

Dye Resist Effects on Sulphamic-Acid-Treated Wool

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ABSTRACT

Dye resist effects achieved on sulphamic-acid-treated wool were investigated in respect of curing temperature and dyestuff type. It was found that there is a significant difference between the pH of aqueous extracts from sulphamic acid treated wool cured at 100°C, 125°C and 150°C. The results from dye exhaustion studies indicate that, for curing temperatures less than 140°C, unbound free sulphamic acid is desorbed from the wool. The desorbed sulphamic acid then changes dyebath pH which, in turn, changes the resist effect achieved. Only when the sulphamic acid is cured above 140°C does complete reaction/pyrolysis of the sulphamic acid take place, giving the best dye resist effect.

Overall it appears that the dye resist effect is highly dependent on the hydrophilic/hydrophobic character of the dyestuffs and substrate. It is demonstrated in this paper that the Inorganicity-Organicity Ratio (IOR) values of the dyes can be used to quantify dye resist effects on sulphamic-acid-treated wool.

1 INTRODUCTION

The sulphamic-acid resist process is currently the most successful dye resist process for wool; however, the curing temperature is high and may damage the wool. If the curing temperature could be reduced from 150°C to the drying temperature normally employed for wool (100–120°C) or, if possible,

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to room temperature, then this process could be widely employed in the wool textile industry. A study of dye resist effects on sulphamic-acid-treated wool, particularly in terms of curing temperature, is therefore considered to be most important.

The question arises as to why sulphamic acid plays a role only at high temperature (140–150°C). If the mechanisms associated with these reactions could be elucidated, then a method could be developed to enable sulphamic acid to react with wool at low temperature and hence have sufficient substantivity to withstand subsequent washing or dyeing processes.

According to the results of Cameron *et al.*,¹ the optimised conditions for maximum uptake of sulphamic acid are to treat the wool with a solution containing 20% sulphamic acid, 20% urea and 0.1% Lissapol TN450 for 30 min at 40°C, followed by padding, drying at 80°C and curing at 150–160°C for 4–5 min.

Thus wool fabric was treated with sulphamic acid and the dye resist effects were investigated using different curing conditions and dyestuffs. The results of these studies have led to a possible explanation for the nature of the reaction between sulphamic acid and wool.

2 MATERIALS AND METHODS

2.1 Materials

The wool fabric employed in this study was a scoured and decatized 2/2 twill, weight 270 g m⁻², supplied by John Vicars Fabrics, Sydney. All chemicals were of analytical grade and were supplied by Ajax Ltd.

A series of acid dyes were selected which have different numbers of sulphonate groups but the same chromophore. In addition, one Irgalan-type metal complex dye and one Lanazol-type reactive dye were selected. (Note: The structures of the latter two dyes were revealed to the authors on the condition that the trade names were not disclosed herein.) The *Colour Index* (CI) names and the CI numbers for these dyes are given in Table 1. The chemical structures of the dyes are given in Fig. 1.

2.2 Purification of dyes²

The commercial dye (10 g) was dissolved in boiling DMF (400 ml); the solution was filtered and the dye (free of inorganic material) was precipitated by the addition of acetone (100 ml) or trichloroethylene (100 ml). The precipitated dye was removed by filtration, washed with acetone or trichloroethylene and dried below 50°C. The procedure was repeated until the absorbance of a solution of given concentration was optimised.

TABLE 1
Dyestuffs Used

Commercial name	Colour index name	Colour index number	Chemical structure ^a	No. of —SO ₃ ⁻ groups
Acid Red 88 (Aldrich)	CI Acid Red 88	CI 15620	I	1
Crystal Scarlet (Aldrich)	CI Acid Red 44	CI 16250	II	2
Amaranth (Aldrich)	CI Acid Red 27	CI 16185	III	3
Acilan Ponc 6R (F.By)	CI Acid Red 41	CI 16290	IV	4
Azo Rhodine G	CI Acid Red 1	CI 18050	V	2
Carbolan Crimson BS	CI Acid Red 138	CI 18073	VI	2
Lanasol type	—	—	VII	2
Irgalan type	—	—	VIII	0

^a See Fig. 1.

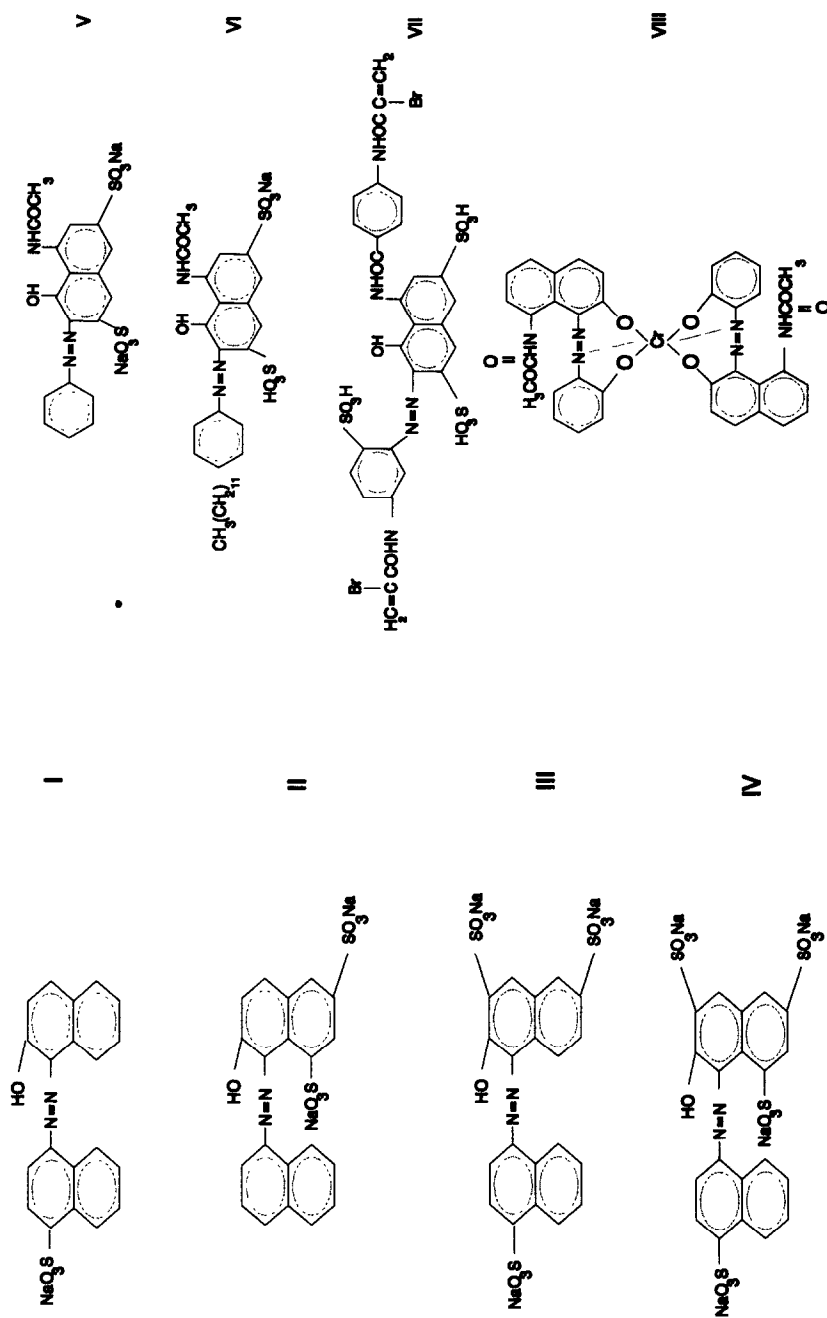


Fig. 1. Dye structures.

2.3 Application of sulphamic acid to wool

Wool samples were treated with sulphamic acid by a pad-dry-bake procedure. The wool was first impregnated with a solution containing sulphamic acid (20%, w/w), urea (20%, w/w) and Lissapol TN450 (ICI) (0.1%, w/w). The wool samples were then padded on a vertical pad mangle (Konrad Peter AG; Liestal M2F-50) to achieve 70% wet pick-up. The padded samples were dried at 85°C for 15 min and baked for 5 min at the chosen curing temperature. The samples were then rinsed thoroughly in water (50°C).

2.4 Dyeing methods

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*.³ Dyeings were conducted to achieve 0.5% depths (pure dye) at a liquor ratio of 100:1.

Dye exhaustion curves were determined by withdrawing samples of dyebath liquor at appropriate times and measuring the absorbance of the samples at the wavelength of maximum absorption with a Cary 210 UV-Visible spectrophotometer (Varian). The percentage exhaustion, E_x , was then calculated by the formula:

$$E_x = \left(1 - \frac{E_t}{E_0} \right) \times 100$$

where E_t is the optical density at time t and E_0 is the optical density at time 0.

The dyed samples were then used for the measurement of the dye resist effect.

2.5 Determination of pH of the aqueous extract of sulphamic-acid-treated wool

The pH of the aqueous extracts of sulphamic-acid-treated wool was determined by the method described in AS 2001.3.1⁴ using an Orion model 520A pH-meter (Orion Research Inc.). The extraction procedure was as follows. Wool samples were boiled in distilled water for 1 h under reflux, and the pH of the cold aqueous extract was measured. The pH variations during the dyeing procedure were also measured.

2.6 Dye resist evaluation

Dye resist percentage was quantified by calculating the K/S values of the dyed sulphamic-acid-treated and untreated wools and then using the

formula given below. The reflectance values were obtained using a Gardner Neotec Spectrogard colour computer system (Pacific Scientific).

$$\text{Dye resist (\%)} = \frac{(K/S)_{\text{ut}} - (K/S)_{\text{tr}}}{(K/S)_{\text{ut}}} \times 100$$

where K denotes absorption coefficient, S scattering coefficient, subscript 'ut' untreated wool, and subscript 'tr' treated wool.

3 RESULTS AND DISCUSSION

3.1 The pH variation of sulphamic-acid-treated wool at different curing temperatures

It can be seen from the results given in Table 2 that there is a significant difference between the pH of the aqueous extracts from the sulphamic-acid-treated wool cured at 150°C and extracts from the sulphamic-acid-treated wools cured at 100°C and 125°C. Clearly, little reaction has taken place between sulphamic acid and wool at 100°C. The free sulphamic acid is readily extracted by boiling water and the pH of the extract is quite low. On the other hand, extensive reaction takes place between sulphamic acid and wool at 150°C. Consequently, the pH of the aqueous extract is relatively high.

It can be seen from the data given in Fig. 2 that the pH changes observed under boiling-dyebath conditions are consistent with the aqueous extraction data for sulphamic-acid-treated wool given in Table 2. All sulphamic-acid-treated wool samples exhibited lower pH values than those for untreated wool in the dyeing liquor. The sulphamic-acid-treated wool cured at 150°C had a fairly stable pH of *c.* 4.5 during the dyeing cycle. Hence it would appear that all of the sulphamic acid present in the wool is bound acid. For the case of the sulphamic-acid-treated wool cured at 100°C, the pH of the dyebath initially dropped to *c.* 2.8 and continued to fall during the dyeing cycle. Hence free sulphamic acid was being desorbed from the wool, suggesting

TABLE 2
pH of Aqueous Extracts

<i>Curing temperature (°C)</i>	<i>pH</i>
100	2.54
125	3.08
150	4.62

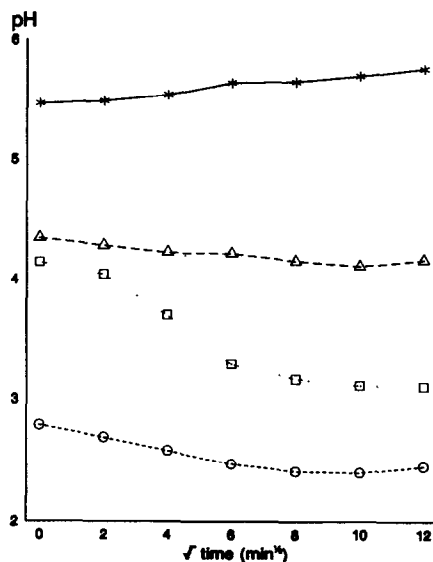


Fig. 2. pH variation (Lanasol-type). Curing temperature: (*) untreated; (O) 100°C; (□) 125°C; (Δ) 150°C.

that the sulphamic acid is not bound to the wool when cured at 100°C. The sulphamic-acid-treated wool cured at 125°C behaves as if the sulphamic acid has partially fixed to the wool.

3.2 Dye exhaustion curves

When the dye exhaustion curves for the eight dyes employed in this study were examined, it could be seen that the exhaustion behaviour allows the dyestuffs to be divided into two groups.

The data given in Fig. 3 for CI Acid Red 88 are typical of the dyeing

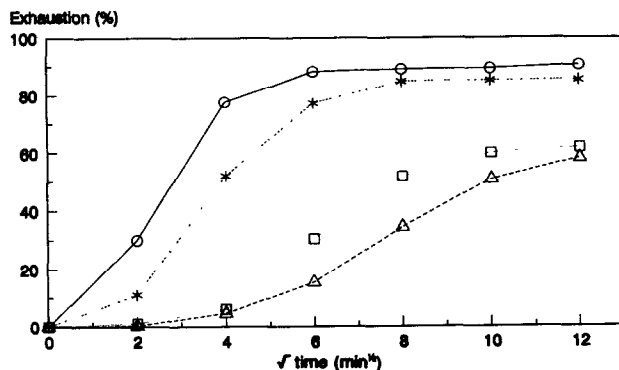


Fig. 3. Rate of CI Acid Red 88 exhaustion on sulphamic-acid-treated wool. Curing temperature: (O) untreated; (*) 100°C; (□) 125°C; (Δ) 150°C.

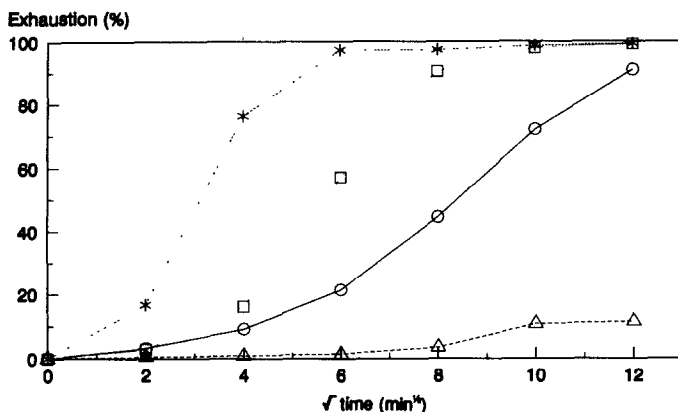


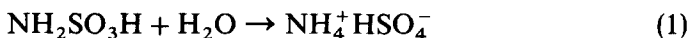
Fig. 4. Rate of Lanazol-type exhaustion on sulphamic-acid-treated wool. Curing temperature: (O) untreated; (*) 100°C; (□) 125°C; (Δ) 150°C.

behaviour of dyes in the first group. In this first group, all dyes exhibit dye resist effects on the sulphamic-acid-treated wools. The resist effect, as indicated by the reduced exhaustion of the dyebath, improves as the curing temperature increases from 100°C to 150°C.

The second group of dyes exhibits quite different behaviour. The data given in Fig. 4 for the Lanazol dye are typical. The exhaustion of these dyes is assisted when applied to wool cured at 100°C but resisted when applied to wool cured at 150°C. These assist effects are caused by the pH changes discussed above.

4 DISCUSSION

At room temperature, aqueous solutions of sulphamic acid are very stable, but at elevated temperatures, rapid hydrolysis occurs as follows.⁵



Decomposition tends to be very rapid above 136°C, whilst at lower

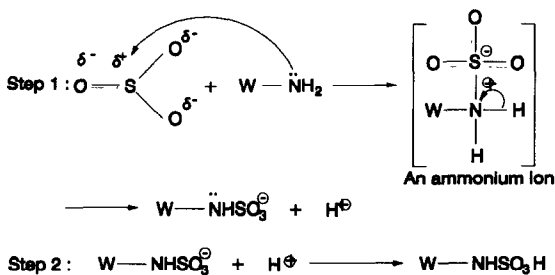
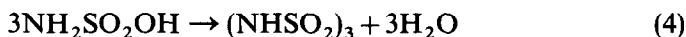


Fig. 5. Reaction mechanisms of sulphur trioxide with basic amino groups of wool amino acids. W = wool.

temperatures decomposition proceeds more slowly.⁶ Thus the decomposition temperature of sulphamic acid has a close correlation with the extent of the dye resist effect observed in wool. The pyrolysis of sulphamic acid results in a whole series of sulphamides, sulphonic acids and polysulphimides,⁷ and it is also possible that sulphamic acid decomposes to sulphur trioxide and ammonia.⁸ The reaction formulae may be represented as follows:



where sulphamic acid can be represented by $\text{NH}_2\text{SO}_2\text{OH}$ or $^+\text{NH}_3-\text{SO}_3^-$, the zwitterionic state.

In dye resist treatments using sulphamic acid, owing to the high curing temperature (150°C), sulphur trioxide and ammonia reaction products [eqn (5)] would predominate, although all the reactions [eqns (2), (3), (4)] could participate. The sulphur trioxide, from reaction (5), would participate in subsequent reactions. At the same time, around this temperature, destruction of some amino acids will occur. It is well known that amino, amide and disulphide groups and many other amino acids including aspartic acid, threonine, serine, valine, tyrosine, lysine, arginine and histidine are partly destroyed by heat.⁹ Furthermore, the formation of *O*-serine hydrogensulphate was confirmed in the amino acid analysis of sulphamic-acid-treated wool.¹⁰ Therefore these amino acids and sulphur trioxide could react with each other covalently.

The reaction mechanisms can be postulated as shown in Figs 5 and 6.

In these reactions, sulphur trioxide acts as a Lewis acid because the sulphur atom is slightly electron-deficient, whereas oxygen atoms have a slight excess negative charge due to the difference in electronegativity of

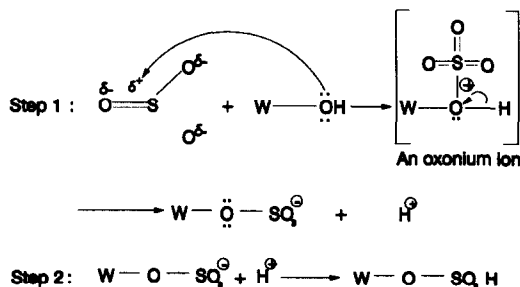


Fig. 6. Reaction mechanism of sulphur trioxide and hydroxyl groups of wool amino acids.
W = wool.

oxygen and sulphur. Therefore in step 1, SO_3 , which is a Lewis acid, would react with Lewis bases, such as the hydroxyl group or the basic amino group, which have unshared electron pairs on the oxygen or on the nitrogen, to form an oxonium ion or an ammonium ion, respectively, as transition states $\text{W}-\text{O}^+\text{H}-\text{SO}_3^-$ or $\text{W}-\text{N}^+\text{H}_2\text{SO}_3^-$.

As the transition states are unstable, the oxonium ion or ammonium ion would immediately gain electrons from the hydrogen, and would then reach a stable state as wool sulphonate and wool sulphamate groups, respectively.

Hence, below 136°C , sulphamic acid may be difficult to decompose to sulphur trioxide and so it would exist as unreacted free sulphamic acid in the wool. Obviously, therefore, the amount of free sulphamic acid would increase as the curing temperature decreases.

The dye exhaustion behaviour can be explained as follows. For the Group 1 dyes (e.g. Fig. 3), where dyeing is carried out under strong acid conditions, the unbound sulphamic acid would not significantly affect the dyebath pH. However, for Group 2 dyes (e.g. Fig. 4), which are applied under weak acid conditions, the dyebath pH would decrease significantly owing to the desorption of the unbound sulphamic acid.

Therefore, in reactive dyeing or metal complex dyeing, which are carried out in weak acid conditions, the exhaustion curves of sulphamic-acid-treated wool cured at 100°C would show a high dye assist effect, while for sulphamic-acid-treated wool cured at 150°C , it would exhibit a slight dye assist effect depending on the dyestuff.

4.1 IOR values

The dyeing process involves three principal components, namely dyestuff, substrate and water. Hence, in order to understand the overall process, one must elucidate the extent of the interactions between these components. Although much work¹¹⁻¹³ has been done to give some guidelines in this area, this subject has not yet been completed and is still being studied. Examples of the approaches that have been applied are the HLB method,¹¹ the IOR method¹² and the QSAR method.¹³ The IOR value can be easily calculated from the organic functional groups and therefore the IOR method¹² was applied to examine the dye resist results for the dyes employed in this study.

Table 3 gives the dye resist and IOR values for four of the acid dyes employed in this study. It can be seen from the data that the IOR values correlate well with the number of sulphonate groups on the acid dyes. These results also show that the dye resist effect is highly correlated with the IOR values of the dyestuffs.

The structures of CI Acid Red 1 and CI Acid Red 138 are essentially the

TABLE 3
Dye Resist Effects

<i>Dye</i>	<i>Curing temperature (°C)</i>	<i>IOR</i>	<i>Dye resist (%)</i>
CI Acid Red 88 (one $-\text{SO}_3^-$)	100	2.5	34.7
	125	2.5	45.8
	150	2.5	66.5
CI Acid Red 44 (two $-\text{SO}_3^-$)	100	4.4	30.5
	125	4.4	43.4
	150	4.4	88.8
CI Acid Red 27 (three $-\text{SO}_3^-$)	100	6.3	29.6
	125	6.3	42.2
	150	6.3	95.3
CI Acid Red 41 (four $-\text{SO}_3^-$)	100	8.1	25.5
	125	8.1	90.3
	150	8.1	98.5

same except that CI Acid Red 138 contains a dodecyl group, thereby making it more hydrophobic than CI Acid Red 1. The data given in Table 4 reflect this difference in hydrophilic/hydrophobic character with CI Acid Red 1 and CI Acid Red 138 having IOR values of 5.3 and 3.2, respectively.

It can also be seen in Table 4 that the Irgalan dyestuff used in this study is the most 'hydrophobic' dye in the set, with an IOR value of 1.3. The IOR value of the Lanazol dye falls between that of CI Acid Red 88 and CI Acid Red 44.

TABLE 4
Dye Resist Effects

<i>Dye</i>	<i>Curing temperature (°C)</i>	<i>IOR</i>	<i>Dye resist (%)</i>
Lanazol type	100	3.6	-56.8
	125	3.6	8.2
	150	3.6	98.0
Irgalan type	100	1.3	-15.8
	125	1.3	10.5
	150	1.3	35.2
CI Acid Red 1	100	5.3	28.8
	125	5.3	62.8
	150	5.3	94.5
CI Acid Red 138	100	3.2	-20.6
	125	3.2	32.6
	150	3.2	77.2

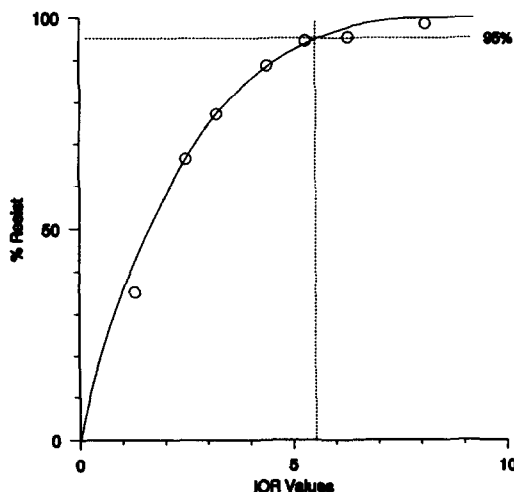


Fig. 7. Percentage resist on wool cured at 150°C versus IOR values.

These results demonstrate that the dye resist effect achieved with the sulphamic acid process is highly dependent on the IOR values of the dyes employed. The resist percentage values for wool cured at 150°C versus IOR value data for the dyes that exhibit ionic/hydrophobic dyeing mechanisms (i.e. excluding the Lanazol reactive dye) are plotted in Fig. 7.

It can be readily seen that, in order to achieve dye resist values of greater than (say) 95%, the dyestuffs employed in the dyeing must have IOR values greater than *c.* 5.5. Such dyestuffs are, of course, polysulphonated and hence more hydrophilic in character than the dyes that are poorly resisted by the sulphamic-acid-treated wool.

Sulphamic acid is a very effective resist for reactive dyes (e.g. Lanazol dyes) because the sulphamic acid treatment effectively blocks the nucleophilic sites in the wool and hence prevents fixation of the dyes to the wool.

5 CONCLUSIONS

The best dye resist effect for the dyes examined in this work is achieved on sulphamic-acid-treated wool cured at *c.* 150°C. Below this temperature, a dye assist effect is exhibited for reactive and metal-complex dyestuffs due to the characteristics of sulphamic acid itself. Dye resist effects depend upon the dyes themselves.

These findings indicate that, for curing temperatures less than 140°C, unbound sulphamic acid is desorbed from the wool during dyeing, with a consequent lowering of dyebath pH.

The dye resist effect is highly dependent on the hydrophilic/hydrophobic character of the dyes and substrate. With the exception of reactive dyes, this work shows that the IOR values of the dyes should be greater than 5.5 in order to achieve dye resist values of better than 95% on sulphamic-acid-treated wool.

IOR values can be used as an important tool in the evaluation of the hydrophilic/hydrophobic character of dyes. This technique should be of great value in future work on dye resist processes.

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