

Crosslinking Nucleophilic Dyes on Wool

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ABSTRACT

Nucleophilic amino-alkyl dyes have been synthesised by the simple expedient of reacting existing reactive dyes with ethylene diamine. These dyes when applied to wool behave as acid dyes, although there is a small amount of covalent bonding to the fibre, presumably through Michael addition at dehydroalanine residues formed from cystine degradation.

If substantive crosslinking agents could be applied then it might be expected that excellent dye-fibre covalent bonding could be achieved to produce dyeings with very high wet fastness properties. The crosslinking agent might be added either before, during or after the amino-alkyl dye application; the latter procedure should, in principle, give the most level dyeings. Crosslinking agents evaluated include hexamine, triacryloylamino-hexahydro-s-triazine, methylene-bisacrylamide and 2-chloro-4,6-di(aminobenzene-4'-sulphatoethylsulphone)-s-triazine. Hexamine and methylene-bisacrylamide are available commercially but the other agents were synthesised. Results obtained are very promising and offer potential wool dyeing methods which have better levelness than existing reactive dye systems.

1 INTRODUCTION

It may be predicted that reactive dyes will assume greater importance in wool dyeing due to a growing perception that chrome and premetallised dyes are environmentally undesirable. Arguments may be advanced against this viewpoint but nevertheless in some areas of the world legislation has resulted in zero chrome dye usage. Thus whatever the reasonableness of the argument, it is important that alternative procedures exist, capable of dyeing wool to the same level of deep shades with the same all-round excellent

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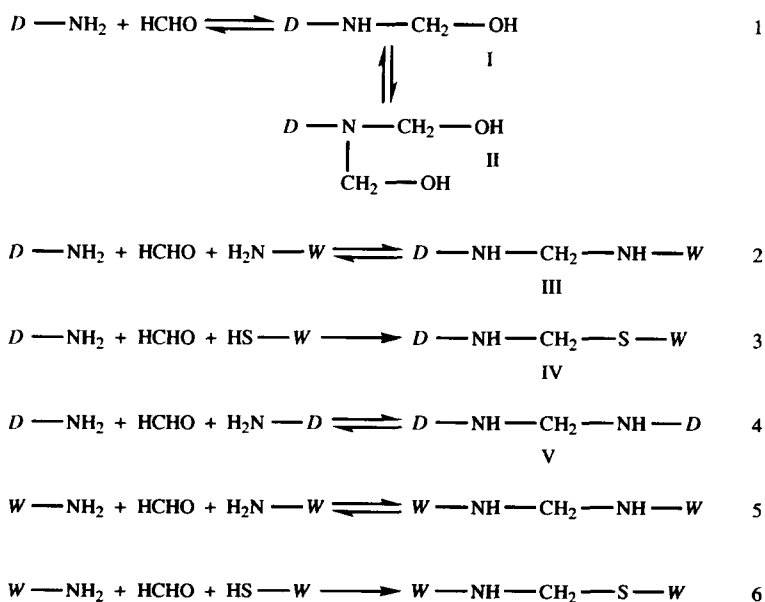
fastness properties currently achievable with chrome dyes.

Reactive dyes on wool suffer from problems of incomplete fixation in deep shades, necessitating some form of alkaline clearing treatment to obtain maximum wet fastness, and a lack of migrating ability which can inhibit their application in such areas as piece and hank dyeing.¹ These problems may, in principle, be solvable by developing fibre substantive crosslinking agents for application with nucleophilic dyes; the crosslinker may be applied either with the dye or as a post-treatment.

A number of crosslinkers are already available but it may be necessary to synthesise new ones to achieve the very best performance. Readily available crosslinking agents include multifunctional epoxides, aldehydes, carbodiimides, vinylsulphones, isocyanates, acrylamides and various reactive polymers.²

Particularly useful nucleophilic dyes for use in a wool/crosslinker system are amino-alkyl dyes, conveniently prepared from the reaction of halotriazinyl dyes with ethylene diamine^{3,4} or vinylsulphone dyes with ammonia.⁵

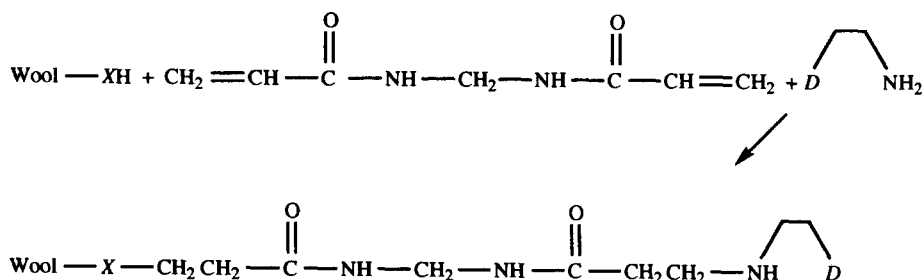
The commonest and cheapest crosslinker is formaldehyde; however environmental concerns militate against its use. Hexamine, a formaldehyde donor, has been employed⁶ to fix nucleophilic amino-alkyl dyes on wool; the active crosslinker, formaldehyde, is produced at the boil. Results achieved by this method were very encouraging in terms of dye levelness and fixation in full shades. Dye is permanently bonded to the fibre according to the following reaction possibilities:



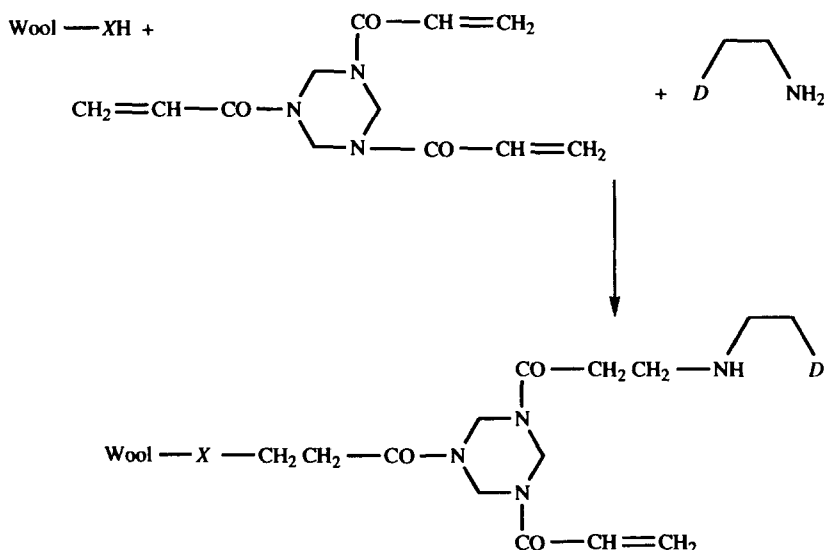
Scheme 1. Reaction of wool nucleophiles and amino-alkyl dye with formaldehyde (W = wool; D = dye).

Reactions 2 and 3 in Scheme 1 will lead to the formation of covalent dye-fibre bonds and reactions 5 and 6 will form additional fibre crosslinks, which may reinforce the physical properties of the fibre. Reaction 4 may also produce improved dye wet fastness by doubling molecular size. However, only the so-called thioalkylation reaction shown in reactions 3 and 6 will lead to stable bonds, all other reactions being reversible; thus reaction 3 is important if adequate dye-fibre bonding is to occur.

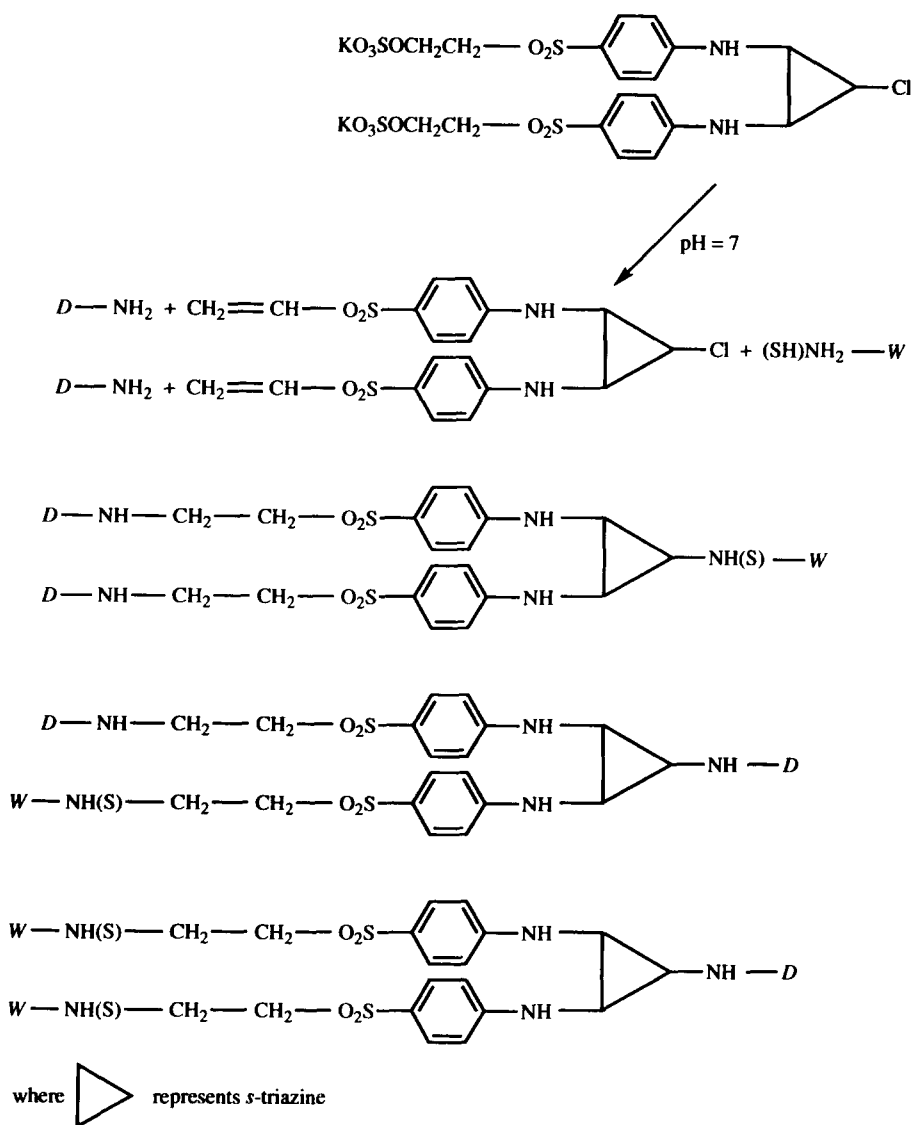
Two compounds, methylene-bis-acrylamide⁷ and triacrylamino-hexahydro-*s*-triazine⁸ have also been evaluated as reactive crosslinking systems to fix amino-alkyl dyes on wool. Dispersions of these crosslinkers react with amino-alkyl dyes and nucleophilic sites in wool keratin (wool-XH) according to Schemes 2 and 3.



Scheme 2. Reaction of wool nucleophiles and amino-alkyl dye with methylene-bis-acrylamide.



Scheme 3. Reaction of wool nucleophiles and aminoalkyl dye with triacrylamino-hexahydro-*s*-triazine.



Scheme 4. Reaction of nucleophilic dyes with XLC and wool.

A water-soluble, fibre substantive crosslinker, 2-chloro-4,6-di(aminobenzene-4'- β -sulphatoethylsulphone)-1,3,5-*s*-triazine (XLC) was first patented by Wool Development International; its substantivity and reactivity towards wool have been reported,⁹⁻¹¹ but its potential to fix nucleophilic dyes on wool is a novel feature and is reported in this paper. As it is a precursor of a bifunctional vinylsulphonyl compound, it would give two reactive double bonds when present in boiling dye baths with a pH ≥ 6 . Due to the presence

of the two strong electron-withdrawing sulphone groups, the two double bonds are more reactive than those in triacroylamino-hexahydro-*s*-triazine.⁸ Furthermore, XLC also contains one monochloro-triazine reactive group which is less reactive than the vinylsulphonyl residue. Since the compound contains reactive groups of different reactivities, it should readily form covalent bonds between selected nucleophilic dyes and the wool fibre. The reaction of XLC with amino-alkyl dye and the wool fibre may be shown by Scheme 4.

The above scheme shows the ideal formation of dye–XLC–wool linkages. As reaction takes place in a random manner, the following products could also be produced:

- (i) dye : XLC = 3 : 1,
- (ii) XLC : wool = 1 : 3.

Clearly products (i) and (ii) are undesirable since they do not lead to covalent attachment of the dye to the fibre.

2 EXPERIMENTAL

2.1 Materials

A wool serge fabric (2/2 twill, botany serge supplied by Parklands) was used throughout this work.

All chemicals, other than the crosslinking agent, were Analar grade quality. XLC was prepared according to the method described by Lewis.¹² The monochloro-triazine dye used in these studies was Procion Red H8BN (Zeneca) (CI Reactive Red 58).

The amino-alkyl dye was prepared from CI Reactive Red 58 by reaction with ethylene diamine as described previously.^{3,4,6}

2.2 Dyeing of wool

The wool fabric was wetted in the buffer solution required for subsequent dyeing for about 15 minutes and then squeezed to remove the excess solution before being placed into the dyebath. All dyeings were carried out in 100-ml sealed stainless steel dyepots housed in a Rotadyer (John Jeffreys) laboratory dyeing machine, at a liquor-to-goods ratio of 20 : 1. The dyebath was set at the required pH using a citric acid/disodium hydrogen phosphate buffer. Dyeing commenced at 30°C and the temperature was raised to the boil over 40 min and maintained at the boil for the required length of time.

2.3 Measurements

The uptake of dye by wool was measured by sampling the dyebath before and after the dyeing process. The absorbance of the diluted dye solution was measured at the wavelength of maximum absorption (λ_{\max}) of the dye using a UV-visible Spectrophotometer (Phillips Pye Unicam PU8600). Dyebath exhaustion was calculated using the following equation:

$$\text{Exhaustion \%} = 100 (1 - A_1/A_0) \%$$

A_0 , A_1 = Absorbance of dye solution before and after the respective process.

Measurement of the extent of dye–fibre covalent bonding or dye fixation was carried out by stripping any unfixed dye from the dyed material using 25% aqueous pyridine (100°C, LR = 10:1). This stripping treatment was carried out repeatedly using fresh aqueous pyridine until no further dye was removed. The K/S values (λ_{\max}) of the stripped, dyed samples were then measured using an I.C.S. Micromatch colour measurement system from which the extent of fixation of dye was calculated using the following equations:

$$\text{Total dye applied fixed (T\%)} = \text{dye exhaustion (\%)} \cdot (C_2/C_1)$$

$$\text{Degree of fixation of dye absorbed (F\%)} = (C_2/C_1) \cdot 100\%$$

C_1, C_2 = K/S values of dyed samples before and after stripping respectively.

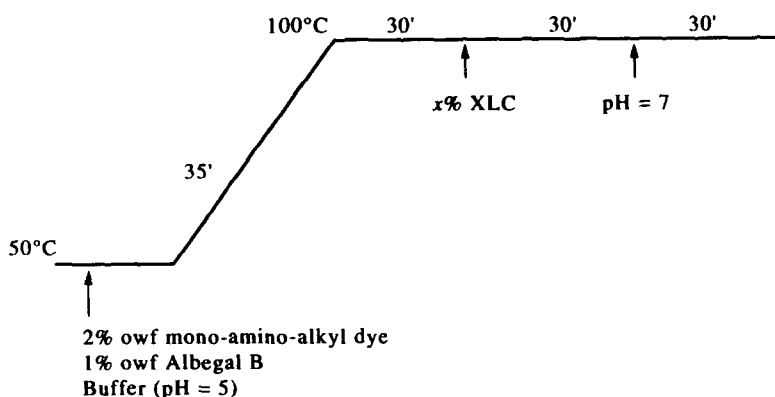
Colour fastness testing: fabrics were tested according to BS standard procedures. Specific tests used were: BS CO2, CO3 and CO4 (1978): colour fastness to washing; BS E04: colour fastness to perspiration.

3 RESULTS AND DISCUSSION

3.1 Effect of XLC concentration on dye fixation

A level of 2% owf mono-amino alkyl dye and different XLC concentrations were used in this study. The dyeing was carried out initially at pH 5 and proceeded according to the dyeing profile shown in Scheme 5. The experimental results are given in Table 1.

The results in Table 1 indicate that dye fixation increases with increasing XLC concentration but reaches its highest value when 3% owf XLC was used. The presence of more XLC in the dyebath might bring about more crosslinks within the wool fibre, which would impair dye penetration into the fibre. It should be noted that under weakly acidic to neutral conditions XLC has good substantivity for wool⁹ and this clearly is important in determining its effectiveness as a dye–fibre crosslinking agent.



Scheme 5. The dyeing profile employed for different XLC concentrations.

The low 'background' fixation (32%) of amino-alkyl dye on wool in the absence of crosslinker is of interest; it is proposed that this reaction occurs due to the normal β -elimination reaction of cystine in wool to give dehydroalanine residues. This is illustrated in Scheme 6.

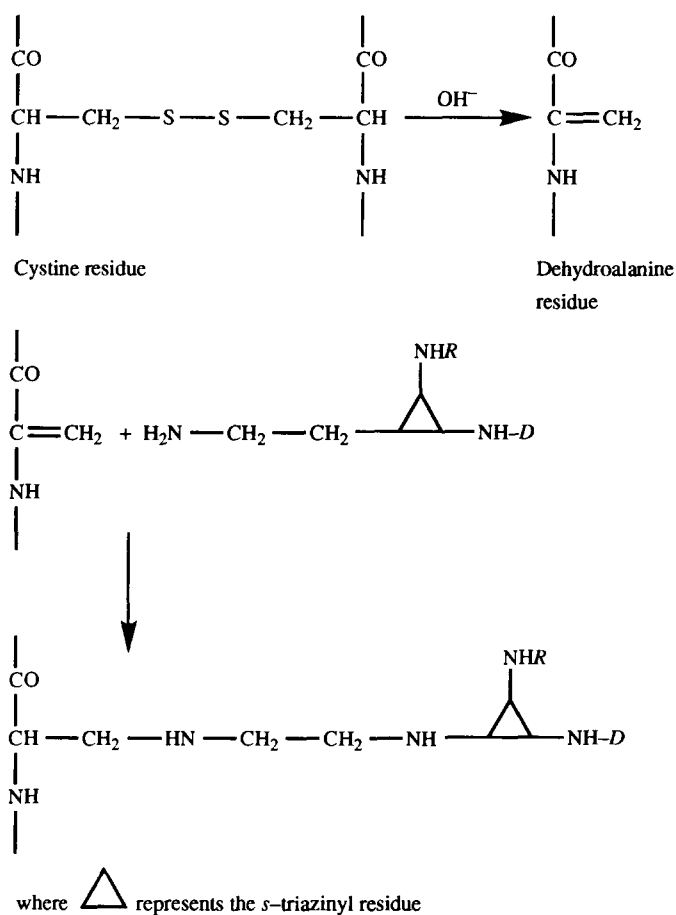
3.2 Effect of duration of fixation time on dye fixation

The wool fibre was dyed with 2% owf mono-amino-alkyl dye, 2% owf or 3% owf XLC respectively, at pH 5. After the dyebath pH value was adjusted from 5 to 7, dyeing was continued for different lengths of time. The dyeing profile is as shown in Scheme 5 and the results are given in Table 2.

From the results in Table 2, it can be clearly seen that the dye fixation was not increased on prolonging the fixation time. Due to the high reactivity of XLC, 30 min is long enough to complete the reaction.

TABLE 1
Effect of XLC Concentration on Dye Fixation

XLC conc. (% owf)	Colour yield (K/S)		$E^0\%$	$F^0\%$
	Before extract	After extract		
0	24.62	7.88	97	32
1	24.14	19.59	92	81
2	24.01	21.53	91	90
3	24.26	23.28	93	96
4	24.52	22.93	93	94



Scheme 6. Fixation of amino-alkyl dyes on wool in the absence of crosslinker.

TABLE 2
Effect of Fixation Time on Dye Fixation

Fixation time (min)	XLC conc. (% owf)	Colour yield (K/S)		E%	F%
		Before extract	After extract		
30	2	24.01	21.53	91	90
60	2	25.89	22.93	97	89
30	3	24.26	23.28	93	96
60	3	25.05	23.64	95	94

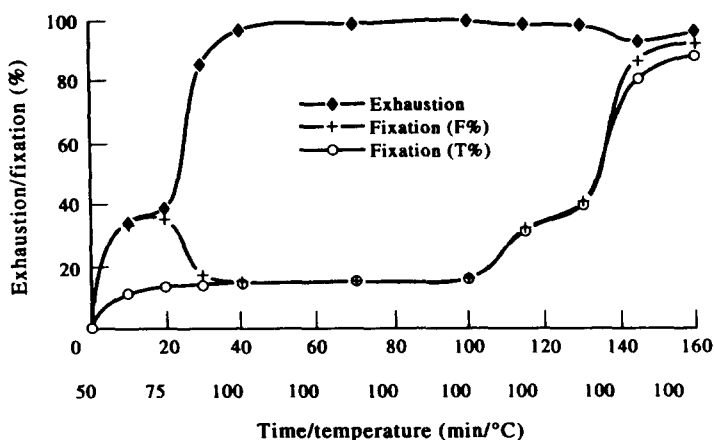


Fig. 1. Exhaustion/fixation curves from the amino-alkyl dye/XLC method.

3.3 Level dyeing of the amino-alkyl dye XLC system on wool

Levels of 1% owf mono-amino-alkyl dye and 3% owf XLC were used in this investigation. The dyeing profile was similar to that described in Scheme 5 except that boiling was for 60 min; 3% XLC was then added, boiling continued a further 30 min and the pH then adjusted to 7.0 and boiling continued a further 30 min. Exhaustion and fixation values, determined at regular intervals, are plotted in Fig. 1.

The big gap between exhaustion and fixation in the early stages of dyeing clearly indicates the potential for level dyeing. Commercially available reactive dyeing systems for wool do not show this large difference between uptake and fixation and are thus only suitable for application in machinery with a high degree of fibre-liquor interaction (e.g. package or soft-flow jet); this new system would thus offer the dyer a real chance to level dye wool in all its forms to reactive dye standards.

3.4 Dyeing fastness

The dyed samples for all the fastness tests were produced using 2% owf of both the mono-amino-alkyl dye and its parent dye (CI Reactive Red 58) according to the dyeing profiles described in Scheme 5. Table 3 shows the wash, perspiration and light fastness of dyeings produced by the amino-alkyl dye plus XLC method compared with the fastnesses achieved by the conventional reactive dyeing method using the unmodified dye. It is seen that with the new dyeing method, perspiration fastness of the dyeings produced is as good as that from dyeings by the conventional reactive dyeing method while the new method produced dyeings of even better wash and light fastness.

TABLE 3
Colour Fastness of Different Dyed Samples

		<i>Amino-alkyl dye plus XLC method</i>	<i>Conventional dyeing method</i>
Wash fastness			
Test standard		CO4	CO3
Effect on pattern		4	3-4
Cotton staining		3	1-2
Wool staining		3	4-5
Perspiration fastness			
Effect on pattern	Base	4-5	4-5
	Acid	4-5	4
Cotton staining	Base	3-4	4
	Acid	4	4-5
Wool staining	Base	4	4-5
	Acid	4-5	5
Light fastness		7	6

4 CONCLUSIONS

Dyeing of wool with improved levelness and good fastness properties has been achieved by using specially prepared amino-alkyl dyes and an asymmetrical cross-linking agent — XLC.

It was found that optimum results were obtained by applying the nucleophilic dye to the wool fibre from a dyebath set at pH 5 and 50°C. This dyebath was raised to the boil, dyeing continued at this temperature for 30-60 min, XLC added and after a further 30 min at the boil the dyebath pH was adjusted to 7 with disodium hydrogen phosphate; another 30 min fixation time completed the dyeing process. The dyeings produced in the presence of crosslinker were fast to pyridine extraction, confirming that the amino-alkyl residue had reacted covalently with XLC which in turn reacted with nucleophilic sites in the fibre.

The large gap between rate of dye fixation and rate of dye exhaustion underlines the potential for level dyeing offered by the nucleophilic dye/substantive crosslinker system.

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