Dyes and Pigments **20** (1992) 109–121

Dye Resist Effects Achieved on Reactive Resist Treated Wool

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(Received 26 May 1992; accepted 22 June 1992)

ABSTRACT

Four reactive dye resist agents containing s-triazine-based reactive groups were synthesised and the dye resist effects achieved on wool were evaluated. The order of the dye resist effects achieved was found to be consistent with the IOR (Inorganicity Organicity Ratio) values of the dyes that dye wool by ionic/hydrophobic dyeing mechanisms. The dye resist effect achieved with the bifunctional reactive resist (DRB) was superior to that achieved by the monofunctional reactive resist (DRM). The explanation for this difference might be that there are crosslinks introduced by the bifunctional groups of DRB. Low temperature curing can be applied to produce tone on tone effects or dark colour resist treatments in the case of the bifunctional reactive resist (DRB). Full white resist effects seem to be difficult to achieve with reactive resists in normal dyeing. If higher levels of fixation and crosslinking could be achieved, then the perfect dye resist process may still be feasible.

1 INTRODUCTION

A viable dye resist agent must be completely cured and bound firmly to the wool substrate in order to achieve satisfactory dye resist effects.

Increasing the substantivity between the substrate and the dye resist agents is one of the most important factors needed to improve dye

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Dyes and Pigments 0143-7208/92/$05.00

resist effects. In order to increase this substantivity, one possible effective dye resist method would be to covalently bind the dye resist agents to the wool substrate using suitable fibre reactive groups.

Attempts were thus made to produce reactive dye resist agents for wool by the addition of low-temperature-curing reactive groups to the anionic-dye-repelling aryl group.

A suitable model structure for reactive dye resists can be proposed as follows:

$$X—NH—Ar—[(SO_3)^-]_n$$

where X represents a suitable fibre reactive group, NH is a bridging group, Ar is an aryl group, and SO_3^- functions both as a water-solubilising group and an anionic dye 'repelling' group. If X (reactive group) can be reacted and cured at low temperature, then these reactive resists should exhibit a low-temperature curable dye resist effect.

The cold pad batch process, developed by Lewis and Seltzer,[1] allows dyeing to be carried out at low temperature with the very reactive s-triazine-based fibre reactive dyestuffs. This process may be applied to wool under mildly acidic conditions, in order to minimise the hydrolysis of dichlorotriazine dyestuffs, giving high fixation efficiency. Based on this process, it was considered that a low-temperature-curable dye resist effect might be similarly achieved by treatment of wool with an s-triazine-based fibre reactive agent in a cold pad batch process. Preliminary work, however, utilising several s-triazine derivatives indicated that a perfect dye resist could not be achieved with a monofunctional resist agent. Therefore, in order to achieve a more effective resist, a bifunctional system containing two s-triazine fibre reactive moieties was designed and synthesised. This paper reports the results of an investigation of resist effects for each synthesised compound.

The general synthesis route for the four reactive resists is shown in Fig. 1.

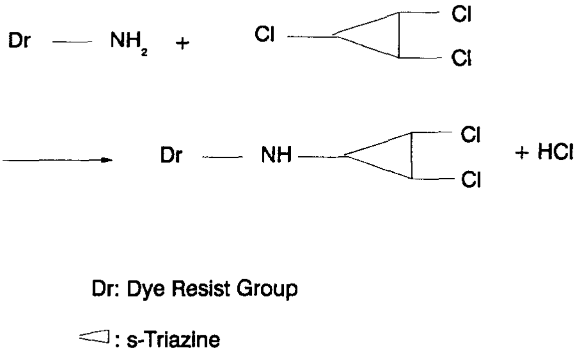

Fig. 1. Synthesis route for reactive resists.

2. PREPARATION AND APPLICATION OF S-TRIAZINE BASED REACTIVE RESISTS

2.1 Materials and methods

2.1.1 Materials

The wool fabric used in this work was a scoured and decatised 2/2 twill, weight 270 g/m^2, supplied by John Vicars Fabrics, Sydney. 2,5-Diamino benzene sulphonic acid (90% assay), cyanuric chloride (99% assay) and sulphanilic acid (99% assay) were supplied by Aldrich. All other chemicals employed were of analytical grade. Lissapol TN 450 was supplied by ICI (Australia) Ltd. Table 1 gives the codes and chemical names of the four synthesised reactive resists employed in this work. The chemical structures of the four reactive resists are given in Fig. 2.

2.1.2 Dyes

A series of six acid dyes which have different numbers of sulphonate groups but the same chromophore together with one metal complex dye (Irgalan dyestuff type) were selected as described previously.[2]

2.1.3 Purification of Chemicals

Cyanuric chloride.[3] Cyanuric chloride was crystallised from petroleum ether (b.p. 90–100°C), and dried under vacuum at room temperature.

Sulphanilic acid.[4] 100 g sulphanilic acid in about 500 ml 1N sodium carbonate solution was boiled, then filtered and made strongly acid with hydrochloric acid. The solution was then neutralised with 1N sodium carbonate. The hot solution was cooled to 0°C with stirring and the precipitate of sodium sulphanilate was filtered off. The crystals were dissolved in 500 ml distilled water and the solution was filtered and

TABLE 1
The Codes for, and Chemical Names of, the Reactive Resists

Code	*Name*	*Structure (Fig. 2)*
DRM	2,4-Dichloro-s-triazin-6-yl-*p*-aminophenyl-sulphonic acid sodium salt	I
DRB	2,5-Bis(2,4-dichloro-s-triazin-6-yl)-aminophenyl-sulphonic acid sodium salt	II
DRS	2,4-Dichloro-s-triazin-6-yl-*p*-aminosalicylic acid sodium salt	III
DRN	2,4-Dichloro-s-triazin-6-yl-amino-8-naphthol-3,6-disulphonic acid sodium salt	IV

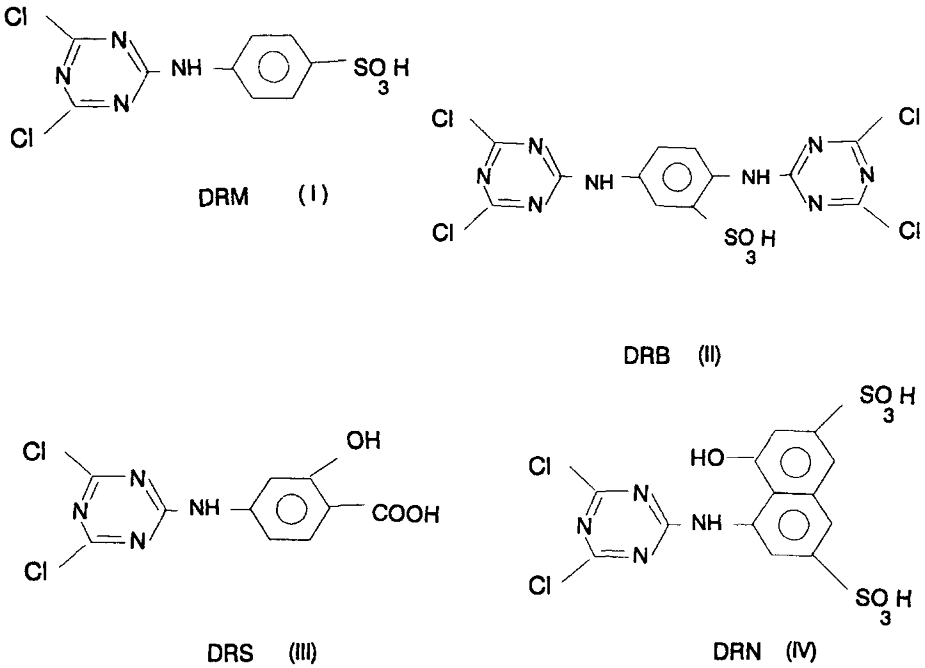

Fig. 2. Chemical structures of the reactive resists.

then acidified with concentrated hydrochloric acid. The material was then recrystallised from hot distilled water and dried at 120°C overnight.

1-Amino-8-naphthol-3,6-disulphonic acid (ANDA).[5] Sodium carbonate (20 g), to make the solution slightly alkaline to litmus, was added to a solution of 100 g of the dry ANDA in 750 ml of hot distilled water, followed by 5 g of activated charcoal. The suspension was stirred for 20 min and filtered by suction. The ANDA was precipitated by adding approximately 50 ml of conc. HCl, then filtered by suction and washed with distilled water. This purification procedure was then repeated. The ANDA was dried overnight in an oven at 60°C and stored in a dark glass bottle.

Synthesis of 2,4-dichloro-s-triazin-6-yl-p-aminophenylsulphonic acid sodium salt (dihydrate) (DRM). The method used was based on that described by Lewis and Pailthorpe.[6] 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 h after which time 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%).

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 h 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%.

Synthesis of 2,4-Dichloro-s-triazin-6-yl-p-aminosalicylic acid sodium salt (dihydrate) (DRS).[7] Cyanuric chloride (32 g) was dissolved in 100 ml acetone, ice-cold, with constant stirring, to which was added 25 g of the sodium salt of *p*-aminosalicylic acid dissolved in 60 ml water, 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 acetone in order to remove excess cyanuric chloride. The product was dried to constant weight. The yield achieved was 97%.

Synthesis of 2,4-dichloro-s-triazin-6-yl-amino-8-naphthol-3,6-disulphonic acid sodium salt (DRN).[8] 38 g ANDA (H Acid) was dissolved in 1N sodium bicarbonate solution, the solution 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 (2:1; 100 ml) at 0°C over 3 h. 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 salted out using saturated NaCl solution. The DRN product was filtered and vacuum dried at room temperature. The yield achieved was 70%.

2.1.4 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 $60F_{254}$ 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).

2.1.5 *Application of resist compounds*

The four reactive resists were applied to wool fabric (3 g) by a pad-cure technique. The treatment solution contained (wt/wt): active compound X%, sodium acetate 10%, urea 20% and Lissapol TN 450 0·1%. The fabric was impregnated and passed through a vertical pad mangle (Konrad Peter AG) set to achieve approximately 70% wet pick-up, then batch-rolled around a small cylinder, sealed in a polythene bag and cured for a specific time and temperature. The samples were washed off for 30 min in running tap water at 50°C and then dried.

2.1.6 *Determination of weight gain*

Weight gain was determined on the basis of oven dry weight measured before and after the application of the reactive resist compound. Fabrics were dried to constant weight in a circulating oven at 90°C for 2 h.

2.1.7 *Dyeing of wool fabric*

All dyeings were carried out in a thermostatically controlled dyebath (John Jeffreys Dye Master Engineering Co.). The dyeing methods employed were as given in the Colour Index.[9] Dyeings were conducted to achieve 0·5% depths (pure dye) at a liquor ratio of 100:1.

In order to compare the dye resist effects, competition dyeings were also carried out with a 2:1 ratio of untreated to resist-treated wool. The dyed pieces were then washed off at 50°C and dried.

2.1.8 *Dye resist evaluation*

Dye resist (%) was quantified by first calculating the K/S values of the dyed resist treated and untreated wools and then using the formula given below. The reflectance values were obtained using a Gardner Neotec Spectrögard Colour Computer System (Pacific Scientific).

$$\text{Resist percentage} = \frac{(K/S)\text{ut} - (K/S)\text{tr}}{(K/S)\text{ut}} \times 100$$

where ut : untreated wool
tr : resist treated wool
K : Absorption Coefficient
S : Scattering Coefficient

and

$$K/S = \frac{(1 - R)^2}{2R}$$

3 RESULTS AND DISCUSSION

3.1 Synthesis

Although a number of patents and journal articles[10–12] describe the synthesis methods which condense cyanuric chloride to amino aromatic sulphonic acids, it was found that the published procedures did not give satisfactory results. Therefore the methods developed in this work were based on optimisation according to the claims of each patent and journal article and preliminary experiments.

3.2 Characterisation of products

All compounds have melting points above 250°C. Some products were analysed as the dihydrate. The structures of the synthesised compounds were confirmed by elemental analysis and IR spectroscopy. The results from the elemental analyses and appropriate IR spectral data are given in Table 2. The data from elemental analyses and IR spectra showed that all four synthesised products were in good agreement with the expected values. Ring stretching modes were observed for the triazine functional group at 1560–1520 cm^{-1}.[13] This result clearly indicates that all four compounds have a triazine group.

3.3 Weight gain

The weight gains achieved when the synthesised reactive resist compounds were applied to wool by the pad-cure method are given in Fig. 3.

TABLE 2
Elemental Analyses and IR Data

Product code	*Yield (%)*	*Elemental composition*			*IR (cm^{-1})*
		C	*H*	*N*	
DRM	92	[E][a] 27·40 [F][b] 27·53	1·72 1·84	21·30 21·25	1180, 1560, 3300
DRB	90	[E] 28·51 [F] 27·50	2·39 2·20	14·78 13·61	1190, 1560, 3400
DRS	97	[E] 33·45 [F] 33·10	2·53 2·94	15·60 14·57	1190, 1570, 3300
DRN	70	[E] 33·42 [F] 32·98	1·72 1·31	11·99 11·45	1180, 1560, 3300

[a] [E]: Expected value.
[b] [F]: Found from elemental analysis.

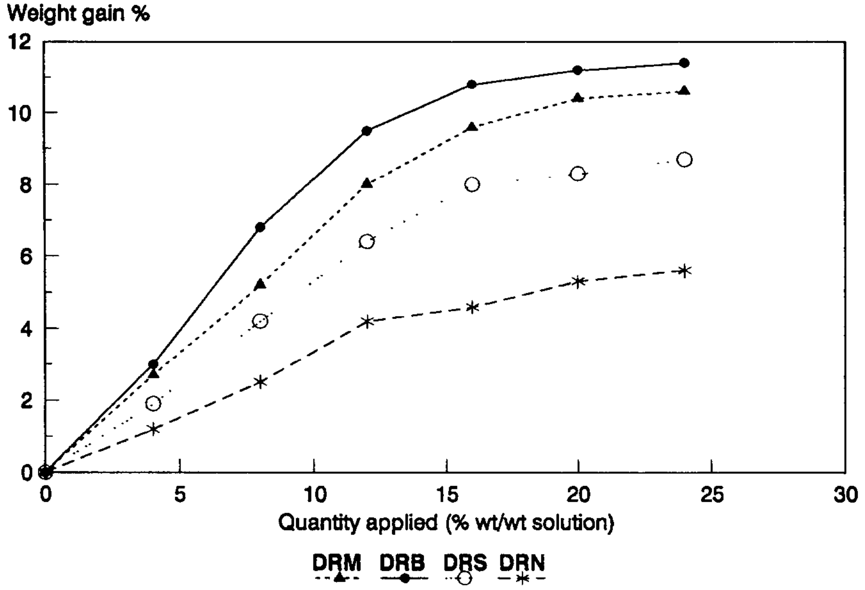

Fig. 3. Weight gain vs amount of dye resist compound applied by the pad-cure method with fixation at 80°C and 24 hours.

For all four reactive resists, the maximum weight gain appears to be achieved at an application level of about 14% owf (20% wt/wt, 70 % wet pick-up). DRB achieved the highest weight gain of *c*. 11%, whereas DRM achieved *c*. 10%. The weight gains achieved with DRS and DRN were only *c*. 8% and 5%, respectively.

In an attempt to explain the weight gain results for DRB, DRM, DRS and DRN, the IOR (Inorganicity Organicity Ratio)[2] values of synthesised compounds were calculated and are given in Table 3. It can be seen that the order of the weight gains is consistent with that of the IOR values of the reactive resists except for DRN, which gave the lowest weight gain and yet has the highest IOR value. It must be concluded that other factors such as molecular configuration, in addition to ionic/hydrophobic mechanisms, could affect the achieved weight gains.

TABLE 3
IOR Values of Reactive Resists

Code	*IOR value*
DRB	7·54
DRM	6·96
DRS	5·96
DRN	8·65

Since the inductive effect of the electron-withdrawing nitrogen on the *s*-triazines activates the reactive centres on the carbon atoms of *s*-triazines more than those of other heterocycles, it would be anticipated that the leaving groups in the *s*-triazines should be more easily substituted than those of other heterocycles. Moreover, the electro-negativity of the leaving groups adjacent to the reactive centres also partly contributes to the increased reactivity of the reactive centres.

It can be seen from the results given in Fig. 3 that the DRB-treated wool achieves a higher weight gain than the DRM-treated wool. One might be tempted to deduce that this difference arises because the DRB reactive resist contains two *s*-triazine reactive moieties which leads to a higher degree of fixation of DRB to the wool fibre.[14,15] When the weight gain data are recalculated in terms of millimoles/g reactive resist fixed to the wool, a different pattern emerges.

As can be seen from the data provided in Table 4, DRM has actually achieved the highest fixation of active compound.

Thus, since both DRM and DRB are monosulphonated species, DRM has actually introduced the greatest number of sulphonate groups into the wool. DRN is a disulphonated reactive resist and, even though the weight gain (5·3%) is lower than that achieved by DRB (11·4%), the DRN-modified wool has only slightly less sulphonate groups than does the DRB-treated wool.

The DRS-modified wool, with a weight gain of 8·3%, has 0·26 mmol/g of carboxylic acid residues. This concentration is similar to the number of sulphonate groups to be found in both the DRB- and DRN-modified wools.

3.4 Dye resist effects

For those dyes that dye wool by ionic/hydrophobic mechanisms, the % dye resist data has been plotted against the IOR values of the dyes for

TABLE 4
Weight Gain Data Expressed as mmol/g

CPD	*MW*	*WG%*	*mmol/g*	*mmol/g* SO_3^-	*mmol/g* COO^-
DRM	331·12	10·6	0·32	0·32	—
DRB	470·05	11·4	0·24	0·24	—
DRS	323·08	8·3	0·26	—	0·26
DRN	511·23	5·3	0·10	0·20	—

CPD—Reactive Resist Compound.
MW—Molecular Weight.
WG%—Weight Gain %.

the four dye resist agents and sulphamic acid in competition dyeing and normal dyeing (see Figs 4–5). These graphs show that there is a non-linear relationship between % Resist and IOR values.

These results confirm that the dye resist effects achieved with the reactive resists are highly dependent on the IOR values of the dyes employed to dye the reactive resist treated wool.

It is obvious from the data provided in Figs 4 and 5 that sulphamic acid (SA) modified wool gives a superior dye resist, for the seven dyes examined, to any of the four reactive dye resist agents synthesised in this work. This result is quite explicable when one considers that an 8·5% weight gain for sulphamic-acid-treated wool represents *c.* 0·88 mmol/g of sulphamate and/or sulphonate groups in the SA-modified wool. This amount far outweighs the 0·32 mmol/g achieved with the DRM-modified wool.

Of the four reactive resists synthesised in this work, DRB gives the highest dye resist effect for the seven dyestuffs examined. This result is particularly interesting when one considers that, whilst DRB achieves the highest weight gain (11·4%), DRM actually achieves the highest addition of sulphonate groups (0·32 mmol/g) to wool (see Table 4). Of course, DRB is a bifunctional reactive resist because it contains two *s*-triazine reactive groups. Thus there is a higher probability of reaction between DRB and wool as compared with the reaction of DRM and wool. Since DRB has two *s*-triazine reactive groups it is highly likely that DRB may cross-link the wool. Such a cross-linking action could greatly reduce both

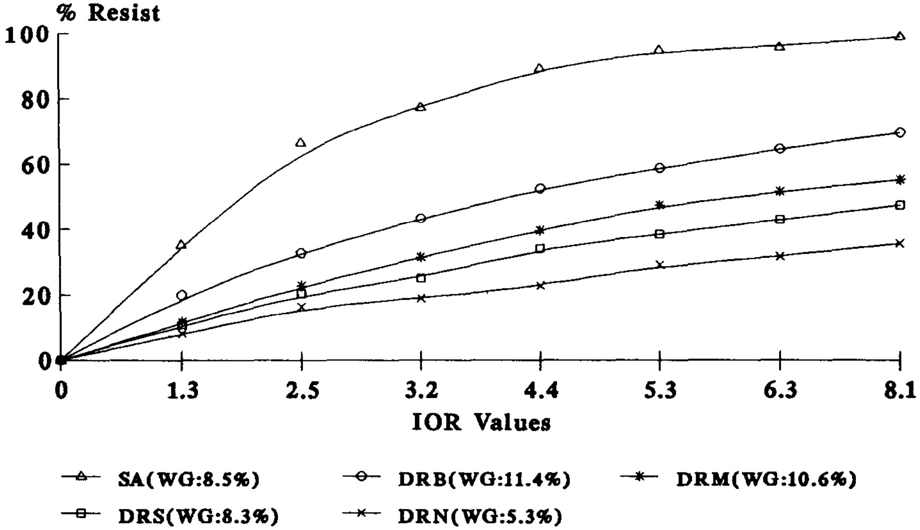

Fig. 4. % Resist on reactive resist treated wool versus IOR values (normal dyeing).

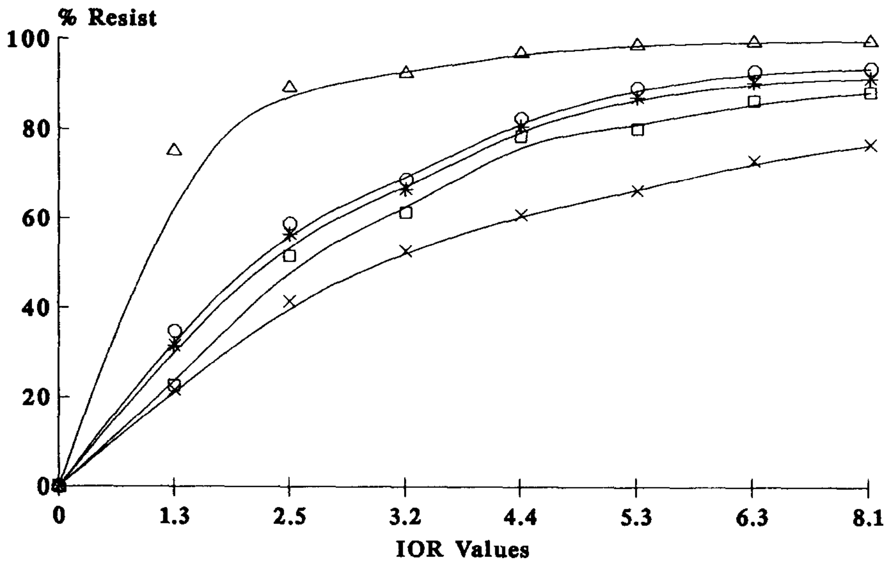

Fig. 5. % Resist on reactive resist treated wool versus IOR values (competition dyeing) (for key see Fig. 4).

the diffusion coefficients of the dyes in the modified wool and the free volume available within the modified fibre to accommodate the dyes. Modica *et al.*[16] also found a decrease of the affinity towards acid dyes after bifunctional group treatment of wool.

DRN-modified wool has 0·20 mmol/g of added sulphonate groups yet gives a very poor dye resist to the seven dyes employed in this study. Since the total added sulphonate groups for DRB- and DRN-modified wools are similar, being 0·24 and 0·20 mmol/g, respectively, the bifunctional nature of DRB leading to cross-links in the wool becomes a plausible explanation.

The DRS-modified wool contains 0·24 mmol/g of carboxylate groups and exhibits reasonably good dye resist effects to the seven dyes employed in this study. However, it is obvious from the data presented in Figs 4 and 5 that DRB- and DRM-treated wools give the best dye resist effects, with the DRB-treated wool being superior. Even so, full white resists (100% resist) were not achieved with any of the four reactive resists synthesised in this project. Sulphamic-acid-treated wool remains the best dye-resisted wool especially to dyes with high IOR values and to reactive dyes.

Although the IOR values can be used as an important tool in the evaluation of the hydrophilic/hydrophobic character of substances, it must be noted that there are limitations and that the molecular configurations of different chromophores may have to be considered. However, for similar chemical structures of the same chromophore, IOR values can be well utilised. Therefore knowledge of IOR values (or HLB, or QSAR values) enables one to make accurate predictions about dye resist effects. These predictions make it possible for one to achieve some degree of control over these dye resist processes. For example, if we can calculate the IOR values from the chemical structures, we can predict the dye resist effects and choose appropriate dyestuffs depending upon the requirements of the dye resist effects.

The main drawback of these reactive dye resist methods is that 20% wt/wt must be applied in order to achieve satisfactory tone on tone effects. In practice, usually less than 4% owf reactive dyestuff dye is applied to fix on the substrate. This 20% wt/wt amount may be a limitation to widespread application in industrial use. However, it seems to be necessary to treat above 20% in order to modify the wool substrate sufficiently to block the wool's reactive sites and achieve tone on tone effects. This problem may be solved by pretreatment or aftertreatment of the reactive resists using other techniques such as cross-linking fixing agents.

4 CONCLUSIONS

Four reactive dye resist agents containing *s*-triazine-based reactive groups were synthesised and evaluated.

Low-temperature curing can be applied to produce tone on tone effects or dark colour resist treatments in the case of the bifunctional reactive resist (DRB).

The orders of the dye resist effects achieved were found to be consistent with the IOR values of the dyes that dye wool by ionic/hydrophobic dyeing mechanisms. Therefore, knowledge of IOR values enables one to make accurate predictions about dye resist effects. These predictions make it possible for one to achieve some degree of control over these dye resist processes.

The dye resist effect achieved by the bifunctional reactive resist (DRB) was superior to that of the monofunctional reactive resist (DRM). The explanation for this difference might be that there are cross-linking effects between the bifunctional groups of DRB and the wool substrate. Hence these bifunctional reactive groups play a physical blocking role together with other ionic repulsion forces. This effect could be the basis for future work.

Full white resist effects seem to be difficult to achieve with reactive resists and the reactive resists achieved herein are not as good as the sulphamic acid resist process. If higher levels of fixation and cross-linking effects could be achieved, then the perfect dye resist process may still be feasible.

The drawback of these reactive dye resist methods is that the reactive resist must be applied above 20% wt/wt in order to achieve satisfactory tone on tone effects. This amount may be a limitation for the process application in widespread industrial use.

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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