

# Hercosett-57 Resin Deposition on Wool and Modified Wools

R. S. ASQUITH, K. L. GARDNER, W. S. MCGAREL, and M. S. OTTERBURN, *Department of Industrial Chemistry, The Queen's University of Belfast, 21 Chlorine Gardens, Belfast BT9 5DL, North Ireland*

## Synopsis

A study has been made of the uptake of a commercial polyaminoamide resin (Hercosett-57) by wool fibers. The effect of various chemical pretreatments on the uptake of the resin was monitored in order to investigate the mechanism of bonding of the polymer with the wool. From the results obtained it would appear that the deposition of the resin is not controlled by simple chemical reaction with the fiber. Surface treatments to the wool fibers and adhesion play a more important part in the resin-bonding process. Insoluble chlorinating agents such as DCCA and Chloramine T proved more effective in bringing about resin deposition than did the more widely used acid chlorination treatments, which use free chlorine in solution.

## INTRODUCTION

The treatment of wool with the polyamino-amide-epichlorhydrin resin, Hercosett-57, is now well established as a commercial shrink-proofing process,<sup>1</sup> although the nature of the interaction between the resin and the substrate is still not fully understood. Prior to application of the resin a prechlorination treatment is performed on the wool, in order to achieve satisfactory deposition of bound resin on the surface of the fiber. The chlorination treatment seems to be the most effective pretreatment,<sup>2</sup> although it has the disadvantage of causing a weight loss of the wool of approximately 2.0%. As a process it also has the operational disadvantage of causing the release of chlorine to the atmosphere from the chlorination bath.

The present work was carried out to determine the mechanism of deposition of the resin onto the wool fiber and to investigate alternative methods of pretreatment which would obviate the disadvantages of acid-chlorination.

## EXPERIMENTAL

### Samples

Hercosett-57 resin was obtained from Hercules Chemical Corporation Inc. and from International Wool Secretariat, Ilkley, Yorkshire. The wool used throughout this work was Merino 64's quality.

### Wool Pretreatments

(1) *Chlorination-neutralization*: A sample was immersed for 30 sec in a bath containing 40 ml sulfuric acid (98%) and 200 ml sodium hypochlorite (1.45  $\text{gl}^{-1}$ )

available chlorine) diluted to 1:1. The treated sample was then neutralized for 30 sec in a solution containing  $10 \text{ gl}^{-1}$  sodium carbonate and  $4 \text{ gl}^{-1}$  sodium sulfite, and then rinsed in water and dried.

(2) *Sodium hydroxide*: A sample was treated for 1 hr at  $65^\circ\text{C}$  in 0.1 M sodium hydroxide and then washed and dried.

(3) *Urea*: A sample was treated for 16 hr at room temperature in 8 M urea, washed and dried

(4) *Tributyl phosphine (TBP)*: A sample was shaken for 24 hr at room temperature, under nitrogen in a solution containing 25 ml Tris Buffer (2 M, pH 8), 225 ml water, 250 ml propan-2-ol, and 1.5 ml tributyl phosphine. The sample was washed and dried.

(5) *Alcoholic potassium hydroxide*: Treatment of the sample was for 2 hr at room temperature in 250 ml of a 1.0% solution. Sample was then washed and dried.

(6) *Urea-bisulphite (UBS)*: Treatment of the sample for 1 hr at  $65^\circ\text{C}$  was carried out using 500 ml of the following solution: urea ( $500 \text{ gl}^{-1}$ ), sodium metabisulphite ( $30 \text{ gl}^{-1}$ ) adjusted to pH 7. The sample was washed and dried.

(7) *Dichlorocyanuric acid (DCCA)*: Sample was treated for 30 sec in a bath (3 liter) containing the required amount of DCCA (0.53% available chlorine, based on 100% "pickup"), 5 ml sulfuric acid, adjusted to pH 2 with acetic acid. The sample was then squeezed through a pad-mangle, passed through a normal neutralizing bath, washed, and dried.

(8) *Chloramine T*: Sample was treated for 30 min at  $40^\circ\text{C}$  in 400 ml (0.5%) sulfuric acid containing the required amount of chloramine T (1%–3% available chlorine). The sample was washed with water, dilute ammonia and water, and dried. Treatment in the presence of sodium chloride was as above with 10% weight per volume (w/v) of the salt added to the bath.

### Resin Application

A pretreated wool sample (5 g) was immersed for 30 min in 250 ml of a solution containing Hercosett-57 ( $5 \text{ gl}^{-1}$ ) and sodium bicarbonate ( $10 \text{ gl}^{-1}$ ). The sample was thoroughly rinsed and dried.

### Analysis of Hercosett-57 on Wool by Gas Chromatography

Samples (500 mg) of resin treated wool were hydrolyzed for 18 hr by refluxing in 100 ml of hydrochloric acid (6 M). The adipic acid produced was extracted using  $2 \times 25 \text{ ml}$  portions of diethyl ether and the ether evaporated off at  $40^\circ\text{C}$ .

Methanolic-hydrogen chloride solution (1 ml), which contained  $5 \text{ mg ml}^{-1}$  of pimelic acid, was then added to the residue.

Aliquots ( $10 \mu\text{l}$ ) of this solution were injected into a gas chromatograph (column 2 m, 2.5 mm packed with: 3% SE-30 on Chromasorb G. AW, DMCS). The column was kept at  $110^\circ\text{C}$  for 2 min and then increased to  $190^\circ\text{C}$  at a rate of  $15^\circ\text{C min}^{-1}$ . The injection temperature was maintained at  $250^\circ\text{C}$ .

The ratio of the adipic acid peak to that of the pimelic acid was determined by adding 1 ml of the standard methanolic-HCl solution containing 5 mg pimelic acid to 5 mg adipic acid.

### Chlorination of Nylon 6:6

10 g of nylon 6:6 (MN  $2.1 \times 10^3$ ) fabric was treated for 1 hr at pH 4 in sodium hypochlorite (10%) solution, acidified with acetic acid. After washing and drying the *N*-chlorinated product (NC-66) was dissolved in benzene at 50°C and centrifuged to remove impurities. The product was isolated by precipitation with ether. Iodometric titration showed 92% of the nylon was *N*-chlorinated.

### Chloride Ion Release

Chloride ion release in the Hercosett-NC-6:6 reaction was determined using an Activion (Type 00315001) electrode and an Ag-AgCl reference electrode, using potassium nitrate (2 M) to maintain constant ionic strength.<sup>4</sup>

### Shrinkage Tests

These tests were performed on treated and untreated wool fiber samples using the Cubex Washing Procedure.<sup>5</sup>

### Measurement of Contact Angle

Contact angles were measured in an aqueous solution containing Hercosett (5 g liter<sup>-1</sup>) and sodium bicarbonate (10 g liter<sup>-1</sup>). The samples were totally immersed in the solution and the receding contact angle measured. A polarizing microscope was used for observation. All measurements were carried out at 20°C  $\pm$  1°C.<sup>6</sup>

### Cysteic Acid Analyses

Wool samples were hydrolyzed in 6 N HCl in sealed ampoules (under N<sub>2</sub>) for 18 hr. The acid was removed by lyophilization. Each sample was then analyzed on a Technicon amino acid analyzer and the cysteic acid concentration measured. Nor-Leucine was used as the internal standard.<sup>7</sup>

### Determination of Percent Available Chlorine

The percent available chlorine on the samples was determined by back titration of liberated iodine by 0.1 N sodium thiosulphate.

## RESULTS AND DISCUSSION

In any study of the uptake of resin by a substrate it is necessary to have an accurate method for the estimation of the bound resin. Various methods are available.<sup>8-10</sup> The method of Swanepoel et al.<sup>8</sup> was found to be the most useful and was investigated. The method was modified and improved so that the sensitivity was increased. For the necessity of repetitive analyses and ease of procedure, methylation with acetyl chloride-dry methanol was preferred to diazomethane. The gas chromatographic method thus developed and described in the experimental section was used throughout this work.

Previous work has shown that chlorination improves the uptake of Hercosett

resin by wool.<sup>2,11</sup> In the present work it was found that prechlorinated wool had 600% more resin bound than had untreated wool, using a 1% Hercosett solution at pH 8. Clearly, this pretreatment has a considerable effect on the amount of resin bound to the wool and yet the reasons for this are unclear, particularly since the treatment is extremely rapid and very little penetration of the fiber occurs. The possible mechanisms of resin deposition could be accounted for by either (a) oxidation of the disulphide bonds to cysteic acid residues, or (b) surface damage which increases adhesion of the resin for the wool surface.

Hypochlorite treatments which are industrially satisfactory could possibly introduce two different reactive sites or ionic sites by which the resin could bind to the wool. These are cysteic acid and/or *N*-chloroimine sites. It has previously been claimed that increasing the number of anionic sites, such as cysteic acid, increases the binding of the resin which contains cationic azetidinium sites.<sup>1</sup> It has also been suggested that covalent reaction between several groups such as amino or thiol groups in the wool with the resin could take place. Accordingly in order to study the possibility of any ionic interaction between cysteic acid sites and the resin, various different treated wool samples were examined and the cysteic acid content and resin uptake compared. The results are shown in Table I.

From these results it appeared that the presence of some cysteic acid did assist deposition of the resin. However, while the treatments listed do in many cases introduce cysteic acid residues into the fiber surface and enhancement of resin deposition also occurs, there is no direct correlation between cysteic acid content and the amount of resin bound to the wool. Thus for example Chloramine T treatment introduces a high cysteic acid level and there is a relatively high-resin uptake, whereas the acid-hypochlorite treatment introduces about the same amount of cysteic acid, but the resin uptake is much lower. Further, dichloro-cyanuric acid treatment causes a considerable enhancement of resin deposition, but only a small amount of cysteic acid is formed. It, therefore, appears that other factors are involved.

The possibility that *N*-chloroimine groups could be introduced during the prechlorination seemed plausible for two reasons; firstly the very short time of chlorination employed could lead to a general reaction taking place to a greater extent at the surface, rather than specific oxidation of disulphide bonds and secondly, previous workers have observed that chlorinated wool always possesses residual oxidizing power which would be characteristic of the presence of *N*-chloroimine groups.<sup>12</sup> The presence of such groups is, however, difficult to determine due to traces of hypochlorite and the effect of the neutralization pro-

TABLE I  
Comparison of Cysteic Acid Content in Wool with Resin Uptake

Treatment	Resin uptake (%)	Cysteic acid content ( $\mu$ moles $g^{-1}$ )
Alcoholic-KOH	1.20	12
Acid-Hypochlorite	1.44	55
Dichlorocyanuric acid	3.05	9
Chloramine T	3.45	50
Chloramine T-NaCl	4.65	58
Untreated	0.25	8

cedure. To avoid such difficulties it was decided to proceed by analogy using *N*-chlorinated nylon 6:6 which had previously been prepared and characterized.<sup>13,14</sup>

The results of the studies of reacting Hercosett-57 (1%; pH 8) with *N*-chlorinated nylon are shown in Figure 1. The molecular weight of the resin (by specific viscosity measurement) was found to initially increase, indicating that it was being crosslinked. However, the ultimate molecular weight of the resin suggested that the chloroimine groups in the nylon were oxidizing the resin and the molecular weight was only slightly greater than the initial value. The rate of release of chloride ions supported these findings, although the amount of chloride ions released was only one third of the theoretical amount known to be present in the form of  $\text{—NCl}$  groups. The influence of these latter groups is thus not very important with only a limited extent of reaction taking place. It would appear therefore that in the case of wool the neutralization stage after chlorination, although essential to remove excess chlorine, serves little purpose in removing chloroimine groups.

### Surface Effects

Of the possible effects of prechlorination that are occurring an important factor is whether penetration of the fibers by the hypochlorite reagent is necessary or whether due to the rate of reaction only surface reaction is necessary. Accordingly a number of different pretreatments prior to the resin application were selected. These treatments were deliberately chosen to study the comparison of the effect of reaction specifically on the fiber surface, with treatments which could penetrate throughout the wool fiber. The results of these experiments are shown in Table II. Treatments 1–2 are surface treatments only and treatments 3–5 are general treatments.

From Table II the effect of general treatments do increase the resin uptake

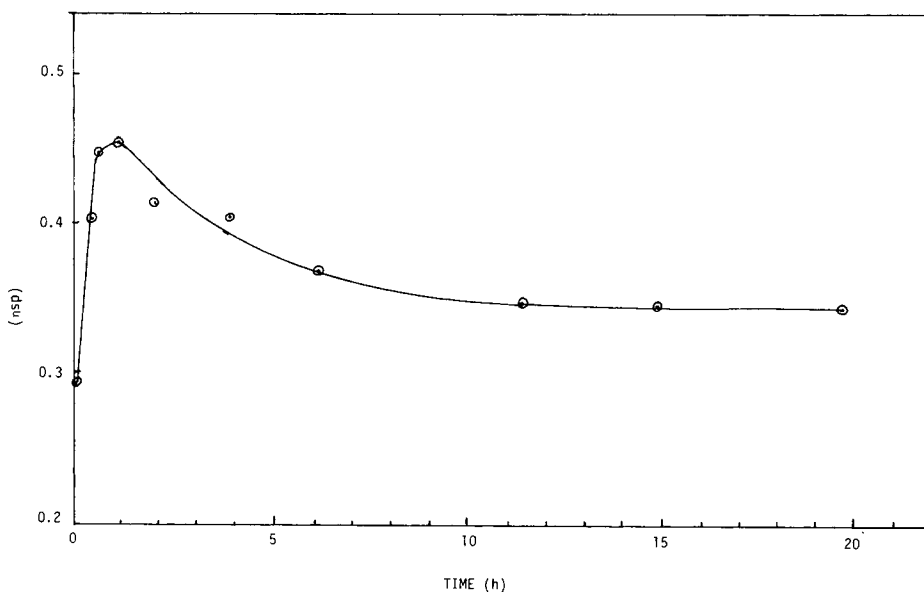


Fig. 1. Viscosities of resin + *N*-chlorinated nylon 6:6 vs time.

TABLE II  
Comparison of Surface with General Pretreatments of Wool with Resin Uptake

Treatment	Resin uptake (%)
(1) Chlorination-neutralization	1.44
(2) Alcoholic-KOH	1.20
(3) NaOH	0.42
(4) Urea-bisulphite (UBS)	0.60
(5) Tributyl phosphine (TBP)	0.70
(6) Untreated	0.02

but pretreatments specifically confined to the fiber surface are equally if not more effective in this aim. Following these results the surface effect of the fiber in relation to adhesion was studied.

### Adhesion Effects

In the bonding of polymeric resins to wool many different parameters have been observed to affect the actual adhesion mechanism.<sup>15</sup> Although a prime factor is thought to be due to a weak interfacial layer, associated with this is the influence of wetting and contact angle. To observe the adhesion effect of Hercosett-57 on wool a series of different pretreatments were carried out and the contact angle between the wool and resin was compared with the resin uptake, Figure 2.

From these results it appears that bonding of the resin to the fiber is directly related to the surface adhesion forces. Chlorination treatments are clearly the optimum type of pretreatment, which suggests that surface modification and

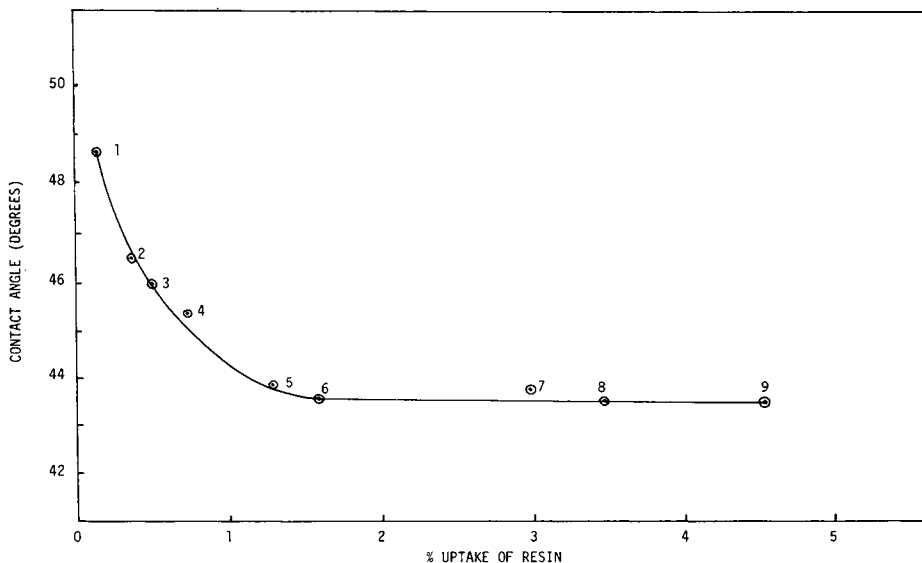


Fig. 2. Contact angle vs percent uptake of resin by wool after pretreatments: (1) untreated; (2) NaOH; (3) 8 M urea; (4) TPB/propan-2-ol; (5) alcoholic KOH; (6) acid chlorination/neutralization; (7) DCCA; (8) chloramine T; (9) Chloramine T + NaCl.

the introduction of surface ionic charge play an important role in resin binding, while covalent interaction is of little significance. Different types of chlorination pretreatment were therefore examined in order to overcome the previously mentioned disadvantages of the acid-hypochlorite system. Two treatments, dichlorocyanuric acid (DCCA) and Chloramine T are shown in Figures 3 and 4. The latter treatment is of particular interest as Alexander et al.<sup>17</sup> have previously shown that *N*-chloroimine derivatives gave improved shrink resist when the treatment was carried out in the presence of added salt. No satisfactory ex-

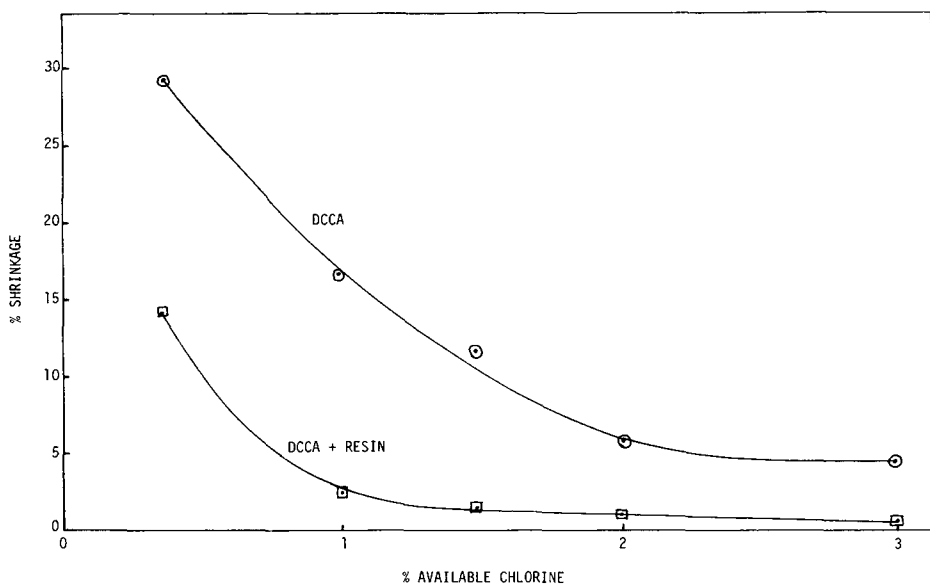


Fig. 3. Percent shrinkage of wool vs percent available chlorine (DCCA).

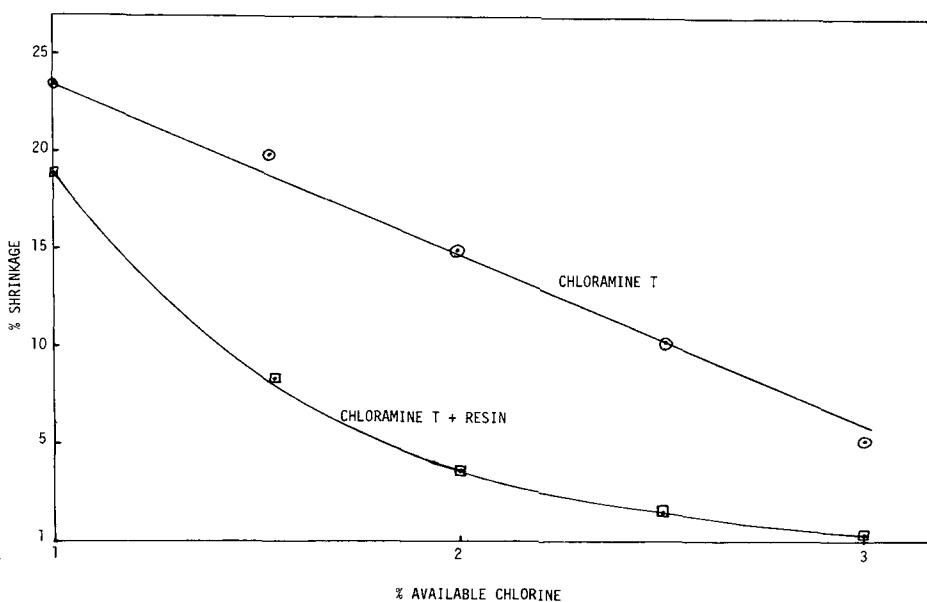


Fig. 4. Percent shrinkage of wool vs. percent available chlorine (chloramine T).

planation has yet been found for this effect. From the results obtained in this work a possible explanation could be that this relatively insoluble compound is deposited on the fiber surface where it decomposes and performs a surface chlorination reaction. This view is supported by the finding that more resin is bound to the wool after the Chloramine T treatment than a chlorination treatment where the hypochlorite ions are released in solution. The DCCA compound is also relatively insoluble and also probably performs a surface chlorination on the wool fiber.

## CONCLUSIONS

From the results obtained it would not seem that the effects of the prechlorination stage applied to wool prior to the deposition of Hercosett-57 resin can easily be explained by simple chemical reaction with the fiber. Thus, although both chlorination and other treatments are capable of introducing cysteic acid residues into the fiber subsequent deposition of resin on the treated fibers does not show any direct correlation with cysteic acid content. Equally, studies of *N*-chlorinated nylon 6:6 and its reaction with the resin indicated there is some measure of crosslinking reaction within the resin on exposure to the *N*-chloropolyamide; this is of insufficient significance to explain the considerable differences between the deposition of the resin on the untreated and prechlorinated wools, respectively.

Results with different pretreatments on the wool prior to resin application indicate that surface modification of the wool is sufficient without interactions within the fiber to govern the extent of subsequent resin deposition. Further, from measurements of contact angles it can be concluded that this is the defining factor which determines the ease of deposition of the resin. The greater effectiveness of relatively insoluble chlorinating agents (e.g., Chloramine T and DCCA) as compared with aqueous chlorine would suggest that these reagents by precipitation on the surface of the fiber are more capable of producing specific surface modification than is chlorine.

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