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Reactions of β-Sulphatoethyl Sulphone Crosslinking Agent with Wool. Part V: Effects during Reactive Dyeing

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ABSTRACT

The application of the crosslinking agent 2-chloro-4,6-di(-aminobenzene-4-β-sulphato-ethylsulphone)-1,3,5-s-triazine (XLC) was investigated during the reactive dyeing of wool with Remazol Brilliant Blue R (CI Reactive Blue 19) using the manufacturer's recommended dyeing conditions. Amino acid analysis and tests for crosslinking were used to show that the compound reacted and crosslinked the fibre even more extensively during the reactive dyeing cycle than was previously observed with shorter treatments. The yield of soluble wool gelatins was significantly reduced by the application of both dye and XLC. Exhaustion of the reactive dye was found to be relatively unaffected by the simultaneous application of XLC. Fastness tests indicated that the compound generally had little effect on the fastness ratings of the reactive dyeings. Slight improvements in the wool staining

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ratings were often observed for these dyeings and at high concentrations of XLC and reactive dye the change of shade ratings were found to be adversely affected.

1 INTRODUCTION

The application of the new chemical crosslinking agent, 2-chloro-4,6-di(-aminobenzene-4-β-sulphato-ethylsulphone)-1,3,5-*s*-triazine (XLC), to wool, and the effect of pH on its application has been reported. Stripping tests were performed to help gauge the effectiveness of XLC in this application.[1] The purpose of this present work is to examine the ability of this compound, as claimed by Lewis,[2] to reduce the damage to wool which occurs during the dyeing process. Since one possible mechanism by which damage in dyeing may be reduced lies in the ability of the compound to crosslink the fibre, this process was investigated by the use of various wool solubility and swelling tests.[3] Reactions of the compound within specific morphological regions of the fibre have also been analysed by using wool fractionation procedures to isolate different protein components of the fibre.[4] At the primary level of protein structure, reaction of the compound with specific amino acid residues has been determined by amino acid analysis.[5]

The ability of XLC to reduce the yield of soluble proteins or wool gelatins, and to fix these protein fragments to the fibre, suggests that these effects could impart improved fastness to reactive dyeings. One of the possible causes of the fastness problems associated with reactive dyeings at deep shades was thought to arise from the presence on the fibre surface of dyed, non-fast wool gelatins. It was envisaged that fastness improvements could possibly be achieved by fixing these coloured protein fragments to the fibre, or crosslinking them *in situ*, such that they would no longer be water soluble. Fastness ratings would therefore be improved, while at the same time the integrity and mechanical strength of the wool fibre would be maintained.

This proposed mechanism was examined by incorporating XLC in the dyebath during the reactive dyeing of wool under the manufacturer's recommended dyeing conditions. A range of dyeings from light to heavy shades was produced. The exhaustion of both XLC and dye were monitored, and the extent of crosslinking as well as the yield of soluble wool gelatin following this treatment were determined. Amino acid analysis was carried out, and the effect of XLC on the fastness ratings of the dyeings under several standard fastness tests was also determined.

2 EXPERIMENTAL

This work constitutes an investigation of the effects of XLC on wool during reactive dyeing. Conditions were chosen such that the simultaneous application of XLC and Remazol Brilliant Blue R (FH) (CI Reactive Blue 19) was as close to the manufacturer's recommended procedure for reactive dyeing as was possible under laboratory conditions.[6]

2.1 Application procedure

All dyeings were carried out with 10·0 g wool samples, at a liquor ratio of 30 : 1 using a Jeffries laboratory dyeing machine. The general dyeing cycle used is shown in Fig. 1. An acetic acid–sodium acetate buffer at a concentration of 0·05 M was found to be adequate for holding the dyebath pH constant in the desired range (pH 4·7–5·5) throughout the dyeing cycle. An aliquot (50 ml) of a 0·3 M acetate buffer, after addition of other dyebath components, was diluted to 300 ml to give a buffered dyebath of the appropriate pH and concentration. For all depths of shade, the dyebaths were set with 3% $(NH_4)_2SO_4$ (o.w.w.) and 1% Albegal B (o.w.w.), together with Remazol Brilliant Blue R and XLC as required.

For light depths of shade (1% dye), the dyebath was set at pH 5·5. The hold period at 98°C in the dyeing cycle (Fig. 1) was 45 min, after which the fabrics were removed, rinsed thoroughly with cold water, and air dried at room temperature.

For medium depths of shade (3% dye) the dyebath was set at pH 5·0, with a hold period at 98°C of 70 min, followed by cooling to 80°C in 10 min. At this temperature the fabric was given an alkaline after-treatment

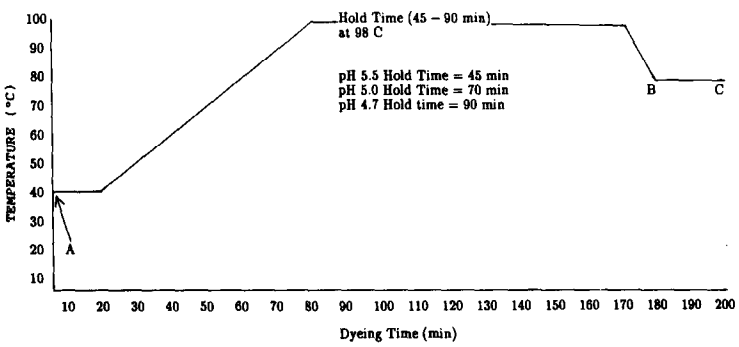

Fig. 1. General dyeing cycle. (A) Set dye bath 1% Albegal B (o.w.w.), 3% $(NH_4)_2SO_4$ (o.w.w.), 0·05 M acetate buffer, dye, XLC sample for XLC determination, then enter wool fabric (10·0 g). (B) Ammonia treatment, addition of ammonia (35% w/w) to pH 8·5. (C) Rinsing of fabric with cold water and drying at room temperature. Dyeing pH = 5·5 for 1% dye, 5·0 for 3% dye and 4·7 for 5 and 10% dye.

by adding ammonia (35% w/w, 7·8 ml) to adjust the dyebath to pH 8·5. After 15 min at 80°C and pH 8·5, the fabric was thoroughly rinsed with water and air dried at room temperature.

Dyeing was carried out at pH 4·7 for heavy depths of shade (5% and 10% dye). The hold time at 98°C was 90 min, followed by an alkaline after-treatment with ammonium hydroxide at pH 8·5 (5% shade required 10·6 ml and 10% required 13·6 ml of 35% ammonia), rinsing and drying at room temperature.

The following dyeings were produced:

(i) Dye alone at 1% (pH 5·5), 3% (pH 5·0), 5% and 10% (pH 4·7);
(ii) XLC at 1%, 3%, 5% and 10% for dyeings at 1% dye (pH 5·5), 3% dye (pH 5·0), 5% dye (pH 4·7) and 10% dye (pH 4·7);
(iii) XLC alone at 1%, 3%, 5% and 10%, for each of the three dyeings cycles, at pH 5·5, 5·0 and 4·7.

2.2 Measurement of exhaustion

The exhaustion of XLC was measured by sampling the dyebath before the wool was entered, and just before the alkaline after-treatment process. Samples were treated as detailed in Section 2.1 and XLC determined by HPLC.

The exhaustion of Remazol Brilliant Blue R was determined by measurements of optical density using a Philips Model PU8820 spectrophotometer. The residual dyebath, after cooling overnight, was made up to a volume of 500 ml. A sample of this was then filtered through a disposable 45 μm filter (Gellman), to remove insoluble XLC which precipitates during the alkaline after-treatment. The absorbance of the clear filtrate was then measured using the following formula:

$$\text{Percentage exhaustion} = \frac{[\text{Initial amount of dye} - (0{\cdot}5\ A/\varepsilon l)]}{\text{Initial amount of dye}} \times 100 \quad (1)$$

where A is absorbance of dyebath solution; l is path length (cm); ε is extinction coefficient (l g^{-1} cm^{-1}) at 590 nm and 0·02 g l^{-1} dye solution; and initial amount of dye (g) = % shade of dyeing × 0·1.

2.3 Fastness tests

Alkaline perspiration fastness (TM174), severe washing fastness (TM193), and wet and dry rubbing fastness (TM165) tests were carried out on all dyed samples according to the standard IWS test method. (IWS, Ilkley, 1988, private communication).

3 RESULTS

3.1 The application and effects of XLC during reactive dyeing

The simultaneous application to wool of XLC and Remazol Brilliant Blue R was studied. The latter is a monofunctional reactive dye with the same β-sulphatoethyl sulphone reactive groups as present in XLC. The exhaustion behaviour of both compounds was monitored, using a range of concentrations and under conditions chosen in the laboratory to be as close as possible to the industrial dyeing process. The crosslinking abilities of XLC, and its effects on the subsequent yield and composition of the wool gelatins from the dyeings, were examined. The fastness ratings of these dyeings were determined and the effects of XLC assessed.

3.2 Studies on the simultaneous exhaustion of XLC and reactive dye onto wool

The effects of reactive dye concentration on the exhaustion of XLC onto wool, and vice versa, were studied when Remazol Brilliant Blue R and XLC were applied simultaneously to wool. The degree of exhaustion of both reactive dye and XLC were obtained following the manufacturers' recommended dyeing method and shown in Table 1. These data show that, when applied together, the final percentage exhaustion of the reactive dye was substantially greater than that of XLC throughout the range of concentrations and pH studied. The two compounds exhibited competitive substantivity during this application process. For 1% and 3% dye, increasing the concentration of XLC reduced the exhaustion of the dye to a minor extent. The results for 5% and 10% dye, applied at pH 4·7, showed exhaustion values for the dye that were lower in the absence of XLC than in its presence. The differences were quite significant, approximately 6 percentage units at 5% dye and 10 units at 10% dye. Overall there was a slight fall in dye exhaustion with XLC as the dye concentration was raised.

The dramatic effect of concentration (and pH) on the dye, in conjunction with the increase in dye concentration, caused the foregoing effect. Since different buffer pH values and dyeing cycles were used for the various dye concentrations, they may not be compared directly, but one would expect the exhaustion of the dye to fall with increasing amounts of XLC at the very high dye concentrations used. The exhaustion of the reactive dye was, in general, not adversely affected by the inclusion of XLC in the dyebath and adequate exhaustions, usually greater than 85%, were achieved for up to 10% dye.

The presence of dye had a much greater effect on the exhaustion of XLC than the latter had on that of dye; 1% dye had little effect, but as

TABLE 1
Exhaustion Data for the Simultaneous Application of XLC and Remazol Brilliant Blue R to Wool

Dye applied (%, o.w.w.)	*XLC applied (%, o.w.w.)*	*Dyeing pH*	*Dyeing time at 98°C*	*Exhaustion of XLC (%)*	*Exhaustion of dye (%)*
0	1	5·5	45	96·9	
	3			90·1	
	5			89·8	
	10			79·3	
1	0	5·5	45		97·7
	1			94·3	97·5
	3			91·8	95·8
	5			85·8	94·1
	10			82·2	88·1
0	1	5·0	70	98·9	
	3			96·0	
	5			92·4	
	10			83·6	
3	0	5·0	70		95·8
	1			81·6	94·9
	3			85·8	93·2
	5			79·9	91·5
	10			80·5	93·2
0	1	4·7	90	96·9	
	3			96·9	
	5			93·8	
	10			85·8	
5	0	4·7	90		86·4
	1			78·2	92·4
	3			86·7	91·8
	5			84·7	91·8
	10			71·4	92·1
10	0	4·7	90		75·1
	1			72·5	84·7
	3			72·2	84·7
	5			66·9	83·6
	10			65·7	86·7

the concentration of dye was further increased its retarding action on the exhaustion of XLC became more pronounced. The presence of 10% dye depressed the exhaustion of XLC by up to 27 percentage units. However, considering the total weight of the two compounds being taken up by the fibre, a reasonable exhaustion level for XLC of 66–73% was still achieved at this high concentration of dye.

The percentage exhaustion values observed for Remazol Brilliant Blue R in this work did not necessarily show that the dye was more rapidly taken up by wool than XLC, as the dye was a commercial product. As such, it would have been diluted with salts, whereas XLC was a pure compound. The absolute concentration of dye was therefore likely to have been much lower than XLC for equal percentage values (o.w.w.), as the two compounds had similar molecular weights (dye = 627, XLC = 750). Due to these uncertainties about the molar concentration of dye, the relative uptake of the two compounds could not be assessed. The work did, however, demonstrate that reactive dyeings to deep shades could be attained during the simultaneous application of XLC, without there being a detrimental effect on dye uptake.

3.3 The crosslinking effects of XLC during the reactive dyeing of wool

The performic acid/ammonia solubility test and the swelling behaviour of wool in formic acid have been used to assess the crosslinking ability of XLC when applied during the reactive dyeing cycle.[3] The solubility and swelling properties of the wool samples treated with XLC and reactive dye at pH 5·5, pH 5·0 and pH 4·7 are shown in Figs 2–7.

For each pH and concentration of dye, the performic acid/ammonia solubilities decreased considerably, and the swelling factor $V_c^{5/3}$ increased with increasing XLC applied to the wool. These data gave clear evidence

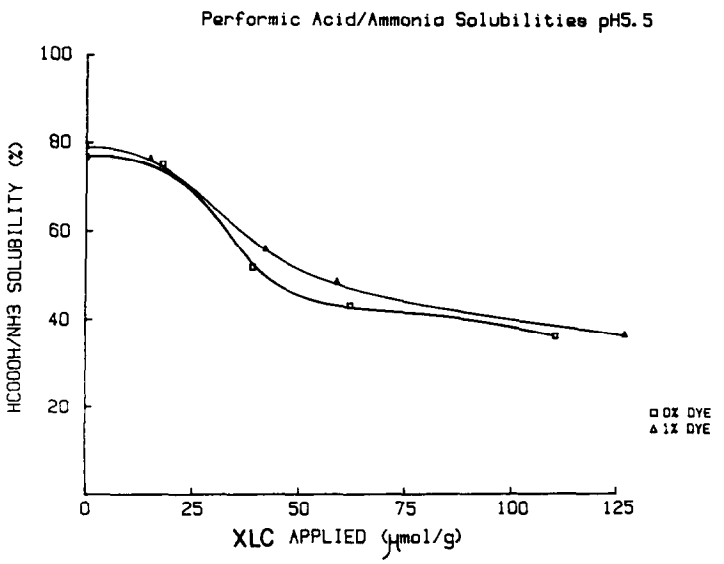

Fig. 2. The solubility properties of wool treated with XLC and reactive dye at pH 5·5.

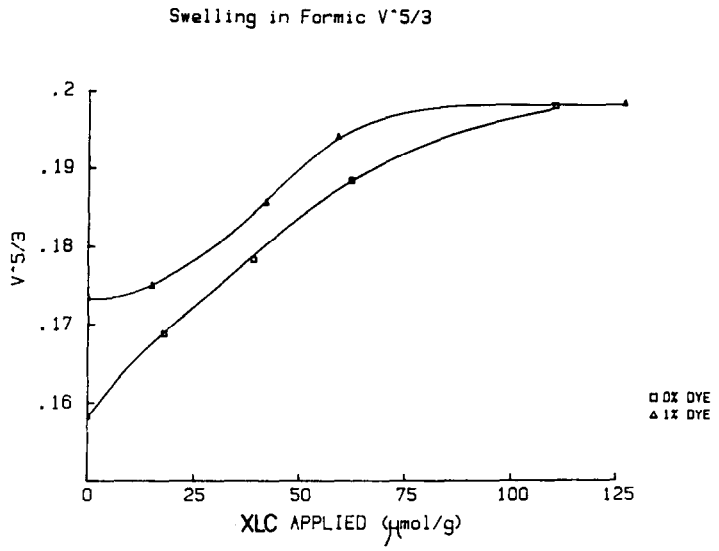

Fig. 3. The swelling properties of wool treated with XLC and reactive dye at pH 5·5.

that the compound was crosslinking the fibre during the reactive dyeing process. When the results of the undyed samples were compared with those found previously,[3] it was evident that crosslinking was more extensive using the reactive dyeing cycle and the longer reaction time, than when using the short application time used in the foregoing sections. For example, the pH 5 results may be compared directly: for 10% XLC

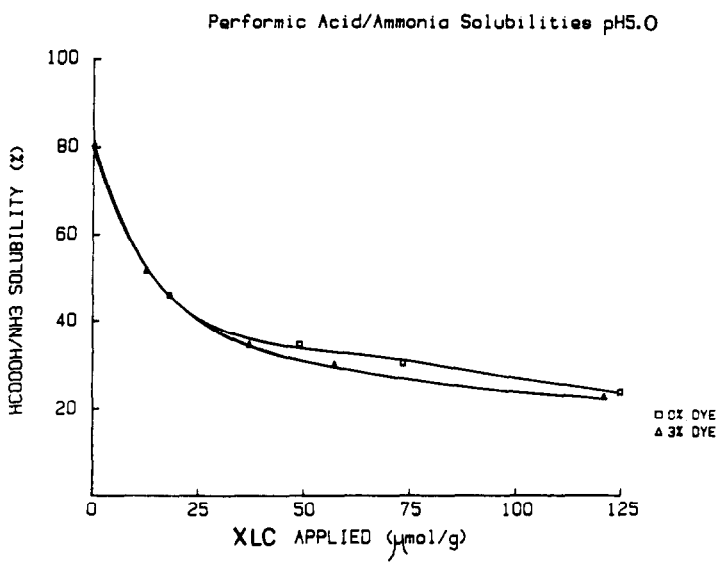

Fig. 4. The solubility properties of wool treated with XLC and reactive dye at pH 5·0.

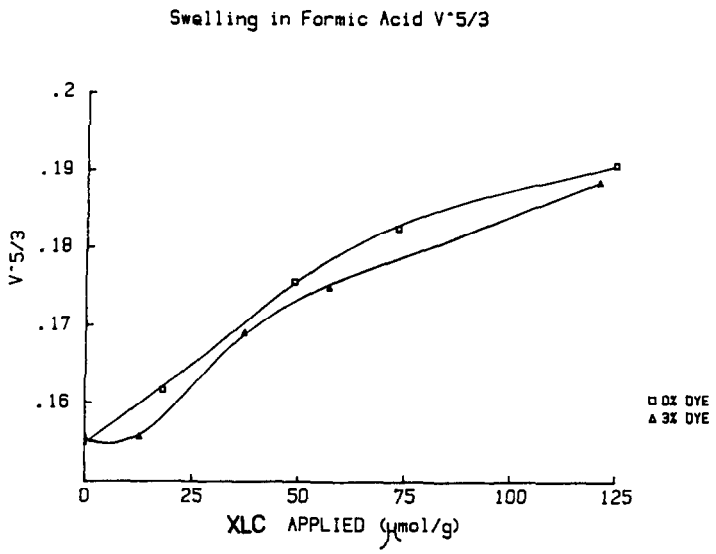

Fig. 5. The swelling properties of wool treated with XLC and reactive dye at pH 5·0.

(o.w.w.), using the reactive dyeing cycle, 125 μmol XLC g^{-1} of wool was applied and the subsequent PA/NH_3 solubility was measured as 23·6% (cf. Fig. 4); for the short application time, 104 μmol XLC g^{-1} was applied and the PA/NH_3 solubility was 37·6% (Ref. 3). It would appear that the longer cycle permitted greater exhaustion and reaction of the compound, which increased the degree of fibre crosslinking. It is also

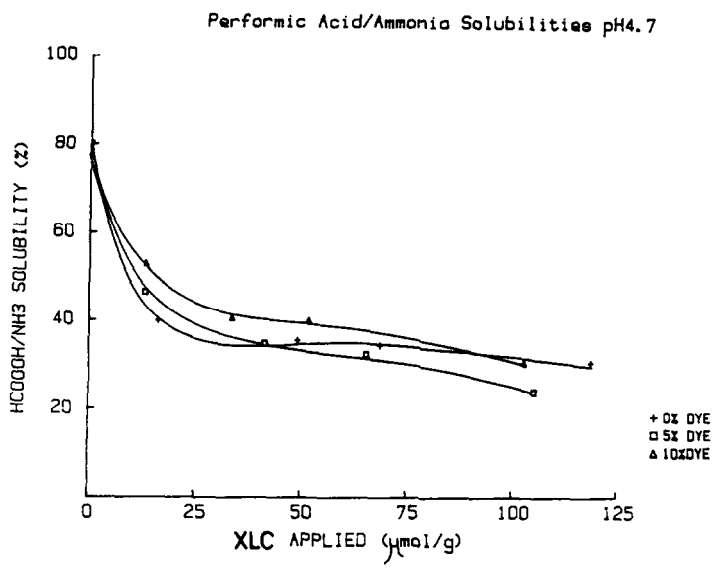

Fig. 6. The solubility properties of wool treated with XLC and reactive dye at pH 4·7.

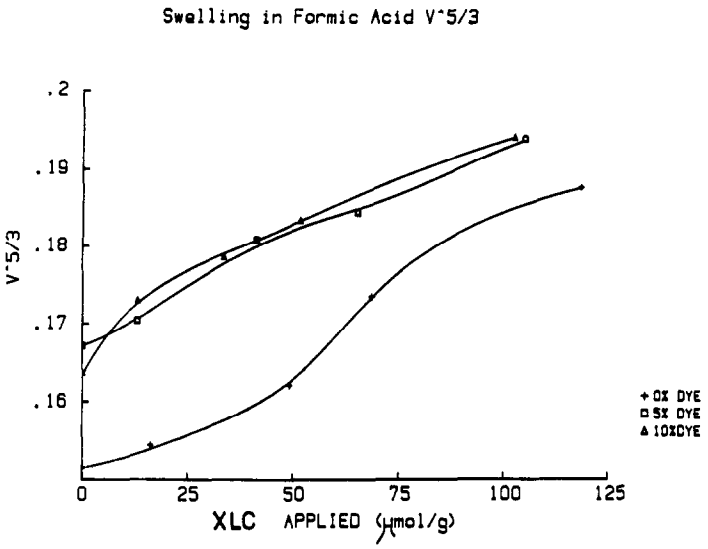

Fig. 7. The swelling properties of wool treated with XLC and reactive dye at pH 4·7.

possible that the alkaline after-treatment used at the end of the reactive dyeing cycle may have promoted a greater reaction of the compound with the fibre.

The application of dye alone to the fibre increased the solubility of the wool relative to the blank dyed controls. This change was only small (maximum of 3·1 percentage units), but did indicate that the monofunctional reaction of the dye did not show any apparent crosslinking effect with this test, and demonstrated the validity of the test for detecting crosslinking. For concentrations up to 5% (o.w.w.) the dye did not impede the crosslinking effects of XLC, and a substantial fall in PA/NH_3 solubility was observed with increasing XLC applied at pH 5·5, pH 5·0 and pH 4·7 (cf. Figs. 2, 4 and 6 respectively). However, with low concentrations of XLC and 10% dye, the reduction in solubility was not as great as in the absence of the dye (cf. Fig. 6). It is possible that the monofunctional reaction of the dye blocked potential reaction sites (Lys or His) close to where XLC would be initially attached, and therefore reduced to some extent the probability of crosslinking. This effect would be expected to be more important as the dye concentration increased. The solubility of these samples (10% dye) was still lower than those of pH 5 with the short application time,[3] and the compound was clearly still able to crosslink the fibre despite the presence of 10% dye.

From Figs 3, 5 and 7, it may be seen that the formic acid swelling of wool was restricted to an increasing extent as higher concentrations of dye were applied. This clearly demonstrated the sensitivity of this test to

TABLE 2
Amino Acid Composition of Wool Treated with XLC at pH 4·7 using Reactive Dyeing Cycle with 0% Dye

Amino acid residue	*Blank treated wool*		*XLC applied (μmol g⁻¹), pH 4·7, 0% dye*					
			16		*69*		*119*	
	(μmol g⁻¹)	*(mol %)*	*(μmol g⁻¹)*	*(mol %)*	*(μmol g⁻¹)*	*(mol %)*	*(μmol g⁻¹)*	*(mol %)*
Asp	595	6·28	582	6·27	512	6·50	441	6·40
Glu	1122	11·85	1123	12·09	988	12·54	850	12·33
Ser	968	10·22	950	10·24	830	10·54	719	10·44
Gly	795	8·40	787	8·48	675	8·57	581	8·44
His	70	0·74	66	0·71	29	0·37	23	0·33
Arg	593	6·26	590	6·35	453	5·75	398	5·78
Thr	539	5·69	526	5·67	457	5·80	407	5·91
Ala	517	5·46	515	5·55	447	5·67	376	5·45
Pro	631	6·66	624	6·72	543	6·90	486	7·05
Tyr	345	3·64	346	3·72	275	3·49	231	3·35
Val	522	5·52	516	5·55	441	5·59	336	5·31
Met	40	0·42	40	0·43	38	0·48	36	0·53
1/2 Cys	1185	12·51	1030	11·09	1042	13·23	1071	15·55
Ile	282	2·98	281	3·03	220	2·79	178	2·59
Leu	746	7·88	777	8·37	579	7·34	457	6·64
Phe	260	2·75	285	3·07	214	2·72	180	2·61
Lys	260	2·75	248	2·68	135	1·72	89	1·29

Values given in mol g^{-1} and mol % ± 8%.

a monofunctional type reaction. The swelling was further restricted for all pH values by application of XLC, and this restriction was much greater in magnitude than the effect produced by the dye. Although this test could not be used in isolation to prove crosslinking, in conjunction with the results of the performic acid/ammonia solubility tests these effects indicate a crosslinking reaction of the fibre by XLC.

3.4 Amino acid analysis of wool treated with reactive dye and XLC

The results for the amino acid analyses of wool samples treated with XLC and Remazol Brilliant Blue R at pH 4·7 are given in Tables 2 and 3. The concentration of cystine in the dyed samples was not determined since the blue colour of the dye would interfere with the colorimetric assay of this amino acid. The partial amino acid compositions of the dyed samples are therefore reported in μmol g^{-1}, and those of the undyed samples in both μmol g^{-1} and mol %.

TABLE 3
Amino Acid Composition of Wool Treated with XLC at pH 4·7 with 10% Remazol Brilliant Blue R

Amino acid residue	*XLC applied (μmol g^{-1}), pH 4·7, 10% dye*		
	0	*13*	*52*
Asp	520	559	516
Glu	997	1082	1008
Ser	859	930	869
Gly	686	736	693
His	32	33	27
Arg	495	545	474
Thr	469	529	498
Ala	454	485	453
Pro	585	632	606
Tyr	300	322	281
Val	453	491	442
Met	35	38	35
Ile	242	257	227
Leu	640	683	605
Phe	234	261	225
Lys	191	201	137

1/2 Cys was not determined.

The same general conclusions may be drawn from these data as were reached previously for samples treated at pH 5 and 6 with a shorter application time. For the undyed samples treated with XLC at pH 4·7 (cf. Table 2), there was no significant change in the mol% of the majority of the amino acids, except for histidine and lysine. The latter two residues were modified to a greater extent at pH 4·7 with the reactive dyeing cycle than was previously observed for either pH 5 or 6. For example, when 10% XLC was applied at pH 4·7, 55·4% of His and 53·1% of Lys were modified, compared with 35·8% of His and 46·6% of Lys at pH 5 and 46·8% of His and 51·6% of Lys at pH 6. The reason for this difference could be attributed to the incorporation of more crosslinker with the longer application time; 119 μmol XLC g^{-1} was applied at pH 4·7, 104 μmol XLC g^{-1} at pH 5 and 118 μmol XLC g^{-1} at pH 6. It is interesting to compare the functionalities for these three different samples: for pH 5 the functionality was 1·51; for pH 6, 1·48; and for pH 4·7, 1·49. Comparison of the total lysine and histidine residues reacted (functionality times, μmol XLC applied g^{-1}) gave 157 μmol g^{-1} for pH 5; 175 μmol g^{-1} for pH 6; and 177 μmol g^{-1} for pH 4·7. The results of the performic acid/ammonia solubility test for

these samples almost fell in the anticipated order on the basis of lysine and histidine modified: 37·6% for pH 5; 25·3% for pH 6; and 30·5% for pH 4·7. The pH 5 sample had the highest solubility and lowest quantity of basic residues modified, the pH 6 and pH 4·7 samples had virtually the same number of basic residues modified, but the pH 6 sample had a lower solubility. Other factors may be involved in the lower solubility of the pH 6 sample, but within the limits of the accuracy of amino acid analysis, the extent of modification of lysine and histidine residues would appear to account well for the differences in solubility of the treated samples.

Another interesting result for pH 4·7 was the relative degree of reaction of lysine and histidine. Smith *et al.*[5] predicted that histidine should be the favoured reaction site at the more acid pH values of around 4, since it has a much lower pK_a than lysine. Thus, at pH 4·7, better reaction with the imidazole group of histidine was found, in contrast to the higher pH values where a greater percentage modification of the ε-amino group of lysine was observed.

For the samples treated with Remazol Brilliant Blue R (Table 2), a substantial modification of both lysine and histidine was observed for 10% dye (o.w.w.). These residues were further modified by reaction with XLC, the reaction being mainly with the remaining lysine, and only to a minor extent with histidine. It would appear that the first approximately 50% of histidine residues reacted easily, but the next 50% seemed to be less readily modified. This suggests that these histidine residues were less accessible to XLC, and emphasised the point that the morphology of the wool fibre, or the chemical environment in which the residues occur, also affect the reaction of the amino acid residues in wool with potential crosslinking agents.

3.5 Wool gelatin analysis of wool treated with reactive dye and XLC

Wool gelatins were extracted, using the method previously outlined,[5] for fixed times of 2, 4 and 6 h from wool previously treated with XLC and Remazol Brilliant Blue R at pH 4·7 using the reactive dyeing cycle. The effects of these two compounds on the total yield of wool gelatins after these times are shown in Figs 8 and 9. It is clear from Fig. 8 that the yield of wool gelatin was significantly reduced by the presence of 5% and 10% XLC in the dyebath. The yield for 6 h at 10% XLC represented only 19% of the yield from the blank treated control. The compound appeared to be effective at a concentration of 1% (o.w.w.).

It is evident from Fig. 9 that Remazol Brilliant Blue R was also capable of reducing the yield of wool gelatin; for 10% dye, the yield after 6 h represented a minimum of 52% relative to the blank control. This result

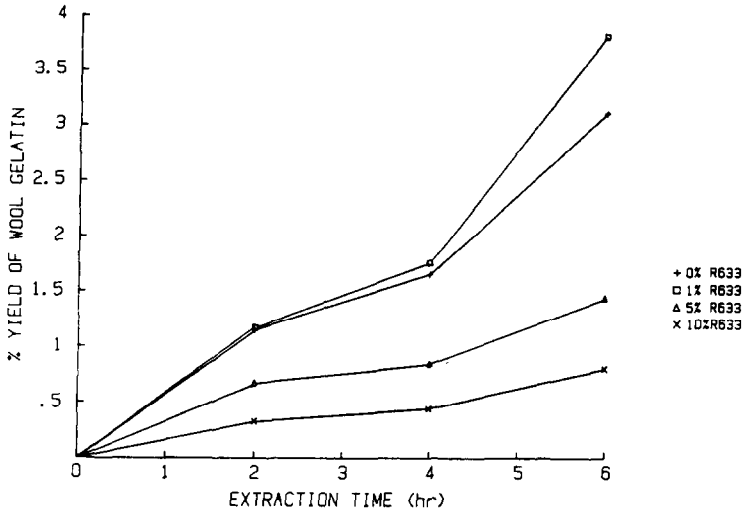

Fig. 8. Wool gelatins extracted from wool treated with XLC at pH 4·7.

is in agreement with the findings of other workers,[7,8] who found that a crosslinking reaction was not a requirement for stabilisation of the non-keratinous proteins or wool gelatins. When XLC was included during the reactive dyeing process, its effect was to reduce still further the subsequent yield of gelatins; for 10% dye and 5% XLC, a minimum yield of 17% was measured for the 6 h sample. A concentration of 1% XLC caused only a small drop in the yield of gelatin with the 10% dyeing.

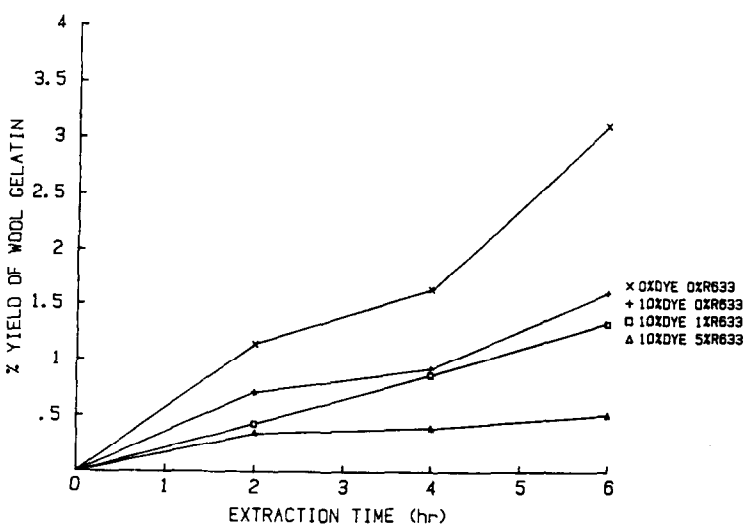

Fig. 9. Wool gelatins extracted from wool treated with XLC and reactive dye at pH 4·7.

TABLE 4
Yield and Amino Acid Composition of Wool Gelatins Extracted After 2 h from Wool Treated with XLC and Remazol Brilliant Blue R at pH 4·7

Amino acid residue	*0% Dye, pH 4·7 XLC applied (μmol g⁻¹)*				*10% Dye, pH 4·7 XLC applied (μmol g⁻¹)*		
	0	*16*	*69*	*119*	*0*	*13*	*52*
Asp	10·2	10·2	9·5	9·6	10·5	10·3	10·1
Glu	12·2	12·2	13·4	15·6	13·7	12·6	14·1
Ser	7·1	6·8	6·7	6·9	5·7	8·0	6·8
Gly	11·8	11·9	13·0	13·2	11·5	12·3	12·2
His	1·8	0·9	0·9	0·7	1·2	0·9	0·8
Arg	7·4	7·2	7·2	6·7	6·7	6·7	6·6
Thr	4·5	4·5	4·3	4·7	4·3	4·8	4·3
Ala	6·6	6·3	5·7	5·5	6·5	6·1	5·5
Pro	7·5	7·9	8·4	8·5	8·4	8·0	8·6
Tyr	4·9	4·9	6·0	5·9	4·9	4·3	5·6
Val	5·3	5·7	5·3	5·5	5·6	5·7	5·2
Met	2·8	3·0	2·7	2·4	2·8	2·4	2·3
1/2 Cys	0·4	0·5	0·7	0·4	1·9	2·5	3·4
Ile	3·2	3·3	3·1	3·1	3·4	3·3	2·9
Leu	7·6	7·9	7·5	6·8	7·6	7·1	6·9
Phe	3·7	4·4	4·3	3·7	3·3	3·4	3·5
Lys	3·1	2·5	1·4	0·9	2·1	1·6	1·1
Percentage yield	1·15	1·17	0·67	0·33	0·72	0·43	0·35

Amino acid concentrations are given in mol %.
Percentage yields of wool gelatin are given as a % of the dry weight of the wool.
Wool gelatins were extracted at pH 2, 100°C.

The amino acid compositions of the wool gelatins extracted at 2, 4 and 6 h are given in Tables 4–6 respectively. For the gelatins extracted after 2 h (Table 4), the changes that occurred with increasing XLC applied were similar to those observed earlier. Lysine and histidine fell with increasing XLC, and there was a rise in the mol % value of glutamic acid. Apart from a slight rise in the mol % value of glycine, the other amino acids did not change greatly in relative concentration. These same observations were also true for the gelatin extracted from wool treated with 10% dye, as well as for samples treated with dye and XLC.

Comparison of the 4 and 6 h compositions with those of the 2 h samples showed that the relative concentration of lysine increased with time for both untreated, crosslinked and reactively dyed wool gelatins. Also, the glutamic acid mol % values for all samples dropped at 6 h to

TABLE 5
Yield and Amino Acid Composition of Wool Gelatins Extracted After 4 h from Wool Treated with XLC and Remazol Brilliant Blue R at pH 4·7

Amino acid residue	*0% Dye, pH 4·7 XLC applied (μmol g⁻¹)*				*10% Dye, pH 4·7 XLC applied (μmol g⁻¹)*		
	0	*16*	*69*	*119*	*0*	*13*	*52*
Asp	9·9	9·4	9·2	9·1	10·8	9·6	9·1
Glu	12·7	10·7	10·3	11·6	12·1	10·9	12·2
Ser	7·2	7·7	7·9	7·2	6·7	6·8	8·2
Gly	11·0	11·7	11·4	11·2	10·1	10·7	11·7
His	1·4	1·7	0·7	0·3	0·8	0·9	0·9
Arg	6·7	7·5	7·2	6·2	7·4	6·7	8·4
Thr	3·8	4·7	4·7	4·4	4·0	4·5	4·7
Ala	5·9	5·7	5·0	4·3	5·5	5·4	6·5
Pro	5·8	8·1	9·9	9·7	7·0	9·2	6·4
Tyr	5·2	5·5	5·6	5·7	5·3	5·6	6·0
Val	6·1	5·7	5·8	5·7	6·2	6·3	6·5
Met	3·1	3·1	3·2	3·3	3·2	3·4	0·9
1/2 Cys	1·4	0·6	2·6	6·3	2·6	3·5	0·8
Ile	3·7	3·3	3·1	2·9	3·7	3·3	3·3
Leu	8·5	8·2	8·0	7·2	8·7	7·9	9·0
Phe	3·9	4·4	4·4	4·0	3·9	4·0	3·6
Lys	3·7	2·1	1·1	0·8	2·1	1·4	1·8
Percentage yield	1·65	1·76	0·85	0·44	0·93	0·87	0·40

Amino acid concentrations are given in mol %.
Percentage yields of wool gelatin are given as a % of the dry weight of the wool.
Wool gelatins were extracted at pH 2, 100°C.

values that were comparable with the untreated wool gelatins. This effect is consistent with the mechanism proposed to explain the high glutamic acid mol % values observed for wool gelatin samples from wool treated with high concentrations of XLC and extracted for 1 h only.[5] This proposal suggested that wool gelatin proteins high in glutamic acid or glutamine reacted poorly with XLC and were stabilised to a minor extent by the compound, whereas those proteins deficient in these residues and higher in histidine and lysine content were greatly stabilised. Consequently, the former group of proteins was still extracted even at high concentrations of XLC, and with the low yields of proteins after a 1 h extraction the relative concentration of glutamic acid in the wool gelatin was high. On this basis, it could therefore be expected that as the time of extraction increased and the total yield of wool gelatin became greater, then the relative concentration of glutamic acid would fall, due

TABLE 6
Yield and Amino Acid Composition of Wool Gelatins Extracted After 6 h from Wool Treated with XLC and Remazol Brilliant Blue R at pH 4·7

Amino acid residue	*0% Dye, pH 4·7 XLC applied (μmol g⁻¹)*				*10% Dye, pH 4·7 XLC applied (μmol g⁻¹)*		
	0	*16*	*69*	*119*	*0*	*13*	*52*
Asp	8·3	7·9	8·4	9·8	9·8	8·7	9·9
Glu	12·0	12·8	11·9	12·1	12·7	12·3	11·1
Ser	7·8	8·8	8·6	8·2	8·0	8·8	7·4
Gly	10·3	10·6	11·5	11·9	10·1	10·7	10·5
His	1·5	1·2	0·8	0·6	1·1	1·0	0·4
Arg	7·8	8·1	8·8	9·2	8·1	8·0	6·8
Thr	4·6	5·0	4·7	4·4	4·9	5·2	4·4
Ala	7·0	6·8	6·2	6·3	7·3	6·8	5·3
Pro	5·4	5·8	6·8	6·6	6·1	6·0	8·8
Tyr	5·0	4·9	5·5	5·6	4·8	5·2	5·5
Val	6·1	5·8	6·3	6·6	6·4	6·3	6·4
Met	1·3	0·6	1·0	1·2	0·9	1·2	3·3
1/2 Cys	1·0	1·1	1·2	0·2	0·6	0·8	4·6
Ile	4·1	3·4	3·2	3·3	3·7	3·5	3·2
Leu	9·3	9·4	8·8	8·6	9·2	9·0	7·7
Phe	4·1	4·4	4·2	4·0	8·7	3·9	3·4
Lys	4·6	3·6	2·2	1·6	3·5	2·7	1·3
Percentage yield	3·13	3·83	1·45	0·81	1·62	1·34	0·52

Amino acid concentrations are given in mol %.
Percentage yields of wool gelatin are given as a % of the dry weight of the wool.
Wool gelatins were extracted at pH 2, 100°C.

to dilution of the high glutamic acid proteins with proteins lower in glutamic acid which were extracted only at the longer times. Such a fall was observed in the present work.

If the composition of the wool gelatin extracted in 1 h from wool treated at pH 5 with 104 μmol XLC g^{-1} (Ref. 5) is compared with the results in Tables 4–6, evidence for the foregoing mechanism may be observed. The mol % value for Glu with 104 μmol XLC g^{-1} at pH 5 extracted for 1 h was 24·9%; at 4 h it was 11·6%; and at 6 h, 12·0%. Thus, in general, for untreated wool, the mol % Glu value for the gelatins remained constant with extraction time, whereas with crosslinked wool samples the mol % Glu was higher at short extraction times due to stabilisation of other Glu deficient wool gelatins, and this value returned to a normal level at longer extraction times due to extraction of other Glu deficient wool gelatins.

Other amino acid which changed significantly in relative concentration with time were proline, glycine, serine, aspartic acid and arginine. These changes suggested that different types of proteins were being extracted with the longer times. With the 1 h extraction, Baumann[7] has stated that, specifically, the cell membrane complex is extracted. With the longer extraction times, other non-keratinous proteins were being solubilised and these came from different morphological regions of the fibre. These processes produced changes in the amino acid composition of the wool gelatin with time, in contrast to the relative constancy (most of the amino acids unchanged in absolute concentration) of composition within a fixed extraction time, despite treatment with a crosslinker.

3.6 The effects of XLC on the fastness properties of wool dyed with Remazol Brilliant Blue R

The results of wool gelatin analysis on the dyed samples demonstrated that XLC and Remazol Brilliant Blue R together stabilised the non-keratinous proteins, and substantially reduced the yield of soluble wool gelatin. The fastness properties of the reactive dyeings were studied to determine whether or not the reduction in the yield of wool gelatins was translated into tangible improvements in the fastness properties of these reactive dyeings.

Three fastness tests were used and the testing was carried out by IWS (IWS, Ilkley, 1988, private communication). The alkaline perspiration test (TM174) determines the resistance of the colour to transfer in a damp alkaline environment and indicates the degree of cross-staining onto white wool and cotton adjacent fabrics. The test is presumed to reflect the conditions that might occur at the end of the washing cycle in an unattended automatic washing machine, where the items are left in contact for prolonged periods of time. The second test used was a severe washing test (TM193), which is used to predict the fastness of the colour to repeated washing cycles using a heavy duty detergent. The third test assessed the wet and dry rubbing fastness (TM165) of the dyeings, by showing the degree of colour staining onto white cotton (which is used as the rubbing material).

The results of the three fastness tests on reactive dyeings co-applied with 1–10% XLC are given in Tables 7–9. With test TM174, for the 1% dyeings, XLC gave improvements of half a point for the staining of wool at 1% and 3% XLC; however, a fall of half a point in change of shade was found for 5% and 10% XLC. With test TM193, again losses of up to half a point for change of shade and wool staining were found for 5% and 10% XLC. The wet and dry rubbing fastnesses (test TM165) for

TABLE 7
TM174 Alkaline Perspiration Fastness Test Results

Dye applied (%, o.w.w.)	*XLC applied (%, o.w.w.)*	*Dyeing pH*	*Change of shade*	*Wool staining*	*Cotton staining*
1	0	5·5	4–5	3–4	4–5
	1		4–5	4	4–5
	3		4–5	4	4–5
	5		4	3–4	4–5
	10		4	3–4	4–5
3	0	5·0	4–5	3–4	4
	1		4–5	4	4–5
	3		4–5	4	4–5
	5		4–5	4	4–5
	10		4–5	4	4–5
5	0	4·7	4–5	3	4
	1		4–5	3	4
	3		4	3–4	4
	5		4–5	3–4	4
	10		4	3–4	4
10	0	4·7	4	2–3	3–4
	1		3–4	2–3	3
	3		3–4	2–3	3
	5		4	2–3	3
	10		3–4	2–3	3

the 1% dyeings were very good, XLC having no effect on the resultant ratings.

Of all the shades studied, the 3% dyeings at pH 5·0 showed the best improvements in fastness ratings on addition of XLC, but these improvements were still only marginal. With TM174, the change of shade values were very good and XLC gave improvements of half a point for both wool and cotton staining when applied at 1–10%. With TM193, the change of shade ratings were improved by half a point for 3% and 5% XLC and between 0·5 and 1 point at 10% XLC. Wool staining was improved from 4 to an excellent 4–5 rating for 3–10% XLC. Cotton staining was excellent, at 4–5 for all the 3% dyeings with this test (TM193). For TM165, dry rub fastness was good but dropped from 5 to 4–5 for the XLC treated dyeings; wet rub fastness was improved at 1% but dropped by half a point with 10% XLC.

For the 5% dyeings at pH 4·7, improvements of half a point in the wool staining of TM174 at 3–10% XLC were found. The change

TABLE 8
TM193 Severe Washing Fastness Test Results

Dye applied (%, o.w.w.)	*XLC applied (%, o.w.w.)*	*Dyeing pH*	*Change of shade*	*Wool staining*	*Cotton staining*
1	0	5·5	3	4	4–5
	1		3	4	4–5
	3		2–3	4	5
	5		3–4	3–4	4–5
	10		3	3–4	4–5
3	0	5·0	3	4	4–5
	1		3	4	4–5
	3		3–4	4–5	4–5
	5		3–4	4–5	4–5
	10		4/3–4	4–5	4–5
5	0	4·7	3–4	3–4	4–5
	1		2–3	3–4	4–5
	3		3	3–4	4–5
	5		2–3	4	4–5
	10		3	4	4–5
10	0	4·7	3–4	3	4
	1		3	3	4
	3		2–3	3	4
	5		3	3–4	4
	10		3	3–4	4

in shade ratings were still good for 5% dye, but a loss of half a point at 3% and 10% XLC was found with this test. With TM193, improvements of half a point in wool staining were again found at 5% and 10% XLC; however, severe losses of dye were suggested by the reductions of 0·5 to 1 point in change of shade ratings. Slight falls also occurred with the wet rubbing fastness ratings for the 5% and 10% XLC treated dyeings.

For the 10% dyeings, only wool staining in TM193 was improved, otherwise the compound only worsened the fastness ratings or caused no change.

Overall, XLC only gave marginal improvements in the fastness ratings. Wool staining was often improved, and this may have been caused by the fixation of dyed wool gelatins. For the deep shades, the colour losses caused by XLC addition were unacceptable. The only set of samples that showed general improvements were the 3% dyeings at pH 5, fastness ratings for which were good for all the tests.

TABLE 9
TM165 Wet and Dry Rubbing Fastness Test Results

Dye applied (%, o.w.w.)	*XLC applied (%, o.w.w.)*	*Dyeing*	*Wet*	*Dry*
1	0	5·5	4–5	5
	1		4–5	5
	3		4–5	5
	5		4–5	4–5
	10		4–5	4–5
3	0	5·0	4	5
	1		4–5	4–5
	3		4	4–5
	5		4	4–5
	10		3–4	4–5
5	0	4·7	4	4–5
	1		4	4–5
	3		4	4–5
	5		3–4	4–5
	10		3	4–5
10	0	4·7	3–4	4–5
	1		3	4–5
	3		3	4–5
	5		3	4–5
	10		2–3	4

4 CONCLUSIONS

It may be concluded from the studies of the application of XLC during the reactive dyeing of wool that unfixed non-fast coloured wool gelatins are not a major contributory factor to the poor fastness ratings of reactive dyeings to deep shades. It was found that the yield of wool gelatins from reactive dyeings at deep shades was extremely low, and other causes, such as insufficient dye fixation or the presence of hydrolysed dye, would appear to be more important in determining the fastness of these dyeings. At best, XLC gave only slight improvements in the wool staining fastness ratings of these dyeings.

Although XLC did not impart any major fastness improvements to the dyeings in this study, the compound was found to be suitable for maintaining the integrity of the fibre during wet treatments. Relatively mild treatments were used in this study, and relatively little damage occurred to the fibre. Future work on this compound should involve more severe

treatments, such as wet treatments above 100°C, where more damage could be expected. Formaldehyde is currently used as a fibre protective agent for high temperature dyeing; however, there would appear to be a need for a less toxic, more environmentally compatible alternative to this reagent.

Some preliminary work was carried out on several crosslinking compounds analogous to XLC. These compounds contained aryl- or alkyl-diacid chlorides as the linking group between the amino groups of two 1-aminobenzyl-4-β-sulphatoethyl sulphone moieties; the linking group in XLC was cyanuric chloride. Two such compounds based on terephthaloyl chloride and sebacoyl chloride were prepared. Exhaustion studies with the terephthaloyl derivative indicated that the compound formed the reactive vinyl sulphone at a slightly lower pH value than that observed with XLC. Although this was not tested, the foregoing observation suggested that this compound would have had an optimum pH for reaction with wool close to pH 5, compared with that of pH 6 for XLC. The performic acid/ammonia solubilities and the swelling in formic acid of wool were both considerably reduced when the wool was treated with up to 10% (o.w.w.) of the terephthaloyl chloride derivative. This indicated that the compound could crosslink wool. Both the sebacoyl- and the terephthaloyl-chloride derivatives are water-soluble and merit closer study in the future.

REFERENCES

1. Smith, B. M., Spedding, P. L., Otterburn, M. S., Lewis, D. M. & Alanach, D. A., *Textile Res. J.*, **61** (1991) 705.
2. Lewis, D. H. & Wool Development International, *European Pat. Appl.* 85 306256 (1985).
3. Smith, B. M., Spedding, P. L., Otterburn, M. S. & Lewis, D. M., *Textile Res. J.*, **62** (1992) 309.
4. Smith, B. M., Spedding, P. L., Otterburn, M. S. & Lewis, D. M., *Dyes and Pigments*, **26** (1994) 277.
5. Smith, B. M., Spedding, P. L., Otterburn, M. S. & Lewis, D. M., *Dyes and Pigments*, **28** (1995) 57.
6. Hoechst *Hostalan Dyes in Dyeing*. July 1984.
7. Baumann, H., *Fibrous Proteins: Scientific, Industrial and Medical Aspects. Proc. Int. Conf.*, eds D. A. D. Parry & L. K. Creamer. Academic Press, London, 1980, Vol. 4, No. II, pp. 299–370.
8. Frohich, H.-G., Hackauf, M. & Chwala, C., *Handbook der Textilhilfsmittel*, eds C. Chwala & V. Anger. Springer-Verlag, Berlin, 1977, pp. 237–51.