# A new approach to the dyeing of silk with sulphatoethylsulphone dyes

D M Lewis and J Z Shao*

*Dept of Colour Chemistry and Dyeing, University of Leeds, Leeds LS2 9JT, UK*

A new approach to the dyeing of silk with sulphatoethylsulphone dyes, based on β-elimination before dyeing, has been investigated. Some factors affecting both β-elimination and dyeing have been studied. The improved dyeing process shows a high degree of dyebath exhaustion and excellent fixation in the absence of salt, thus reducing the risk of environmental pollution from salt and dyes.

## INTRODUCTION

Silk has been called 'the queen of fibres' [1,2], its natural lustre, handle and draping properties being superior to those of many other textile fibres. However, the wet fastness of dyed silk is often unsatisfactory due to the use, in conventional dyeing, of acid, basic or direct dyes, which interact with the silk protein through ionic attraction, hydrogen bonding and van der Waals forces. Hence the use of reactive dyes, which can bind covalently with silk, should become more important in order to meet high wet fastness requirements.

Sulphatoethylsulphone colorants and their vinylsulphone derivatives are a major group of reactive dyes [3], first introduced by Hoechst under the trade name Remazol. The wet fastness and brilliance of the silk dyed with Remazol dyes are good [4–6]. Song has stated that silk can be dyed with Remazol dyes at pH 7–8 and 80°C in the presence of salt [7], while Venugopal has found that vinylsulphone dyes can be employed using long-liquor or pad methods, with the addition of Glauber's salt and soda ash during the dyeing [8]. Hoechst has recommended that exhaust dyeing of silk with Remazol dyes should be carried out at 60°C in the presence of 30–50 g/l Glauber's salt, adding 2 g/l soda ash after the material has been in the dyebath for a few minutes [9].

This paper describes work undertaken to develop an improved dyeing process, in which β-sulphatoethylsulphone dyes were initially fully activated by a pretreatment at pH 8 to give the corresponding free vinylsulphone dyes. The latter were then applied to silk at pH 4.0–4.5 in the absence of salt.

## EXPERIMENTAL

### Materials

Mill-degummed and bleached woven silk twill fabrics were used in the dyeing experiments. Before dyeing, the fabrics were treated in an aqueous solution containing 1 g/l nonionic surfactant (Sandozin NIE (S)) for 10 min at 90°C and a liquor ratio of 50:1, then washed thoroughly in water at room temperature.

Remazol dyes were commercial samples supplied by Hoechst. All chemical reagents were of laboratory grade. Buffered solutions covering the range pH 6–8 were prepared using 0.1 M sodium hydroxide and 0.1 M sodium dihydrogen phosphate, while buffered solutions of pH 4–5 were prepared using acetic acid and sodium acetate.

### Dyeing

All dyeings were carried out using a Werner Mathis AG BFA-16 laboratory dyeing machine with IR heating. The improved dyeing process involved three steps: β-elimination, vinylsulphone dye application and aftertreatment. Unless otherwise stated, β-elimination was carried out in a buffer system (pH 8) for 5 min at 100°C to yield the vinylsulphone dyes. The dyeing process was carried out according to the profile shown in Figure 1. At the end of the process, the sample was rinsed twice in 50–100 ml cold water, and aftertreated in 50 ml Sandozin NIE (2 ml/l) solution for 15 min at 80°C, then rinsed and dried under ambient conditions.

The conventional dyeing method (as practised by industry) was carried out for 40 min at 80°C and pH 7 in the presence of 20 g/l sodium sulphate, using the same

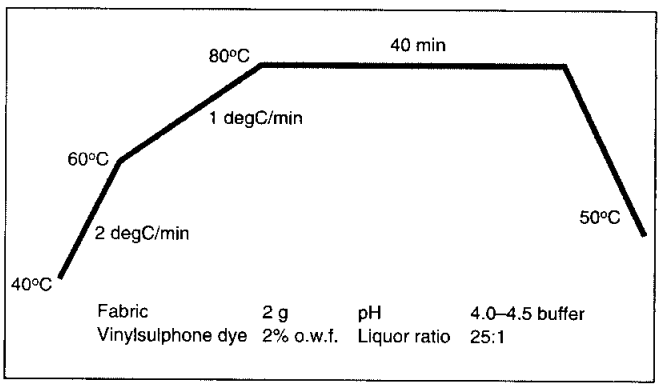



**Figure 1** Dyeing profile used in the present study

*Present address: Zhejiang Institute of Silk Textiles, PR China

time/temperature curve shown in Figure 1. The resultant dyeing was aftertreated in 50 ml of an aqueous solution containing 2 ml/l Sandozin NIE for 15 min at 80 °C.

**Test methods**

The percentage dye exhaustion $E$ was calculated according to Eqn 1:

$$E = \frac{A_0 - A_t}{A_0} \times 100\% \quad (1)$$

where $A_0$ and $A_t$ are the absorbances (at $\lambda_{max}$) of dye originally in the dyebath and of residual dye in the dyebath respectively. The percentage fixation of absorbed dye $F$ was calculated according to Eqn 2:

$$F = \frac{(K/S)_a}{(K/S)_b} \times 100\% \quad (2)$$

where $(K/S)_a$ and $(K/S)_b$ are Kubelka Munk functions of the aftertreated sample and of the just-dyed sample respectively, determined using a Macbeth reflectance spectrophotometer.

The total percentage fixation efficiency ($T$) was calculated according to Eqn 3:

$$T = \frac{EF}{100} \quad (3)$$

The washing fastness test was performed according to BS 1006:C01:1978.

The rate of conversion of the sulphatoethylsulphone dyes to the reactive vinylsulphone and hydrolysed forms was determined using a Varian 5000 high-performance liquid chromatograph (HPLC). Phase A was water containing 0.001 mol tetrabutylammonium bromide, 1 ml acetic acid (20%) and 1 ml potassium hydroxide (5%) in 1000 ml deionised water, while phase B was acetonitrile. The ratio A/B was 64:36 and the flow rate was 1 ml/min. The column employed contained a C18 bonded silica phase.

Dyeing levelness was determined according to the method of Wang and Shao [10]. Five points on a trial sample were determined using a Macbeth ColorEye spectrophotometer. The first point was taken as the standard, with which the other four points were compared. If the maximum $\Delta E$ was less than 0.50, the levelness grade was defined as 1; if the maximum $\Delta E$ was 0.50–1.00, or more than 1.00, the levelness grade was defined as 2 or 3 respectively.

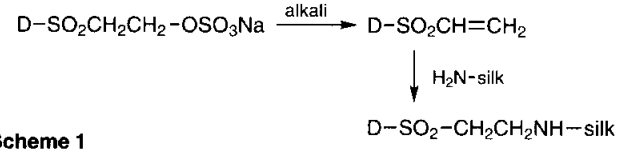
## RESULTS AND DISCUSSION

**Effect of time and pH**

Commercial Remazol dyes usually contain a β-sulphatoethylsulphone group which, under the action of alkali, eliminates bisulphate to produce a vinylsulphone group. The vinylsulphone groups are highly reactive, and under mildly acidic conditions they react with amino groups in the silk fibre via a nucleophilic addition mechanism (Scheme 1). The elimination step is crucial to the improved dyeing process, since the vinylsulphone form gives better exhaustion and fixation than does the sulphatoethylsulphone form.

The effect of time and pH on the formation of the vinylsulphone dye and subsequent hydrolysis were followed using HPLC, and the degree of vinylsulphone formation was measured as a function of pH and time (Figure 2). The formation of the inactive hydroxyethylsulphone dye was also determined (Figure 3). For these studies Remazol Brilliant Blue R (CI Reactive Blue 19, dye **1**) was initially selected.

Figures 2 and 3 show that, in the region pH 4–5, hardly any of the starting dye converted either to the vinylsulphone or the hydrolysed form within 10 min. Raising the pH value to 7–8, however, gave very high conversion rates after only 5–10 min, decreases in the amount of vinylsulphone form being due to the formation of hydrolysed dye. The dye hydrolysed more rapidly at




**Scheme 1**

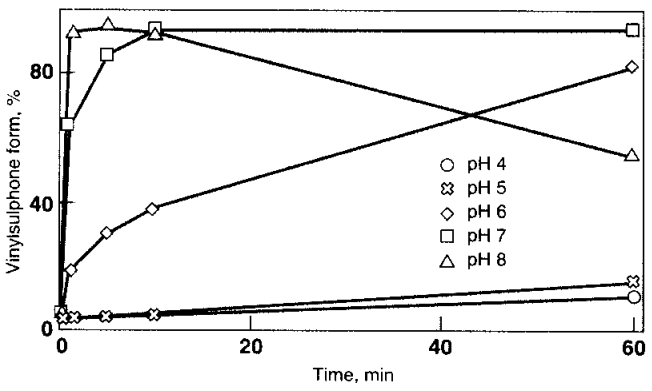



**Figure 2** Rate of conversion of Remazol Brilliant Blue R (1.5 g/l) to its vinylsulphone form at 100°C

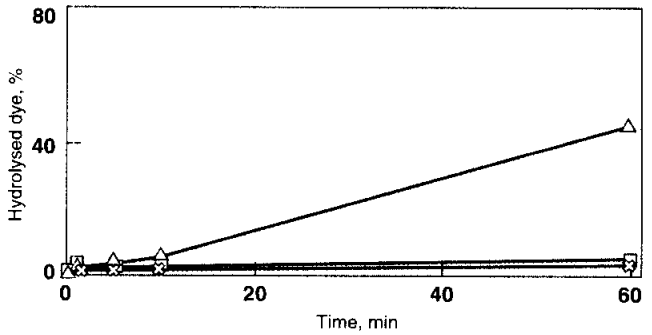



**Figure 3** Rate of hydrolysis of Remazol Brilliant Blue R (1.5 g/l) at 100°C (for key see Figure 2)

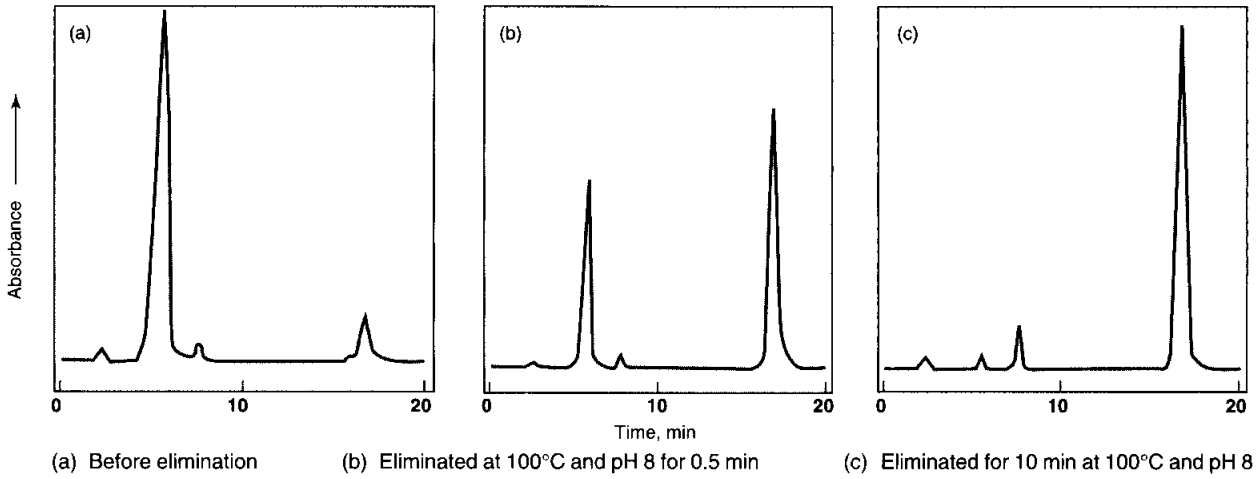



**Figure 4** HPLC chromatograms of Remazol Brilliant Blue R and its derivatives

pH 8 than at pH 7. These results confirm that, in order to achieve sufficient dye–fibre reaction, the optimum pH for conventional dyeing of silk with sulphatoethylsulphone dyes should be in the range 7–8, and that the most suitable pretreatment conditions for Remazol dyes with the improved dyeing process are pH 8 for 5 min or pH 7 for 10 min at 100°C.

Typical HPLC chromatograms of the various derivatives of Remazol Brilliant Blue R are shown in Figure 4. The peak at 6 min is the parent sulphatoethylsulphone form, the peak at 8 min is the hydroxyethylsulphone form and the peak at 17.2 min is the vinylsulphone form. Other Remazol dyes, including Remazol Black B (CI Reactive Black 5, dye **2**), were examined in the above manner and were found to eliminate to the corresponding vinylsulphone dyes under similar conditions.

### Effect of dyebath pH

Dyebaths were set at pH 4, 5, 6, 7 or 8, the dyebaths at pH 5–8 having 20 g/l sodium sulphate added. The effects of pH on the exhaustion and the fixation in both conventional and improved dyeings were determined and the results obtained shown in Figures 5–7. These show that in conventional dyeing the exhaustion and fixation depended to a large extent on dyebath pH. When dyeing with sulphatoethylsulphone dyes at pH 4, maximum exhaustion was achieved, although fixation was very limited, as hardly any sulphatoethylsulphone dye converted to the reactive vinylsulphone form. In this case the sulphatoethylsulphone dye behaved more like an acid dye, bonding with silk by

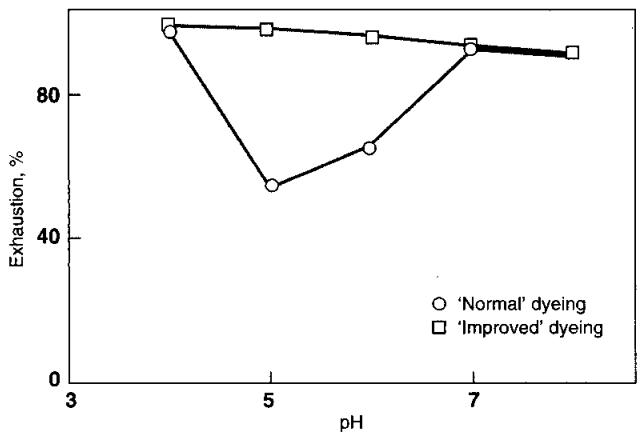



**Figure 5** Effect of dyebath pH on the exhaustion of Remazol Black B (2% o.w.f.)

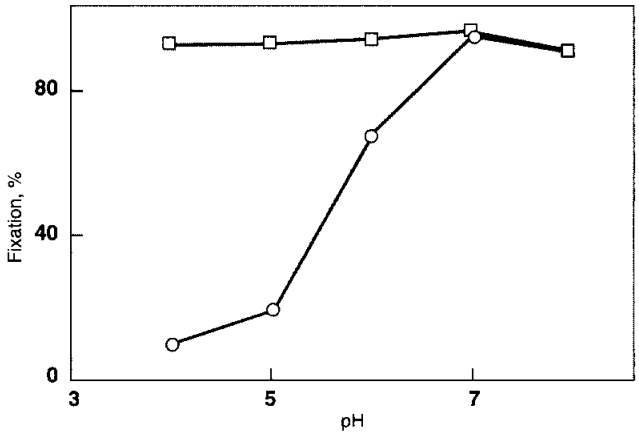



**Figure 6** Effect of dyebath pH on the fixation of Remazol Black B (2% o.w.f.) (for key see Figure 5)

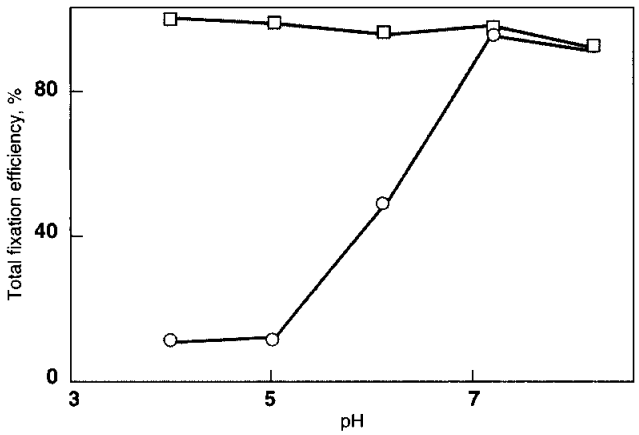



**Figure 7** Effect of dyebath pH on the total fixation efficiency of Remazol Black B (2% o.w.f.) (for key see Figure 5)

ionic attraction. When dyeing with the sulphatoethylsulphone dye in the pH region 5–7, both exhaustion and fixation increased with increasing dyebath pH, owing to the enhancement in the rate of conversion of the dye to the reactive vinylsulphone form.

The situation in the improved dyeing process with pretreated vinylsulphone dye was very different from that pertaining in conventional sulphatoethylsulphone dyeing, i.e. the exhaustion and fixation were virtually independent of dyebath pH, because the vinylsulphone dye reacted equally with silk nucleophiles at any pH in the experimental range (pH 4–8). Undoubtedly, the lack of variation in exhaustion and fixation values from weakly acidic to weakly alkaline conditions would be beneficial in terms of shade reproducibility in practical dyeing.

Moreover it was observed that at pH 5 and 6 the exhaustion obtained using the improved dyeing method was much higher than that from the conventional dyeing method. This was because covalent reactions with the fibre interfered with the equilibrium absorption brought about by non-covalent interactions. Confirmation comes from earlier work on wool, which showed that a hydroxyethylsulphone dye (2% o.w.f. pure dye) gave 22% exhaustion from dyebaths at pH 6, whereas its reactive vinylsulphone analogue, at the same depth of shade, gave 97% exhaustion [11].

### Effect of electrolyte

In conventional dyeing of silk with sulphatoethylsulphone dyes, electrolyte (usually sodium chloride or sodium sulphate) is always needed in order to achieve both adequate dye substantivity for the fibre and exhaustion. The effect of sodium sulphate additions on both conventional and improved dyeing methods using Remazol Black B were evaluated and the results obtained are plotted in Figure 8. This shows that at pH 7, which is above the isoelectric point of the silk fibre, the effect of electrolyte in the improved dyeing method was less than that with the conventional dyeing method. This was probably because after elimination the sulphatoethylsulphone dye was converted to the vinylsulphone form, which has fewer negative charges (sulphonate anions removed), leading to a decrease in ionic repulsion between the anionic dyes and the negatively charged silk. With the improved dyeing method, at pH 4.0–4.5, the exhaustion and fixation were independent of electrolyte concentration and unexpectedly high. This behaviour could be because this pH range is close to the isoelectric point of silk [12], so that anionic dyes could be absorbed initially onto positively charged sites in the silk, via ionic attraction, hydrogen bonding and van der Waals forces. The dyes could then be fixed on the fibres by covalent bond formation with amino groups.

Naturally the use large amounts of electrolyte in conventional reative dyeing has adverse environmental consequences [13]. The improved dyeing method with activated Remazol dyes at pH 4.0–4.5 in the absence of electrolyte could contribute to reducing this problem.

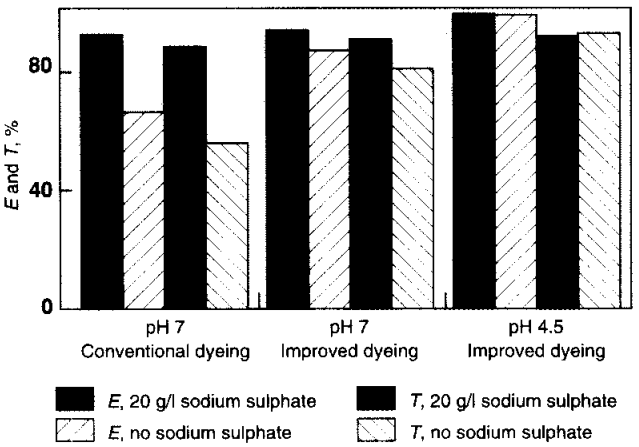



**Figure 8** Comparison of the effect of electrolyte on the conventional dyeing and the improved dyeing method with Remazol Black B

**Table 1** Effect of dye concentration on the improved dyeing process

| Dye[b] | Concn (% o.w.f.) | *E* (%) | *F* (%) | *T* (%) | Washing fastness[a] A | B | C | Levelness |
|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 100 | 97 | 97 | 5 | 5 | 5 | 1 |
| | 3 | 100 | 96 | 96 | 5 | 5 | 5 | 1 |
| | 4 | 98 | 94 | 92 | 5 | 5 | 5 | 1 |
| | 5 | 96 | 92 | 88 | 5 | 5 | 5 | 1 |
| 2 | 2 | 99 | 93 | 92 | 5 | 5 | 5 | 1 |
| | 3 | 98 | 93 | 91 | 5 | 5 | 5 | 1 |
| | 4 | 97 | 92 | 89 | 5 | 5 | 5 | 1 |
| | 5 | 96 | 90 | 86 | 5 | 5 | 5 | 1 |

a A Change in colour
B Staining on cotton
C Staining on silk

b Dye 1 Remazol Brilliant Blue R
Dye 2 Remazol Black B

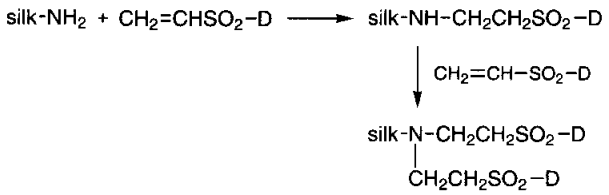
### Effect of dye concentration

Table 1 shows the effect of dye concentration on exhaustion, fixation, washing fastness and levelness in the improved silk dyeing process with Remazol dyes at pH 4.5. Increasing the dye concentration was accompanied by a slight decrease in exhaustion and fixation. Even at a dye concentration of 5% o.w.f., the exhaustion and fixation values were more than 96% and 86% respectively, which may be attributed to lack of steric inhibition and the high reactivity of vinylsulphone groups, leading to two vinylsulphone dye molecules reacting with one silk amino nucleophile (Scheme 2) [14].

At a dye concentration of 5% o.w.f., the dyed silk fabrics showed excellent washing fastness and levelness.

## CONCLUSIONS

The improved method proposed for dyeing with vinylsulphone dyes gives highly reproducible dyebath exhaustion and dye–fibre fixation from weakly acidic to weakly alkaline conditions. Free vinylsulphone dyes are formed after elimination of the sulphatoethylsulphone




**Scheme 2**

dyes, and these form covalent bonds with silk over a wide pH range.

Electrolyte concentration has little effect on exhaustion and fixation in the improved dyeing process. At pH 4.0–4.5 no electrolyte is needed in the dyebath, and the vinylsulphone dyes are initially absorbed by ionic attraction, hydrogen bonding and van der Waals forces, and they then become fixed by covalent bonding. The silk fabrics dyed by the improved process show high wet fastness and levelness.

In the proposed dyeing process the optimum elimination conditions for converting sulphatoethylsulphone dyes to their vinylsulphone analogues are treatment for 5 min at 100°C and pH 8. With the vinylsulphone dyes, the optimum conditions for dyeing are 40 min at 80°C and pH 4.0–4.5 in the absence of salt.

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