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## REDUCING THE WEIGHT LOSS DURING DYEING OF DCCA SHRINKPROOFED WOOL

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# REDUCING THE WEIGHT LOSS DURING DYEING OF DCCA SHRINKPROOFED WOOL

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## ABSTRACT

*The loss of weight when wool shrinkproofed with DCCA is dyed was investigated and methods of reducing this loss by introducing cross-linkages into the protein were examined.*

KEY WORDS: Cross-linkages — dyeing — shrinkproofing — weight loss — wool.

## INTRODUCTION

The major reaction occurring when wool is chlorinated with the alkali salts of dichloroisocyanuric acid (DCCA) is one in which disulphide cross-linkages are severed and converted to polar sulphonic acid residues. Further disulphide scission also occurs during the subsequent antichlor treatment of the wool with sodium bisulphite. In this latter treatment thiol and thiosulphate residues are formed which are less strongly acidic than the sulphonic acid residues but nevertheless highly polar. Polar groups are also formed during the small amount of peptide bond splitting which takes place during the chlorination of wool.

In the shrinkproofing of wool with DCCA a decrease in the cross-linking density of the wool protein therefore takes place while, at the same time, the polar nature of these proteins is increased considerably. Since both these changes are known to promote the solubility of proteins in aqueous media, wool which has been shrinkproofed with DCCA can be expected to be more soluble than untreated wool. This increased solubility is particularly noticeable under more drastic conditions such as sustained boiling during dyeing.

A loss in weight during dyeing, even though it may not be accompanied by any loss in strength or in abrasion resistance, presents an economical problem to the industrialist who purchases his undyed wool and sells his dyed wool materials on a weight basis. The work reported here was carried out with the object of assessing the magnitude of this problem and of finding methods of reducing any high weight losses. The acute concern of part of industry about the possible scope of the problem necessitated that only those avenues which appeared to be the most promising in terms of rapid positive results, and which involved only simple, inexpensive, and readily adaptable treatments were considered. In this context the most promising approach appeared to be one of following the shrink-resist treatment with an after-

treatment in which cross-linkages are introduced into the protein. It was expected that these cross-linkages would decrease the solubility of the protein. If, in addition, the establishment of the cross-linkages could be brought about in such a manner as to reduce the total polarity of the protein, a further reduction in the extent of the dissolution of the wool in the dye liquor was considered likely. Three possible methods based on this approach were investigated.

## EXPERIMENTAL

Unbleached yarn, spun from 64's South African merino wool was used in the experiments.

All treatments were carried out in conventional hank dyeing machines at liquor ratios of approximately 30:1. Initial experiments were carried out on 3 Kg lots of wool but this was ultimately upscaled to 25 Kg lots.

### Chlorination:

The yarns were wetted out at room temperature in a liquor containing 2 g/l sodium chloride and 0.5 g/l Tergitol TMN (a nonionic wetting-agent manufactured by Union Carbide). Sodium dichloroisocyanurate (4% wov) was then added and the pH adjusted to 6.0. After 35 min running the temperature was increased to 35° where it was maintained until the bath was exhausted of active chlorine.

### Antichlor:

Sodium bisulphite (3% wov) was added to the bath containing the chlorinated wool and the pH adjusted to 4.5 with acetic acid. The reaction was then allowed to proceed at 35° for 25 min.

### After-treatments:

Reagents employed in the after-treatments were added directly to the antichlor bath.

- (a) Formaldehyde (5% wov of a 40% solution) was added to the bath, the pH adjusted to 8.0 with ammonia and the circulation continued at 50° for 30 min.
- (b) The same as in (a) except that ethylene diamine (1% wov) was added to the bath together with the formaldehyde.
- (c) Sulfix A (ICI) (2% wov) was activated by standing at 40° for 30 min in an aqueous solution containing an equal weight of trisodium phosphate. This procedure has been shown<sup>1</sup> to convert the sulphato-ethyl compound to the reactive vinyl compound with a minimum formation of the undesirable hydroxy-ethyl hydrolysis product. The activated Sulfix A was then added to the liquor in the dyeing machine, the pH adjusted to 9.0 and the wool allowed to react with the reagent at 50° for 30 min.

The terminal treatment, whether this was the antichlor treatment or one of the after-treatments (a), (b) or (c), was followed by rinsing and drying.

### Dyeing:

Hanks of known dry weight were dyed with a variety of dyestuffs and the recipes were invariably those recommended by the manufacturer of the particular dyestuff concerned. The boiling time was 2 hours throughout except where the actual influence of the time of boiling on the degree of dissolution taking place was investigated.

The dyed wool was rinsed, then dried until completely dry and reweighed. The loss in weight was calculated.

## RESULTS AND DISCUSSION

Formaldehyde has been known for many years as a cross-linking agent for a wide range of materials, in particular proteins and cellulose and the reactions involved are currently understood reasonably well, largely as a result of the work of Fraenkel-Conrat<sup>2</sup>. Cross-linkages may be formed when formaldehyde reacts with thiol groups to form djenkolic acid residues<sup>3</sup>.



The very low concentration of thiol groups in native wool protein is probably responsible for the failure to find any chemical evidence of the presence of djenkolic acid in wool fibres treated with formaldehyde. However, once the thiol content of the fibres has been increased by suitable reduction of some of the disulphide groups, djenkolic acid is formed in measurable quantities<sup>4</sup>. It is therefore probable that shrinkproofed wool, with its higher thiol content, resulting from the antichlor treatment with bisulphite, may form reasonable amounts of the bis-thioether cross-linkages when given a formaldehyde after-treatment.

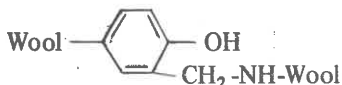
The amino side chains of the lysine residues in wool, react almost instantaneously with formaldehyde at room temperature to form methylol groups. These methylolamine groups cannot react with each other to form cross-linkages and the original representation of cross-linking by formaldehyde through two amino side chain residues



is now considered incorrect. The methylolamine groups can, however, react with amide groups to give stable cross-linkages<sup>2</sup>.



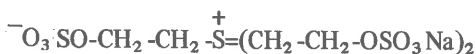
It has also been shown<sup>2</sup> that primary amido groups and amino groups may be linked to phenols through formaldehyde by a Mannich type of reaction but it is not known if two phenolic groups can be bridged in this way. Evidence is available from the work of Alexander *et al*<sup>6</sup> that formaldehyde is involved in the formation of cross-linkages between lysine and tyrosine residues to form an acid-labile residue which probably has the following structure:—



The use of an alkyl diamine together with formaldehyde was prompted by the knowledge that amino groups react rapidly with formaldehyde to form methylolamine compounds — in this particular case a bis-methylolamine compound. As explained above, a methylolamine may react with amido and phenolic groups to produce stable linkages. Since the bis-methylolamine compound is bifunctional, it can react with two groups in the protein and in this way produce cross-linkages.

Instead of creating a bifunctional reagent of required reactivity *in situ* by the combined use of formaldehyde and the alkyl diamine, reagents such as Sulfix A, which already possess this ability and which require no formaldehyde as a necessary ingredient of the cross-linking reagent, may be employed.

Sulfix A, a reagent which was developed for the cross-linking of cotton in order to improve the wet wrinkle recovery, is the disodium salt of tris- $\beta$ -sulphatoethyl sulphonium internal salt<sup>7</sup>.



It is converted by alkali to the trivinyl sulphonium compound,  $^+\text{S}(\text{CH}=\text{CH}_2)_3$ , which can then react with wool to form the following types of cross-linkages:—



The shrinkproofed wool which had been after-treated by any one of the cross-linking methods described above, invariably dissolved less during dyeing than wool which had not been after-treated (see Table I). The results also show that formaldehyde was less effective than either Sulfix A or the combination formaldehyde — ethylene diamine treatment. It was also shown that these protective effects did not break down when the wool was exposed to boiling times of up to 8 hours.

The nature of the various liquors used in the dyeing of the wool with the different dyestuffs differed considerably in terms of pH, and the concentration and the type of added salts and surfactants. These factors, and also the nature and con-

TABLE I

Typical results showing the decrease in weight loss during dyeing when shrinkproofed wool had been after-treated by a cross-linking agent. Results are given for different types of dyestuffs.

After-treatment of Shrinkproofed wool	% Dissolution during dyeing with						
	Reactive	Acid Milling	Acid Milling	Acid Levelling	Acid Levelling	Premetallized (1:2)	Premetallized (1:1)
None	2.6	1.3	1.8	2.9	1.2	2.2	3.0
Formaldehyde	1.5	0.6	1.4	0.9	0.2	1.0	2.6
Formaldehyde + Ethylene Diamine	0.9	0.1					
Sulfix A	1.1	0.1					

centration of the dyestuff used, have a profound effect on the rate of dissolution of the wool in the liquor and a considerable difference between results obtained in different experiments was therefore to be expected. However, the extent of the dissolution which took place when the shrinkproofed (but not after-treated) wool was dyed for two hours at the boil, remained between 1.2 and 3.0% with only a very few exceptions.

The costs of the chemicals consumed in the after-treatment of the wool, plus the added expenditure of running the equipment for an additional 30 min at 50°, must naturally be substantially lower than the value of the gain in weight of the dyed goods. From the results in Table I it would appear that it can be assumed with reasonable confidence that after-treatment with formaldehyde may give a 1% higher yield of dyed wool than without the after-treatment, i.e. the gain per 100 Kg of wool is 1 Kg. The cost of the formaldehyde used in the treatment is about 30–40% the value of a Kg of wool tops and if the cost of the longer treatment is added, the ultimate profit, if any, may be very small. If dyeing is carried out at either the yarn or the fabric stage, the difference in value between the formaldehyde consumed and the wool gained by the reduction in weight loss becomes large. The after-treatment may then offer economic advantages.

Use of the more expensive Sulfix A, or the combination formaldehyde – ethylene diamine treatment, gave higher protection against dissolution than did formaldehyde alone. Dissolution of wool which had received the latter treatment was,

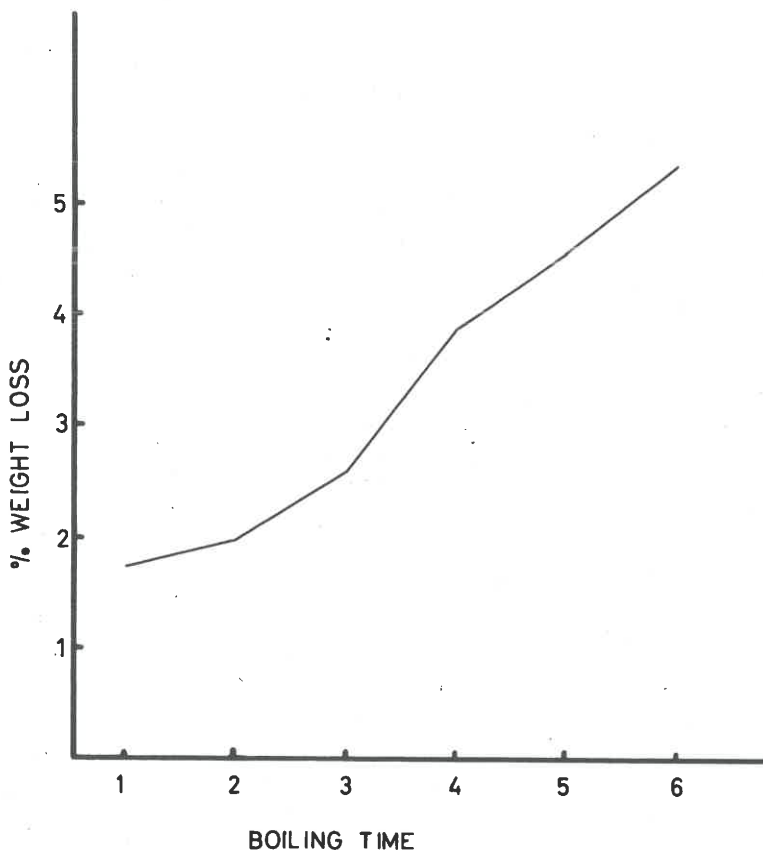


Fig. 1 Percentage weight loss when DCCA-shrinkproofed wool was dyed by boiling for various times.

however, already so low that only limited further improvements by the more potent processes could be possible in terms of absolute gain in weight. The economic benefits of the use of the more expensive after-treatments in these cases are therefore questionable. On the other hand if, as unconfirmed reports which reached us indicated, dyeing conditions do exist where the dissolution of the wool during dyeing may be as high as 7%, the greater protection offered by the more expensive treatments may be justified. It must, however, be emphasized that such high weight losses were never experienced in our investigations when boiling times were 120 min.

Having established that an after-treatment with formaldehyde alone would suffice in what appears to be the majority of instances, the bulk of this investigation



was concentrated on studying the effect of this particular treatment under a wider variety of dyeing conditions.

The boiling times in the dyeings carried out was mostly two hours which was perhaps of the same order as the boiling times employed in many industrial dyeings. As shown in Fig. 1 the time of dyeing had a great effect on the amount of wool dissolved in the dye-bath. This is therefore a further point to consider when the necessity of an after-treatment is contemplated. For example, if wool is going to be dyed only briefly during dyeing, dissolution would be slight and no after-treatment would be justifiable. For longer dyeing times the amount of wool dissolved may become greater and the advisability of the after-treatment may increase. In the case of very long boiling times (e.g. when particularly troublesome matchings are undertaken) it may even be advantageous to employ the combination of formaldehyde and ethylene diamine or alternatively, an agent such as Sulfix A.

None of the after-treatments investigated had any measurable effect on the abrasion resistance, the breaking strength, the dyeing properties, or the appearance and handle of the wool.

### CONCLUSION

The loss of weight during dyeing of wool shrink-proofed with DCCA can be reduced by applying a suitable after-treatment immediately after the antichlor treatment.

The way in which the wool will be dyed will decide whether the after-treatment is economically justifiable and will also indicate whether formaldehyde alone is an adequate inhibitor or whether more powerful agents should be employed.

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