

## Stain Blocking Effects of Dye Resist Agents for Wool

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(Received October 10, 1992)

## 羊毛用 防染劑의 합성과 그 防汚效果

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(1992. 10. 10 접수)

**요 약**— 양모의 반응성 방염처리제(DRB, DRM, DRS, DRN)를 합성하고 이들과 sulphamic acid(SA)를 방염(dye resist) mechanism을 이용하여 방오처리에 응용, 그 효과를 검토하였다. 방오효과는 SA>DRB>DRM>DRS>DRN의 순으로 우수하였다. DCCA 처리 양모의 경우는 SA처리 양모만이 방오효과를 나타내었다. 4종류의 합성된 반응성 방염처리제는 DCCA 처리 양모에 dye assist 효과를 나타내었다. 80% 이상의 방오효과만이 시각적으로 오염을 구분할 수 없었으므로 SA 처리방법은 방오가공에 응용 가능하나, DRB 처리법은 약간의 개선이 필요했다. 이러한 방염처리방법을 방오가공에 응용할 때에 양모 carpet 등의 습윤오염(커피나 주스 등 색소성 오염)의 감소효과가 기대 되어 진다.

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### 1. Introduction

It is obvious that dye resist technology can be applied to stain blocking technology as most stains such as food dyes, are in some form of acid dyes. Therefore it was considered worthwhile to apply these reactive resists to wool and to assess their stain blocking effects. The dye resist mechanism was presumed to be similar to the stain resist mechanism.

Generally, accidental staining occurs at room temperature. Therefore, if a dye resist agent is effective to dyeing or printing procedures which occur at high temperature, it is presumed that this agent may also resist stains which usually occur at room temperature, that is much milder conditions than normal dyeing procedures.

Acidic food colourants, such as C.I. Food Red 17 which most severely stains wool carpets at low temperature, is generally used as a stain to assess stain blocking effects.

This paper describes the stain resist effects to C.I. Food Red 17 when reactive dye resist agents are applied to the wool substrate.

### 2. Experimental

#### 2.1 Materials

The wool fabric used was a scoured and decatized 2/2 twill, weight 270 g/m<sup>2</sup> fabric supplied by John Vicars Fabrics. C.I. Food Red 17 (Commercial name; Hexacol Allura Red 17P) was supplied by Hodgsons Dye Agencies Ltd. and was used without further purification. Citric acid (Analytical

grade) was supplied by Ajax Chemicals. Basolan DC was supplied by BASF.

### 2.2 Synthesis of 2,4-Dichloro-s-triazin-6-yl-p-aminophenyl-sulphonic acid sodium salt (dihydrate) (DRM)

The synthesis method of DRM was based on the report by Lewis and Pailthorpe.<sup>1)</sup> Sulphanilic acid (26 g as a slurry in 100 ml water) was added slowly to cyanuric chloride (28 g as a slurry in 200 ml acetone containing about 100 g ice), whilst maintaining the pH of the solution at 7 by the addition of 2N sodium hydroxide. The reaction mixture was stirred for 1.5~2.0 hours. Thereafter the reaction was judged to be complete once the pH had stabilised at 7. The product was filtered off, washed thoroughly with acetone and then oven dried (yield 92%).

### 2.3 Synthesis of 2,5-Bis(2,4-dichloro-s-triazin-6-yl)-aminophenyl-sulphonic acid sodium salt (dihydrate)(DRB)

Cyanuric chloride (37 g) in acetone (200 ml) and ice was added to a solution of 2,5-diamino benzene sulphonic acid (19 g) as a slurry, whilst maintaining the pH at 7 by the addition of a solution of saturated sodium carbonate. Stirring was continued for 3 hours and the reaction was monitored by TLC. On completion of the reaction the precipitate was filtered off, washed thoroughly with acetone in order to remove any excess cyanuric chloride, and then dried to constant weight. The yield was 90%.

### 2.4 Synthesis of 2,4-Dichloro-s-triazin-6-yl-p-aminosalicylic acid sodium salt (Dihydrate)(DRS)<sup>2)</sup>

Cyanuric chloride (32 g) was dissolved in 100 ml acetone, ice cold with constant stirring, to which 25 g of the sodium salt of p-aminosalicylic acid dissolved in 60 ml water was added, while slowly adding a saturated solution of sodium carbonate and ensuring that the pH did not rise above 7.0. At the end of the reaction (when the pH was stable and the test for p-aminosalicylic acid (TLC) was negative), the contents of the reaction vessel were filtered off and washed thoroughly with ace-

tone in order to remove excess cyanuric chloride. The product was dried to constant weight. The yield achieved was 97%.

### 2.5 Synthesis of 2,4-Dichloro-s-triazin-6-yl-amino-8-naphthol-3,6-disulphonic acid sodium salt (DRN)<sup>3)</sup>

38 g 1-Amino-8-naphthol-3,6-disulphonic acid (ANDA) was dissolved in 1N sodium bicarbonate solution, the solution was diluted to 500 ml and neutralised with acetic acid. This solution and 2N sodium carbonate solution were dropped simultaneously into a well stirred suspension of finely divided cyanuric chloride (20.2 g) in acetone and ice water (100 ml 1:1) at 0°C over 3 hrs. After the reaction was complete (when pH was stable at 7 and the test for ANDA (TLC) was negative) the mixture was filtered. The filtrate was rotary evaporated at 40°C to reduce the solvents and DRN was salted out using saturated NaCl solution. The DRN product was filtered and vacuum dried at room temperature. The yield achieved was 70%.

### 2.6 Characterisation of Products

Melting points were determined on a Gallenkamp Melting Point Apparatus. IR spectra were recorded on a Hitachi Model 260-10 Infrared Spectrophotometer and referred to Nujol mulls mounted onto a disc of NaCl. Elemental analyses were conducted by the School of Chemistry, University of New South Wales. Thin layer chromatography (TLC) was carried out using Merck 60F<sub>254</sub> Silica Gel TLC Foils. A variety of eluents including acetone, water-saturated butanol and ethanol were used. The chromatograms were visualised at 254 nm with a Universal UV Lamp (CAMAG Muttenz Schweiz).

### 2.7 Application of s-Triazine based Reactive Resists

The reactive resists were applied to wool fabric by the exhaustion method derived from that of Bell *et al*<sup>2)</sup>

### 2.8 Sulphamation of Wool

In order to compare the stain blocking effect with dye resist effects, the wool was sulphamic acid treated as follows.

Sulphamic acid (SA)	20% wt/wt
Urea	20% wt/wt
Lissapol TN 450 (ICI)	0.1% wt/wt

(nonylphenylnonaoxyethyleneglycol)

The wool samples were then padded through a vertical pad mangle (Konrad Peter A.G. Liestal M2F-50) to achieve approximately 70% wet-pick-up. The samples were then dried at 85°C for 15 minutes and baked for 5 min at 100°C or 125°C or 150°C in an oven (Hanau Co. Heraeus UT6120). The samples were then rinsed thoroughly in about 50°C warm running water.

### 2.9 DCCA Treatment<sup>4)</sup>

In order to compare the stain blocking effects of untreated wool with those of surface modified wool, wool fabric was chlorinated in a paddle dyeing machine (S. Pegg & Son Textile Engineers PD 2719) at a liquor ratio of 30 : 1. Wool was treated at 20°C with solutions containing 6% w/w of Basolan DC (DCCA; Dichloro isocyanuric acid sodium salt), 10% w/w sodium chloride and 0.01% w/w Lissapol TN 450 (ICI) and adjusted to pH 4.5 with acetic acid. The machine was run for 10 minutes and the temperature raised to 30°C and maintained there for 30 minutes. The wool fabric was given an antichlor aftertreatment with sodium bisulphite (3% w/w) for 30 minutes at 40°C.

### 2.10 Staining Method

Staining was carried out according to the modified method of Harris *et al.*<sup>5)</sup> Preliminary experiments showed that direct immersion in the staining solution was not suitable for a staining test as the sample was not sufficiently wetted to absorb the stain. Therefore, reactive resist treated samples (1 g) were prewetted in 0.1% Lissapol TN 450 solution for 30 min and then hydroextracted. These samples were then immersed in 200 ml of a solution containing 0.056 g/l C.I. Food Red 17 adjusted to pH 2.8 with citric acid and held at room temperature.

The samples were removed from the staining

bath after 30 min and rinsed thoroughly in running water and then deionised water. The excess moisture was absorbed with paper towel and the samples were dried at 95°C until constant weight was achieved. Sulphamic acid treated wool samples were also stained by the same method.

### 2.11 Determination of Stain Blocking Effects

The extent of staining was quantified as the percentage resist, which is obtained on the basis of the following formula. The reflectance values were determined using a Gardner Neotec Spectrogard Colour Computer System (Pacific Scientific Company).

$$SR (\%) = \frac{(K/S)_{u,d} - (K/S)_{m,d}}{(K/S)_{u,d} - (K/S)_{u,ud}} \times 100\%$$

in which: SR = Stain Resist Percentage  
 K = Absorption Coefficient  
 S = Scattering Coefficient  
 $(K/S)_{u,ud}$  = Ratio of K to S obtained from unmodified and undyed wool  
 $(K/S)_{u,d}$  = Ratio of K to S obtained from unmodified and dyed wool  
 $(K/S)_{m,d}$  = Ratio of K to S obtained from modified and dyed wool

## 3. Results and Discussion

### 3.1 Characterisation of Products

All compounds have melting points above 250°C. Some products were analysed as the dihydrate. The structures of the synthesized compounds were confirmed by elemental analysis and IR spectroscopy. The results from the elemental analyses and appropriate IR spectral data were described elsewhere.<sup>6)</sup> The data from elemental analyses and IR spectra showed that all four synthesized products were in good agreement with the expected values.

### 3.2 Exhaustion Curves in Stain Resist Test

Fig. 1 gives the exhaustion curves obtained in

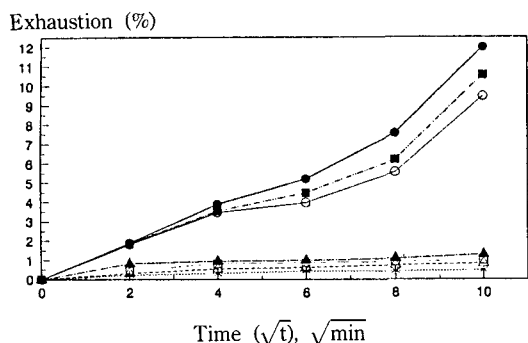


Fig. 1. Rate of acid Food Red 17 exhaustion on DR and pretreated wool.

Untreated ○, SA ※, DRB □, SA and DCCA △, DRB and DCCA ■, DRM ▲, DRM and DCCA ●

the stain resist test. The data clearly demonstrate the outstanding stain blocking achieved with sulphamic acid treated wool as judged by the very low exhaustion of C.I. Food Red 17. Both DRB and DRM treated wools also exhibit good stain blocking effects.

In order to investigate the effects of the surface modification of wool, the wool fabric was DCCA pretreated and then dye resist treated. The results for DCCA pretreated sulphamic acid treated wool and those for DCCA pretreated and DRB or DRM treated wool after the stain test were quite different. The data in Fig. 1 shows that both DCCA pretreated and DRB or DRM treated wools exhibit stain assist effects, whereas the DCCA pretreated sulphamic acid treated wool still gives an excellent stain blocking effect.

The explanation for this result may be that the dyeing character of sulphamic acid treated wool predominates over that of DCCA treated wool, whereas the dyeing character of DRB or DRM treated wool cannot block the dye assist effect produced by the DCCA treatment of wool.

### 3.3 Stain Blocking Effects

The stain resist effect results for all dye resist agents examined are given in Table 1.

Sulphamic acid treated wool shows excellent stain blocking effects. The stain blocking effect of the DRB treated wool is significantly better

Table 1. Stain resist effects after 30 min staining test

	Reflectance (%) (510 nm)	K/S	SR (%)
u, ud	54.43	0.1908	—
Control(u, d)	28.02	0.9245	0
SA	52.75	0.2116	97.3
DRB	43.54	0.3661	76.1
DRM	39.54	0.4622	63.0
DRS	36.47	0.5533	50.6
DRN	30.47	0.7933	17.9
DCCA, SA	45.31	0.3301	81.0
DCCA, DRB	15.36	2.3320	-191.8
DCCA, DRM	13.77	2.6999	-242.0
DCCA, DRS	12.45	3.0783	-293.6
DCCA, DRN	11.98	3.2335	-314.7
DCCA	11.54	3.3904	-336.1

\*SA: Sulphamic acid treated; u, ud: unmodified, undyed; u, d: unmodified, dyed; DCCA: DCCA pretreated; SR: Stain resist effect.

than the DRM treated wool. It must be noted, however, that there is slight staining in the case of DRB treated wool and it is only at an 80% stain resist value (and above) that the sample exhibits no noticeable visual staining. Therefore the DRB treated wool also needs further improvement of the stain blocking effect.

The reflectance curves of the stain resist treated wool are given in Figs. 2 to 5. These curves also confirm the stain resist effects on sulphamic acid treated wool and DRB treated wool.

Whilst the DRS and DRN treated wools give some degree of stain sresist (50.6% and 17.9%, respectively), these compounds are not good enough for commercial application.

The effect of the DCCA pretreatment of the wool is quite dramatic. The DCCA acid chlorination treatment partially removes the cuticle of the wool and increases the ease with which the wool can be dyed. The DCCA-SA treated wool still exhibits a reasonable stain resist to C.I. Food Red 17 with an SR% of 81.0%. Thus it would appear that the sulphamic acid treatment is capable of off-setting most of the dyeing assist effects caused

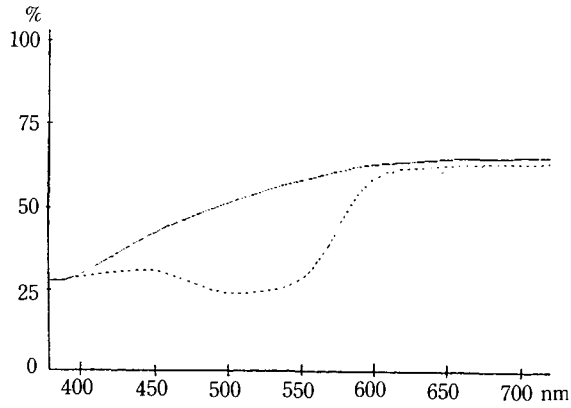


Fig. 2. Reflectance curve of SA treated wool.  
Treated: —, Control: ----

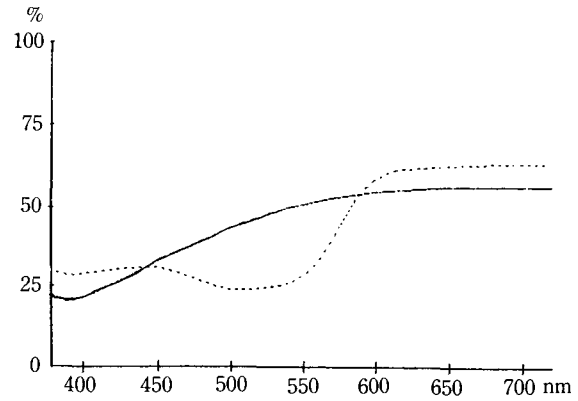


Fig. 4. Reflectance curve of DCCA-SA treated wool.  
Treated: —, Control: ----

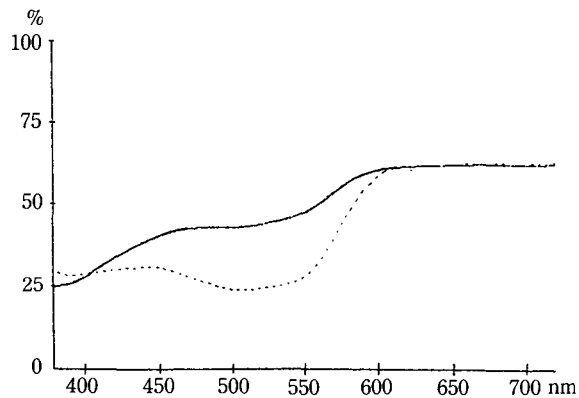


Fig. 3. Reflectance curve of DRB treated wool.  
Treated: —, Control: ----

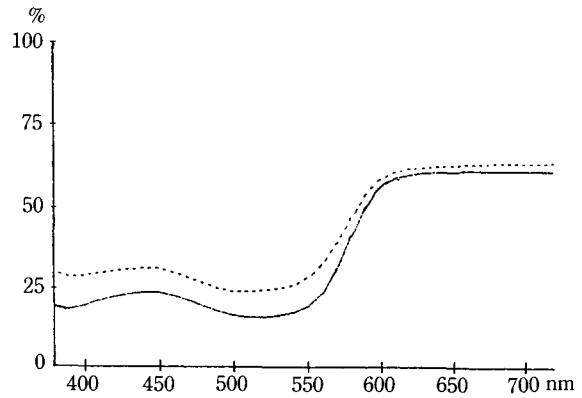


Fig. 5. Reflectance curve of DCCA-DRB treated wool.  
Treated: —, Control: ----

by the DCCA pretreatment.

When applied to DCCA pretreated wool, all four reactive resists synthesized in this study exhibit stain assist effects (see Table 1). Thus the staining (dyeing) assist effect caused by the DCCA pretreatment (-336.1%) swamps the stain resist effects observed with the DR-compounds on untreated wool.

#### 4. Conclusions

All five stain resist treatments examined in this study confer some degree of stain blocking onto the modified wool. The order of effectiveness is SA>DRB>DRM>DRS>DRN. However, when ap-

plied to DCCA pretreated wool, only the sulphamic acid treated wool exhibited a stain resist effect. All four reactive resists synthesized in this study show a dye assist effect on DCCA pretreated wool. Obviously none of these four resist agents is capable of overcoming the dye assist effect conferred on wool by the DCCA treatment.

Sulphamic acid treated wool shows excellent stain blocking effects. The stain blocking effect of the DRB treated wool is significantly better than the DRM treated wool. It must be noted however, that there is slight staining in the case of DRB treated wool and it is only at 80% stain resist value (and above) that the sample exhibits no noticeable staining. Therefore the DRB treated

wool also needs further improvement in stain blocking effects.

### Acknowledgements

This work was supported by a grant from the Wool Research Trust Fund on a recommendation from the Australian Wool Corporation.

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