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Dye-resist Effects on Silk Fabric Treated with Sulphamic Acid and Sandospace R

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ABSTRACT

The reactive molecules sulphamic acid and Sandospace R were applied to silk fabric, and their respective capacity to resist the fixation of acid, metal complex and reactive dyes were compared. Weight gains of 2–8% for sulphamic-acid-treated silk were easily obtained by a pad-dry-cure process and the treated silk exhibited excellent resist effects towards all three dye classes. High weight gains were more difficult to obtain during exhaustion of Sandospace R onto silk fabric and, consequently, dye-resist effects achieved with this reactive agent were inferior to those of sulphamic acid for practical treatment levels. The strength retention, yellowness index and subjective handle of the treated fabrics were also assessed.

1 INTRODUCTION

Attractive coloured patterns on textile fabrics are largely achieved by discharge or resist printing methods.[1,2] Resist methods generally present a preferable alternative, permitting the use of a wider range of dyestuffs with better fastness properties than those applicable to discharge styles. Despite the variety of resist methods introduced for cellulosic textiles,[1] these processes have not been generally suitable for the printing of wool[3] or silk[4] fabrics. Instead, coloured effects on silk or wool fabrics have traditionally been achieved by discharge printing methods. Only relatively recently have

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resist printing (or dyeing) methods, involving the application of reactive resist agents, gained commercial success in the case of wool.[3] Two such reactive resist agents are sulphamic acid,[5] and Sandospace R (Sandoz),[6] both of which effectively retard the fixation of certain (anionic) acid and reactive dyestuffs on wool fabric.[7] While sulphamic acid has been shown to confer a superior dye-resist effect over that of Sandospace R, fixation of the latter reagent may be more conveniently carried out at lower temperature, and is potentially less damaging to the fibre.

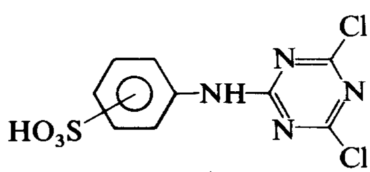
Cameron & Pailthorpe[8] recently investigated the application of sulphamic acid to wool. These workers concluded that reaction occurred predominantly with the hydroxyl-containing amino acid residues and to a much lesser extent with the basic NH_2 groups of wool, presumably resulting in bound sulphate and sulphamate, respectively, according to the following equations:

$$W-OH+NH_2SO_3H \longrightarrow W-O-SO_3H+NH_3 \qquad (1)$$

$$W-NH_2+NH_2SO_3H \longrightarrow W-NH-SO_3H+NH_3 \qquad (2)$$

Although silk fibroin contains a much smaller proportion of nucleophilic amino acid residues compared to wool keratin, the hydroxyl group content of silk is substantial (serine, 12%; threonine, 0·9%; tyrosine, 5%)[9] whereas the approximate values for wool are 10%, 6% and 3%, respectively. Hence a significant degree of reaction can be expected to take place between sulphamic acid and silk. The potential for this reagent to confer dye-resist effects on silk fabric, however, has not been investigated to date.

Sandospace R can be regarded as a colourless reactive dye, based on structure **1**, having a dichlorotriazine reactive group. This reagent is purported to confer dye-resist effects towards acid and reactive dyestuffs when applied to wool, polyamide and silk fabrics.[10] The extent of resist achieved during the dyeing of silk with acid, reactive and metal complex dyestuffs has not, however, been comparatively assessed.



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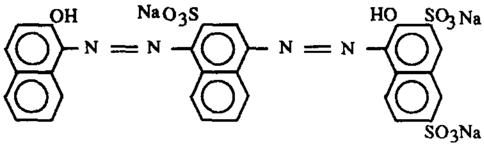
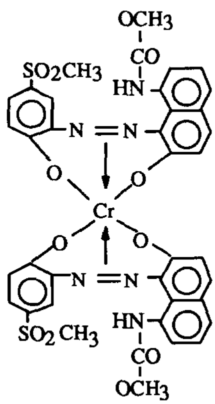
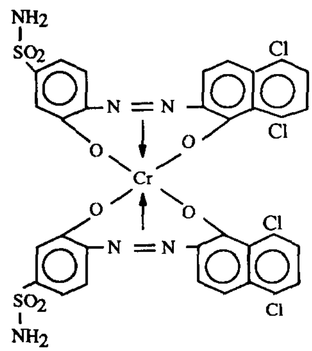
This work has investigated the dye-resist effects obtained towards acid, reactive and metal complex dyestuffs, by the application of sulphamic acid and Sandospace R to silk fabric. Figure 1 gives the structures of some of the dyes used. The strength and whiteness of the treated fabrics were also compared.



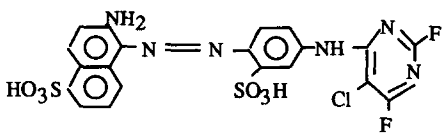
Acid dye : Coomassie Navy Blue type



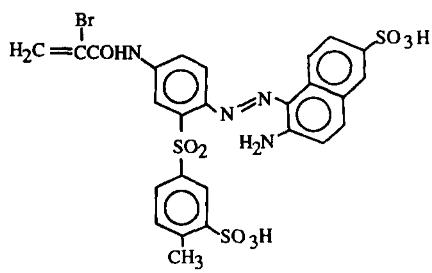
2:1 Metal complex dye: PM-5



2:1 Metal complex dye: PM-4



Reactive dye : Drimalan type



Reactive dye : Lanasol type

Fig. 1. Structure of dye type used in the dyeing process.

2 RESULTS AND DISCUSSION

2.1 Treatment of silk with sulphamic acid

The weight gain of silk treated with sulphamic acid increases markedly with increasing concentration of applied sulphamic acid (Table 1). During the padding procedure, sulphamic acid is presumably absorbed by the fibre resulting in higher weight gains than expected, for the lower treatment levels. The total amount of sulphamic acid substantive to the fibre was determined by acid hydrolysis of the treated silk fibre, followed by precipitation of the sulphate as barium sulphate.[8] For both low and high treatment levels of sulphamic acid, the determined amounts of total sulphate on the fibre were found to correlate well ($< 5\%$ error) with the weight gains obtained in each case (Table 1). Unreacted sulphamic acid, after curing (in the form of free sulphuric acid) may be extracted from the fabric with 4% pyridine–water and determined by titration.[8] In each case the free acid contribution to the

TABLE 1
Properties of Sulphamic-acid-treated Silk

Sulphamic acid (g/100 ml)	*Weight gain (%)*	*Free acid (%)*	*Bound acid (%)*	*Yellowness index*	*Strength retention (%)*
Untreated	—	—	—	1	100
1	1·9	0·3	1·8	17	86
3	3·5	0·3	—	22	88
5	4·6	0·4	—	24	88
10	7·2	0·6	—	23	88
15	9·1	0·8	8·4	23	89

total weight gain was less than 10%. One exception was observed for the lowest treatment level of sulphamic acid, where 0·3% free acid was determined for 1·9% fabric weight gain (that is, 16% of the weight gain is due to the presence of free acid). Hence, the high weight gains obtained for reaction of sulphamic acid with silk fibre are a direct result of covalently bound sulphamic acid within the fibre, and are comparable to those obtained for similar treatment levels of sulphamic acid on wool.[8]

Complete saturation of the serine, tyrosine and threonine residues in silk would lead to an approximate increase in fabric weight of 6%, 2% and 0·4%, respectively. The high weight gains of $>8\%$ obtained for the higher treatment levels of sulphamic acid indicate that a large proportion of these hydroxyl-containing residues participate in the reaction of silk with sulphamic acid, in addition to the smaller proportion of available basic amino acid residues.

Sulphamic-acid-treated silk, even for low treatment levels, has a much higher yellowness index than untreated silk (Table 1). The very high curing temperature (150–160°C) necessary for reaction thus results in a considerable increase in fabric yellowness. A strength loss of 11–14% is also observed although, importantly, the subjective handle of the silk fabric is not noticeably changed.

TABLE 2
Resist Effects of Sulphamic-acid-treated Silk Dyed with Acid Dyes

Sulphamic acid (g/100 ml)	*Resist effect (%)*	
	Coomassie Navy Blue 2RN 140	*Lanasyn Grey BLRN 200%*
1	98·3	97·7
3	99·6	99·2
5	99·8	99·4
10	99·8	99·5
15	99·8	99·5

2.2 Dye-resist effects of sulphamic-acid-treated silk

As expected, the treatment of silk with sulphamic acid confers an excellent resist towards acid dyes (Table 2), similar to that observed in the case of wool.[7] The introduction of an anionic sulphonate group (ionized even at low pH) into the silk fibre by reaction with sulphamic acid is clearly responsible for reducing the affinity of (anionic) acid dyestuffs.

The resist effects obtained for treated silk fabric dyed with three different 2:1 metal complex dyes are shown in Figs 2–4. In addition, the dye-resist behaviour for wool treated with sulphamic acid was carried out for comparison purposes. For all three metal complex dyes a far superior resist is obtained for silk treated with sulphamic acid than for wool, particularly for low treatment levels of sulphamic acid. Dye-resist effects for metal complex dyes on wool are, in general, difficult to achieve as a result of the largely hydrophobic character of these dyestuffs, which are consequently substantive within the hydrophobic regions of the wool fibre.[7] Therefore, unlike anionic acid dyestuffs, 2:1 metal complex dyes do not require the presence of protonated amino groups ($—NH_3^+$) in order to become substantive to the fibre. At high treatment levels of sulphamic acid ($>10\%$ weight gain), however, the increased anionic character of the wool fibre presumably reduces the affinity of these weakly anionic dyestuffs. By comparison, the increase in ionic character of silk resulting from reaction with sulphamic acid, even for very low treatment levels, is apparently sufficient to diminish the hydrophobic interactions necessary for dye substantivity. This difference presumably stems from the relatively more crystalline nature of silk compared with wool. The reaction of sulphamic acid within the limited amorphous regions of silk increases the anionic character of these regions sufficiently, so as to retard significantly the uptake

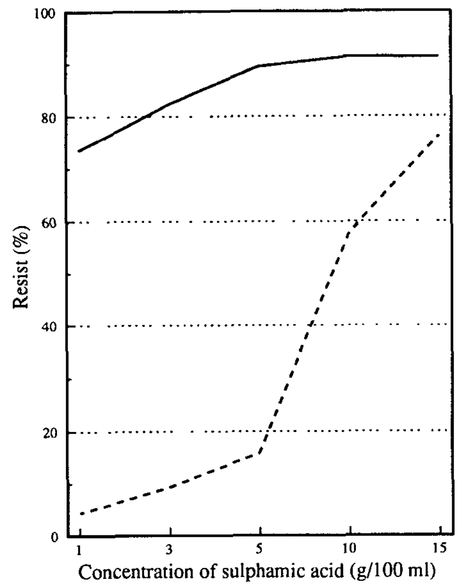


Fig. 2. Resist effect of sulphamic-acid-treated silk and wool dyed with the PM-4 dye. ——, silk; - - -, wool.

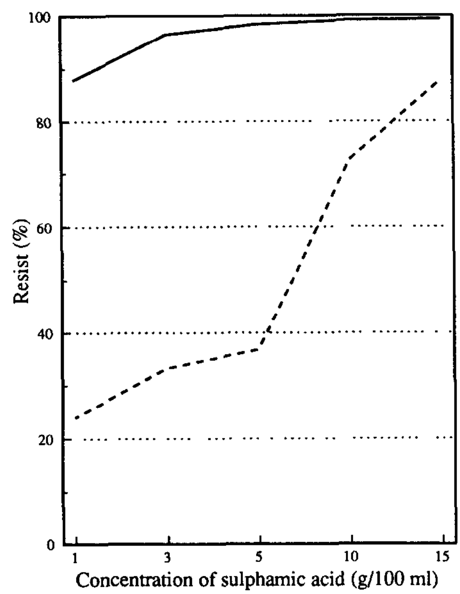


Fig. 3. Resist effect of sulphamic-acid-treated silk and wool dyed with the PM-5 dye. ——, silk; - - -, wool.

of these weakly anionic and large dye molecules. The differences observed between the three metal complex systems may be due to molecular size effects.

Significant differences in dye-resist effects are also observed for the reactive dyeing of wool and silk treated with sulphamic acid (Figs 5 and 6). The most important nucleophilic sites for reactive dye binding in the wool fibre are considered to be the —NH_2 groups of the basic amino acid residues.

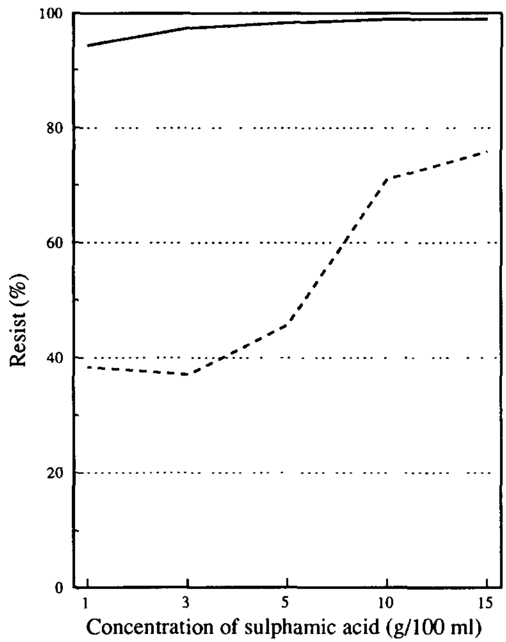


Fig. 4. Resist effect of sulphamic-acid-treated silk and wool dyed with Irgalan Red 2GL KWL 200%. ——, silk; – – –, wool.

In silk, however, these residues are far more limited in proportion than in wool and therefore the dyeing of silk with reactive dyes is necessarily carried out at pH 8–9, where reaction occurs predominantly at the hydroxyl-containing residues.[11] The treatment of silk with sulphamic acid would be expected to block effectively a large proportion of these residues by the formation of bound sulphate (Silk—O—SO_3H). Hence, a significant dye-resist effect can be expected at low treatment levels, as is observed. In the case of wool, the reactive dye sites (—NH_2 groups) are less effectively blocked except at the higher treatment levels of sulphamic acid.

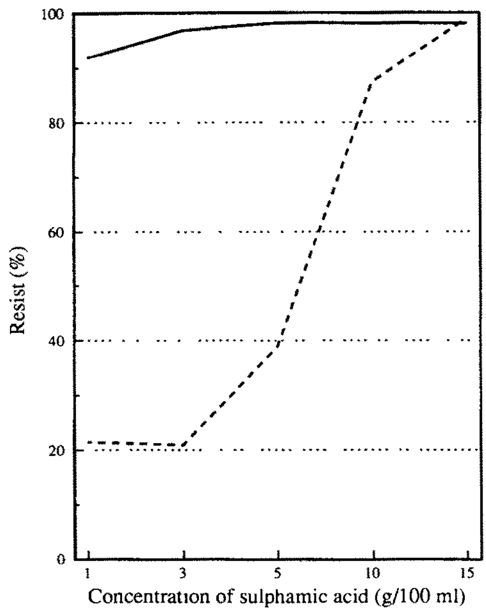


Fig. 5. Resist effect of sulphamic-acid-treated silk and wool dyed with Drimalan Red F-2BL. ——, silk; – – –, wool.

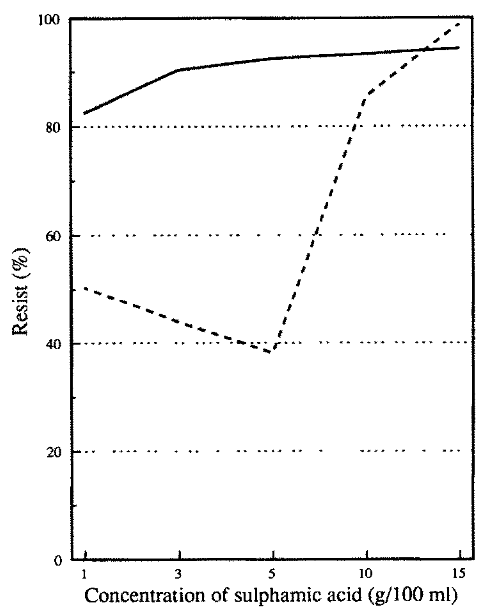


Fig. 6. Resist effect of sulphamic-acid-treated silk and wool dyed with Lanasol Red 6G. ——, silk; – – –, wool.

TABLE 3
Properties of Sandospace R-treated Silk

Sandospace R (% o.w.f.)	*Weight gain* (%)	*Yellowness index*	*Strength retention* (%)
Untreated	—	1	100
2	0·2	2	98
6	0·7	2	97
10	1·1	3	98
15	1·6	3	98
20	2·2	3	98

2.3 Treatment of silk with Sandospace R

Exhaustion of Sandospace R at pH 8 will result in reaction at the hydroxyl residues of the fibre, as in the reactive dyeing of silk. However, these mild treatment conditions of pH and temperature do not confer extensive reaction, as evidenced by the very low fabric weight gain (2%) obtained even for high treatment levels (20%) (Table 3). The treatment of silk with Sandospace R is therefore far more limited in the extent of reaction than in the case of sulphamic acid. Virtually no strength loss, increase in yellowness index or loss of fabric handle was observed.

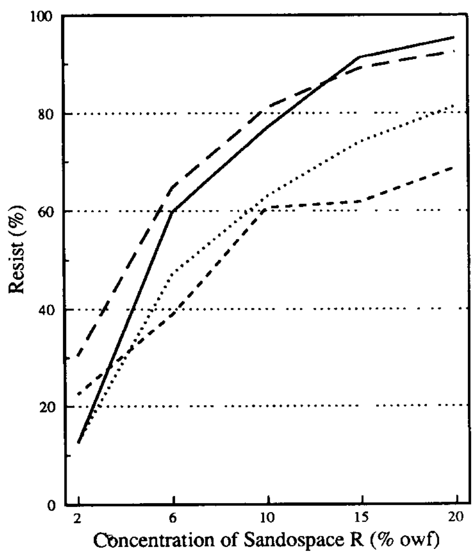


Fig. 7. Resist effect of Sandospace-R-treated silk. ——, Coomassie Navy Blue 2RN 140; – – –, PM-4; . . ., PM-5; — —, Drimalan Red F-2BL.

2.4 Dye-resist effects of Sandospace-R-treated silk

The dye-resist effects observed toward acid, metal complex and reactive dyestuffs are shown in Fig. 7. As expected, the resist effect towards all these dye classes increases with an increasing level of treatment with Sandospace R. For a practical level of treatment, however, the resist effect provided by Sandospace R is inferior to that conferred by sulphamic acid. Comparing the Sandospace R and sulphamic-acid-treated silk fabrics, for a weight gain of approx. 2%, similar levels of dye-resist behaviour are observed for all three dye classes. This is consistent with both these reactive molecules conferring resist effects essentially via the same mechanism of reactive site blocking combined with anionic dye repulsion. A somewhat diminished resist effect is obtained for the metal complex dye systems in the case of Sandospace R treatments, perhaps as a result of the hydrophobic benzene ring in Sandospace R, which may increase the potential for hydrophobic dye–fibre interactions. For all three dye classes a high application level of Sandospace R, to give a weight gain of at least 1%, is necessary in order to confer any significant dye-resist effect.

3 CONCLUSIONS

The treatment of silk with sulphamic acid confers excellent dye-resist behaviour towards acid, metal complex (2:1) and reactive dyestuffs. At all treatment levels, reduction in the breaking strength of the treated fabric is minimal (10–15%), and there is no significant loss of the soft and flexible fabric handle. A high yellowness index, however, is a drawback with respect to obtaining a white resist although, when dyed to achieve tone-on-tone effects, the shades obtained are not diminished in brightness. Even at very low treatment levels, tone-on-tone effects on silk fibre can be achieved successfully with a wide range of dyestuffs. The most striking difference between the resist effects for sulphamic-acid-treated silk compared to those for treated wool is observed for metal complex dyes. This is considered to be due to the less amorphous nature of the molecular system of silk, where the introduction of an anionic moiety has a more pronounced effect on diminishing the substantivity of these large and weakly anionic dye molecules.

High weight gains are difficult to achieve during the exhaustion of Sandospace R onto silk, and thus only marginal dye-resist effects are conferred by this reactive agent. However, tone-on-tone effects may nevertheless be achieved for weight gains of 1–2% and the desirable properties of silk such as whiteness, breaking strength and soft fabric handle are not adversely affected.

4 EXPERIMENTAL

4.1 Materials

Plain-weave silk (32 g/m^2) was obtained from the Australian Silk Wholesalers, Sydney, Australia. Wool fabric (2/2 twill, 270 g/m^2) was supplied by John Vicars Fabrics, Sydney, Australia. Sulphamic acid was purchased from Ajax Chemicals and Sandospace R, in paste form, was supplied by Sandoz Australia.

Three different classes of dyes were used in these experiments—acid dyes, 2:1 metal complex dyes, and reactive dyes—and were obtained from ICI, Ciba Geigy and Sandoz, respectively.

4.2 Methods

4.2.1 Fabric treatment

Silk fabric was treated with sulphamic acid (solution concentrations varied from 10 to 150 g/litre), according to a pad-dry-cure procedure.[8] On attaining a wet pick of 100%, the fabric was dried at 80°C for 5 min and then cured at 160°C for 5 min. Treatment of wool fabric with sulphamic acid was carried out in an identical manner. Sandospace R (2–20% o.w.f. (on weight on fibre)) was applied to silk fabric by aqueous exhaustion at 80°C, according to the recommended procedure.[10] The fabric weight gains were based on the oven-dried weights determined before and after treatment. These values are accurate to $\pm 0{\cdot}3\%$ wt/wt (absolute).

4.2.2 Analyses

The procedures used for the determination of free and bound acid on the sulphamic-acid-treated silk fabrics were identical to those adopted by Cameron & Pailthorpe.[8]

The degree of resist conferred by the treatments with sulphamic acid and Sandospace R was evaluated with three classes of dyestuffs, some of the structures for which are shown in Fig. 1.

The dyes were applied to either silk or wool at 2% o.w.f. according to the manufacturers' recommended procedures for each dye type. Competition dyeings were carried out in each case, with a 3:1 ratio of untreated to treated fabric.

The extent of resist achieved was quantified as follows:

$$\text{Percentage resist} = \frac{K/S_{\text{dye}}\,(\textit{untreated}) - K/S_{\text{dye}}\,(\textit{treated})}{K/S_{\text{dye}}\,(\textit{untreated})} \times 100\%$$

The K/S values of dyed treated and untreated fabrics were calculated from reflected data measured on a Gardner Spectrogard Color System (Pacific Scientific Ltd). The resist effects calculated in all cases are within ±5% error. Yellowness indices (ASTM E-313) were evaluated by comparing the treated fabrics to untreated fabrics using the Gardner Spectrogard Colour System. The breaking strengths of treated and untreated samples were determined according to Australian Standard (AS 2001.2.3-1988) Method A-Ravelled Test. The rate of extension was 100 mm/min on the Instron Tensile Machine.

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