The graft printing of silk fabric in the presence of sulphamic acid

J T Luo

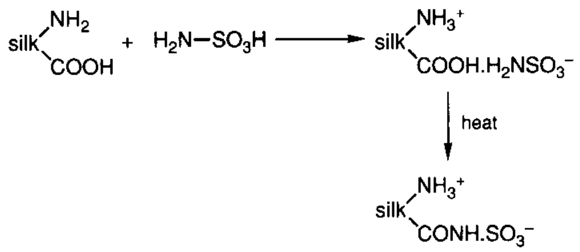
Zhejiang Textile School, NingBo 315010, PR China

The effect of printing silk fabrics in the presence sulphamic acid has been investigated. Sulphamic acid introduces sulphonate groups into silk's structure and confers good resist properties for acid dyes on silk. An increased uptake of basic dyes has also been found. The light fastness of such dyeings was better than on ungrafted silk, being similar to values obtained on acrylic substrates. White and coloured resist effects have been investigated.

INTRODUCTION

In 1955 Sandoz patented a process whereby protein fibres could be treated with sulphamic acid, resulting in a high degree of resist to acid dyes being obtained [1]. Using acid and basic dyes, Cameron and Pailthorpe investigated the dyeing properties of sulphamic acid-treated wool [2]. They found that sulphonate groups were introduced into the structure of wool when it was treated with sulphamic acid. Bell *et al.* found that sulphamic acid-treated wool has increased substantivity for basic dyes, with improved wash and light fastness [3].

Silk is also a protein fibre. When treated with sulphamic acid, the carboxyl end groups of the silk can react with amino groups of the sulphamic acid to introduce the sulphonate groups into the fibre structure. The reaction mechanism could be as illustrated in Scheme 1. The advent of a new practical dye resist treatment, based on sulphamic acid, for the printing of wool has brought about renewed interest in the dyeing behaviour of wool treated with sulphamic acid [4].



Scheme 1

It was thus an aim of this work to investigate graft printing of silk in the presence of sulphamic acid. The special effects obtained by resist printing techniques were studied.

EXPERIMENTAL

Materials

Mill-degummed and bleached twill weave *Bombyx mori* silk fabrics were used throughout. Before use the fabrics were treated with an aqueous solution containing 1 g/l acetic acid and 2 g/l nonionic surfactant (Detergent JU) for 10 min at 60°C and liquor ratio of 60:1. The fabrics were then thoroughly washed at room temperature for 10 min and dried. Sulphamic acid, acetic acid, sodium acetate, dimethyl formamide (DMF) were of laboratory-reagent grade. Glauber's salt, surface-active agent 1227, starch, dextrin and synthetic tragacanth (hydroxyethylated locust bean gum) were of industrial grade.

Commercial acid dyes (CI Acid Blue 83, Green 28, Red 85) and basic dyes (CI Basic Red 13, Violet 14) were used without further purification; their structures are shown in Figure 1.

Graft printing with sulphamic acid

Silk fabric was printed with a paste containing sulphamic acid, urea and starch thickener on a printing table. The fabric was then dried for 15 min at 80°C, treated in an ager or cured, desized and washed. Finally the sample was dried under ambient conditions.

Dyeing with acid dyes

The weighed sulphamic acid-grafted silk fabric samples were introduced into a dyebath containing the required amount of dye (1% o.w.f.), acetic acid (1.5% o.w.f.) and Glauber's salt (10% o.w.f.) at 40°C and a liquor ratio of 80:1. The temperature was then raised to 95°C over 30 min, and dyeing continued for 45 min with continuous stirring. The dyed sample was then removed, rinsed three times and dried under ambient conditions.

Dyeing with basic dyes

The dyebath was set with the following additions: 1% dye, 2% acetic acid, 1% sodium acetate and 0.5% surface-active agent 1227, all percentages o.w.f. The weighed sulphamic acid-graft printed silk samples were introduced into the dyebath at 40°C and a liquor ratio of 80:1. The temperature was then raised to 90°C over 30 min, and dyeing continued for 45 min with continuous stirring. Aftertreatment was the same as for dyeing with acid dyes.

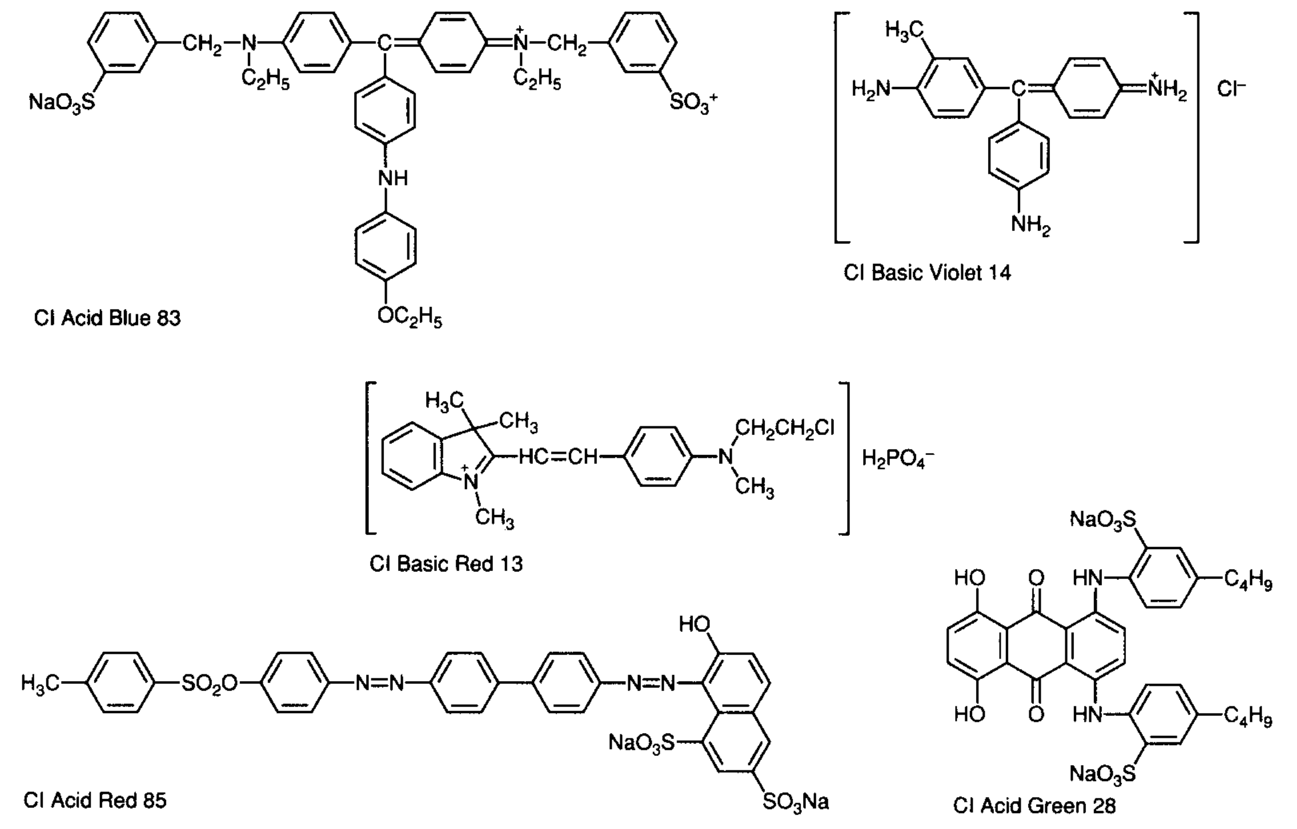


Figure 1 Structures of acid and basic dyes used in the present study

Colour resist printing

The silk fabric was printed with a paste containing an acid dye or a basic dye, sulphamic acid, urea and thickener. The printing aftertreatment was the same as above. Then the printing samples were dyed with another acid dye or basic dye.

The sulphamic acid graft-printed sample was also overprinted with printing paste containing acid or basic dyes, then dried for 15 min at 80°C, and treated in an HT (atmospheric pressure) steamer for 45 min at 130°C, desized and washed. Finally the sample was dried at room temperature.

Test methods

The dye concentration in the fibres was measured spectroscopically following extraction by DMF. The dye uptake as determined according to the method described previously [5].

Evaluation of fastness to washing and light was performed according to standard methods [6]. The fastness to dry cleaning was performed according to Australian Standard 2001.4.16 (colour fastness to dry cleaning, using perchloroethylene (200 ml), 20 steel balls for 30 min at 30°C).

RESULTS AND DISCUSSION

Effect of sulphamic acid concentration

An increase in sulphamic acid concentration in the graft printing paste was accompanied by a significant decrease in the uptake of acid dyes and increase in the uptake of basic dyes (Table 1).

The sulphamic acid graft-printed sample had increased

Table 1 Effect of sulphamic acid concentration in the graft printing paste on dye uptake

Sulphamic acid concn (g/l)	Dye uptake (g/kg) CI Acid Red 85	CI Basic Violet 14
0	7.71	6.23
1	1.35	7.63
2	0.595	8.02
3	0.288	8.34
4	0.078	8.54
5	0.050	8.57

Paste: urea 2 g, starch thickener 25 g, total 40 g, 40 min at 130°C

Table 2 Results with acid dyes on grafting

Dye	Grafted fibre ($\times 10^{-2}$ g/kg fibre)	Ungrafted fibre (g/kg fibre)	Degree of resist (%)
CI Acid Red 85	7.78	7.71	98.9
CI Acid Green 28	3.60	7.86	99.5
CI Acid Blue 83	3.78	8.11	99.5

Table 3 Results with basic dyes on grafted and ungrafted fabric

Basic dyes	Grafted	Dye concn (g/kg fibre)	Wash fastness S	Wash fastness C	Dry cleaning fastness S	Dry cleaning fastness C	Light fastness
CI Basic Violet 14	Yes	8.54	2	2–3	4–5	5	4–5
	No	6.23	1–2	2			2
CI Basic Red 13	Yes	8.48	2	3	4–5	5	4–5
	No	5.47	2	2–3			2

S – Change in shade
C – Staining on whie silk fabric

substantivity for basic dyes and decreased substantivity for acid dyes. The degree of resist for acid dyes was very good and there was also slight staining (Table 2). While dyeing with basic dyes, the dye concentration in the treated fabric samples was 1.37 times that for CI Basic Violet 14 and 1.55 times that for CI Basic Red 13 than in the untreated samples (Table 3).

Effect of urea

Lewin *et al.* found that the inclusion of urea in the treatment liquor led to increased uptake of sulphamic acid when they investigated the grafting of protein fibres with sulphamic acid [7]. Swelling of the silk fibres also increased, leading to enhanced absorption of sulphamic acid. The uniformity of the printed motif was also slightly improved in the presence of urea in graft printing.

Effect of steam ageing or curing

During ageing or curing, sulphamic acid was transferred from the thickener to the fibre, and reacted with it. The effect of the ageing and curing temperatures on grafting was considerable, and the effect of treatment temperature on the fibre itself was also evident. Table 4 shows the effect of ageing temperature and curing temperature on the reaction between sulphamic acid and silk fibre.

A lower temperature may be used in ageing than in curing. There are two possible reasons for this, as indicated below.

(a) The moisture content of the system in ageing is far larger than in curing. In ageing the transfer of sulphamic acid from the print paste to the interior of the fibre, and the reaction between sulphamic acid and fibre are higher than during curing at same temperature. Thus urea must be added to the print paste when curing is used.
(b) The ageing time is longer than the curing time.

Table 5 shows that a significant increase in the amount of basic dye on the fibre was obtained when the ageing time was increased to 40 min or the curing time was raised to 4 min. In contrast, with acid dyes there is a significant decrease in dye concentration on the fibre,

Table 4 Effect of steam ageing temperature and curing temperature on dye concentration and exhaustion

Temp. (°C)	CI Acid Red 85 Concn after ageing (g/kg fibre)	CI Acid Red 85 Exhaustion after curing (%)	CI Basic Violet 14 Concn after ageing (g/kg fibre)	CI Basic Violet 14 Exhaustion after curing (%)
100		38.7		66.7
110		15.3		77.1
115	1.38		7.01	
120	0.575	6.31	7.59	86.3
125	0.255		8.02	
130	0.088	2.60	8.43	92.6
135	0.038		8.49	
140	0.025	0.70	8.49	93.9
150		0.25		94.2
160		0.25		94.1

Paste: sulphamic acid 4 g, urea 2 g, starch thickener 25 g, total 40 g
Ageing time: 45 min
Curing time: 4 min

Table 5 Effect of ageing or curing time on dye concentration and exhaustion

Ageing/curing time (min)	CI Acid Red 85 Concn after ageing (g/kg fibre)	CI Acid Red 85 Exhaustion after curing (%)	CI Basic Violet 14 Concn after ageing (g/kg fibre)	CI Basic Violet 14 Exhaustion after curing (%)
2		4.18		91.2
3		1.0		93.2
4		0.28		93.9
5		0.26		94.0
6		0.20		94.2
20	0.379		8.21	
30	0.091		8.38	
40	0.036		8.44	
50	0.028		8.46	
60	0.025		8.47	

Paste: sulphamic acid 4 g, urea 2 g, starch thickener 25 g, total 40 g
Ageing temp.: 130°C
Curing temp.: 140°C

and raising the treatment temperature will lead to damage of the silk. Yellowing of the silk occurs when the treatment temperature exceeds 140–145°C. Further rises in temperature are accompanied by a significant increase in yellowing. Above 170°C the silk is carbonised. Hence ageing is a more suitable process than curing.

Selection of stock thickener

In printing of silk with acid dyes starch, dextrin or synthetic tragacanth are normally used as the printing paste thickener. In this work the properties of the paste were the same as those in conventional direct printing. Starch thickener typically gave the highest pick-up levels and grafting ratios. However, printing levelness was lower and uneven grafting was readily obtained. Therefore when the grafted sample was dyed with acid dyes, the resist effect differed slightly in different areas of the pattern. With basic dyes this problem did not arise to the same degree.

Starch and dextrin were hydrolysed in the presence of sulphamic acid because of the lower pH, but the viscosity of the printing paste was basically unchanged within 2 h at room temperature. When synthetic tragacanth replaced starch or dextrin as printing thickener the stability of the paste and the level printing properties were excellent, but the grafting ratio was slightly lower.

Dyeing with acid dyes

In the dyeing of the sulphamic acid-grafted fabric with conventional acid dyes the percentage exhaustion was slightly decreased while the amount of dye on the fibre was slightly increased as the dye concentration in the bath was raised. The amount of dye increased from 2.2×10^{-2} to 3.2×10^{-2} g/kg fibre when the dye concentration in the dyebath was raised from 0.5 to 2% o.w.f. Further increases in dye concentration were found to have no effect. Therefore a pastel ground colour is suitable for white resist printing, while a deep ground colour was also suitable for fine patterns.

Table 2 indicates that the degree of resist obtained was also different in dyeing with various types of dyes for sulphamic acid-grafted fibre. The degree of resist obtained for CI Acid Red 85 was the lowest and those for CI Acid Blue 83 and CI Acid Green 28 were similar. There are two possible reasons for this, as indicated below:

(a) CI Acid Red 85 is a linear molecule
(b) CI Acid Blue 83 and CI Acid Green 28 both contain two sulphonate groups attached at both ends of the dye molecule; therefore the interaction between the grafted fibre and these two dyes would be expected to be lower than with CI Acid Red 85.

It was found that the colour of the pattern in the colour resist printing with acid dyes was far less intense than in the direct printing with acid dyes. This suggests that the dye molecules repelled one another during ageing and curing, repulsion taking place between the sulphonate groups and the dye anions.

Dyeing with basic dyes

The dye concentration in the dyebath decreased in direct proportion to the increase of dye concentration on the grafted fabric. This may have been because the sulphonate groups or basic dye sites on the sample grafted with sulphamic acid were greatly increased in number, and far more than in acrylic fibre. Cameron *et al.* found that wool treated with sulphamic acid with 8.5% bound acid has approximately 1000 μequiv./g acidic dye sites [3], while acrylic substrates have an acid group content of between 50 and 150 μequiv./g [8]. Thus the sulphamic acid-treated wool has approximately ten times the number of dye sites normally available in acrylic substrates. The increase of dye sites was also large in grafted silk fabric.

Hence no saturation value within the range of conventional dyeing concentration was observed. A graft-printed sample could give tone-on-tone effects when dyed with basic dyes, i.e. the colour on the graft-printed fabric was more intense than on non-graft-printed areas because the forces of attraction between the sulphamic acid-grafted silk fabric and the dyes would be expected to be greater than those for ungrafted silk fabric.

Table 3 shows that the wash fastness of basic dyes on ungrafted fabric was extremely poor, and the introduction of sulphonate groups into the fibre structure had little effect on improving the wash fastness. A number of aftertreatments were examined to improve this shortcoming. The dry cleaning fastness of basic dyes was excellent (colour change at least 4–5 and staining 5 for all dyes).

Table 3 shows that the light fastness of the sulphamic acid-grafted silk fabric was two to three points higher than for ungrafted silk. This rise in light fastness was attributed to the introduction of sulphonate groups via reaction with sulphamic acid. The colour of patterned samples graft-printed with printing paste containing sulphamic acid, basic dyes and stock paste was deeper than that in conventional direct printing with basic dyes (Table 3).

CONCLUSION

The graft printing of real silk fabric with sulphamic acid gave an excellent resist for acid dyes and assist for basic dyes. With basic dyes the light fastness was improved to the extent that the values obtained were similar to those obtained on acrylic substrates.

REFERENCES

1. S, USP 2 726 133 (1955).
2. B A Cameron and M T Pailthorpe, *J.S.D.C.*, **103** (1987) 257.
3. V A Bell, D M Lewis and M T Pailthorpe, *J.S.D.C.*, **100** (1984) 223.
4. V A Bell, D M Lewis and M T Pailthorpe, Proc. 7th Internat. Wool Text. Res. Conf., Tokyo, Vol. 5 (1985) 89.
5. J T Luo, *J.S.D.C.*, **107** (1991), 117.
6. Third report of the Fastness Tests Coordinating Committee (Bradford: SDC, 1955).
7. M Lewin, P K Issacs and H Schafer, Proc. 5th Internat. Wool Text. Res. Conf., Aachen, Vol. 5 (1975) 73.
8. D Balmforth, C A Bowers and T H Guion, *J.S.D.C.*, **80** (1964) 577.