exhaustion increases significantly until 70 min, probably due to its high substantivity, then gradually increased at the last 60 min until equilibrates at dyeing time (110 min) for both fabrics. It is also clear that the total fixation yield of the dye increases as the dyeing proceeds. This may be due to that the hydrophobic character of the nonionic bis(vinylsulphone) reactive system in the dye, generated from  $\beta$ -elimination reaction of bis (sulphatoethylsulphone) groups, not only imparts high substantivity under the alkaline dyeing but also effectively exhibits high fixation rate.

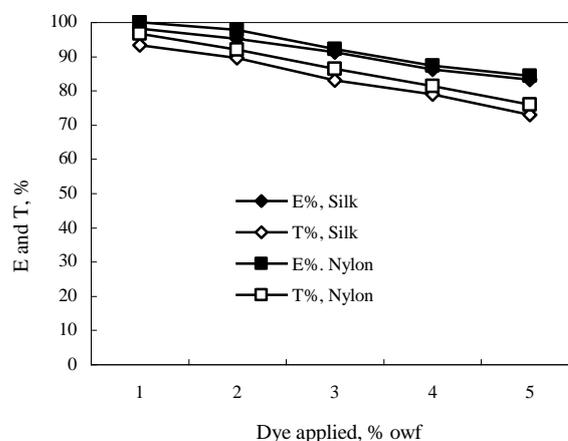


**Figure 2:** Effect of dyeing time on the exhaustion and total fixation of the dye (2% owf) at pH 8 and 100 °C on silk and nylon 6 fabrics.

#### Effect of dye concentration

The study was extended to investigate the effect of dye concentration on the exhaustion and fixation of the dye on silk and nylon 6 fabrics at the optimum dyeing conditions of pH 8 and 100 °C. The results are given in Figure 3 for dyeing concentrations between 1 and 5% owf. These indicate that the extent of dye exhaustion and fixation decrease on both silk and nylon 6 with increasing dye concentration. This is believed to be due to that at low dye concentrations the amount of dye applied would not be enough to saturate the fiber, but on the other hand the lowering of the dye substantivity at higher dye concentration results from increasing dye aggregation, resulting in a decrease in the extent of dye exhaustion and dye-fiber fixation yield. Additionally, at high dye concentration the numbers of available dye sites on the fiber decreases and competitive hydrolysis increases, resulting in a lower extent of exhaustion and fixation yield.

It can also be seen that the dye exhibits a slightly higher values on nylon 6 fabric than on silk fabric.



**Figure 3:** Exhaustion and total fixation at different dye concentrations, pH 8 and at 100 °C on silk and nylon 6 fabrics.

#### Fastness properties

The fastness properties of the dye on both silk and nylon 6, dyed at 2% and 4% owf, liquor ratio 50:1, pH 8 and 100 °C, were investigated and are given in Table 1. The results show that the fastness to rubbing, washing and perspiration of the dyeing on nylon were better than that on silk. This seems reasonable as we have seen that the dye affinity towards nylon 6 is better than that of silk, this suggestion confirmed also by the k/s values. The light fastness values on silk and nylon 6 were identical.

#### 4-Conclusions

A new disazo reactive disperse dye containing two temporarily anionic sulphatoethylsulphone groups has been synthesized and applied to silk and nylon 6 fabrics by exhaust dyeing. The dye displayed high fixation yield when applied to silk and nylon 6 under alkaline conditions. The optimum exhaustion and fixation were achieved at pH 8 and at 100°C for both fabrics.

This dye under these conditions exhibited high build up of being has two temporarily anionic sulphatoethylsulphone groups resulted in the formation of nonionic bifunctional vinylsulphone derivatives which in turn maximize the dye-fiber fixation.

This model of dye has a merit of being combine between highly reactive system represented by the temporarily anionic bis (sulphatoethylsulphone) groups and bathochromic shift effect represented by using aminothiophene moiety derivative (as coupler and diazonium in the same dye molecule)

for achieving a high dyeing performance disazo reactive disperse dye.

**Table 1** Fastness properties and color strength (K/S) of the bis(SES) reactive disperse dye on nylon 6 and silk fabrics

fabric	Dye Conc. % owf	K/S	Fastness to rubbing		Washfastness <sup>a</sup>			Fastness to perspiration <sup>a</sup>						Light
			Dry	Wet	Alt	SC	SN	Alkaline			Acidic			
								Alt	SC	SN	Alt	SC	SN	
Nylon 6	2	15.9	5	5	4-5	5	4	4-5	5	5	4-5	5	4-5	6
	4	20.76	4-5	4-5	4-5	4-5	3-4	4-5	4-5	4	4-5	4-5	4	
Silk	2	9.35	4	4	4-5	4	3	4-5	4-5	3-4	4-5	4-5	3-4	6
	4	12.73	3-4	3-4	4-5	3-4	2-3	4-5	4	3	4-5	4	3	

### Corresponding author

Mohammed F. A

Textile Research Division, National Research Centre, 12622 Dokki, Cairo, Egypt

[fatmaali\\_611@yahoo.com](mailto:fatmaali_611@yahoo.com)

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