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**A Laboratory Investigation of the
Shrinkresist Treatment of Wool with
Polyamide Epichlorohydrin - Polyacrylate
Polymer Dispersions**

by

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A LABORATORY INVESTIGATION OF THE SHRINKRESIST TREATMENT OF WOOL WITH POLYAMIDE EPICHLOROHYDRIN-POLYACRYLATE POLYMER DISPERSIONS

by N.J.J. VAN RENSBURG

ABSTRACT

Some factors affecting the shrinkresist treatment of wool by chlorination followed by a treatment with a polyamide epichlorohydrin (PAE)-polyacrylate dispersion were studied. The addition of certain polyacrylates to the PAE polymer reduced the degree of shrinkage of the chlorinated fabrics. On the other hand, some other polyacrylates had no effect on the shrinkage of the fabrics. The minimum concentration of PAE required in the PAE-polyacrylate dispersion for the successful shrinkresist treatment of the fabrics depended on the level of chlorination, and increased with decreasing levels of chlorination.

KEY WORDS

Wool — shrinkresist — chlorination — polyamide epichlorohydrin polymer — polyacrylate dispersions — area shrinkage.

INTRODUCTION

Many polymers, which differ widely in chemical structure, are available for the shrinkresist treatment of wool⁽¹⁾. The more common types which are at present applied industrially to wool are the polyurethane, polyamide, polyacrylate and silicone polymers. Some of these are applied to wool from an organic solvent medium, but most are applied from an aqueous medium⁽²⁾. Certain polymers can only be applied to wool in the fabric or garment form, while others are more versatile and can be applied at the top, yarn or fabric stage⁽³⁾.

When shrinkresist polymers are applied to wool from aqueous solutions the wool is normally pretreated with oxidising agents, such as chlorine. There are several reagents available for the chlorination of wool, with sodium hypochlorite and salts of dichloroisocyanuric acid (DCCA) the most commonly used ones. The pretreatment of wool with chlorine modifies the fibre surface and facilitates an even spreading of the polymer on the fibre. Both the degree of the surface modification and the uniformity of the treatment from fibre to fibre, are fairly critical and most of the cases where the

shrinkresist treatment of wool with polymers fails, can probably be traced to an inefficient chlorination pretreatment.

One of the polymers which can be applied to wool in top, yarn or fabric form, is Hercosett 70, a polyamide-epichlorohydrin (PAE) polymer⁽⁴⁾. Since its introduction to the textile market about 10 years ago, large quantities of wool have been treated with this polymer. The reaction between PAE polymers and wool has been studied extensively and probably more is known about this polymer than any other used for the shrinkresist treatment of wool. The PAE polymer is a condensation polymer of adipic acid and diethylenetriamine, which has been reacted with epichlorohydrin. The cationic polymer which is then formed contains an azetidinium chloride group.

For technical reasons mixtures of PAE and polyacrylates are sometimes used for the shrinkresist treatment of wool. In these cases relatively *low* concentrations of PAE are employed. (Approximately 10 *per cent* PAE on the mass of the polyacrylate). The PAE in the mixture probably acts as a catalyst or cross-linking agent and reduces the shrinkage of the wool, compared with treatments with the polyacrylate only. The stability of some of the acrylic dispersions is, however, reduced by the presence of the PAE polymer. The polyacrylate polymers are not normally soluble in water and they are usually prepared in the form of aqueous dispersions. These dispersions are heterogeneous and are stabilised by emulsifying or dispersing agents. When mixed with the water-soluble PAE polymer, coagulation frequently occurs, even in the presence of some additional emulsifying agents.

Since very little information is available on the various factors which may affect the shrinkresist treatment of wool with PAE-polyacrylate dispersions an investigation of several parameters pertaining to this field was undertaken.

EXPERIMENTAL

A plain weave wool fabric with a mass/unit area of 130 g/m² was used in this investigation. This fabric has a high shrinking propensity and is similar to the IWS material used for shrinkresist studies. Prior to treatment the fabric was drycleaned for 15 minutes at room temperature in perchloroethylene. Except where indicated otherwise, all chemicals used were of laboratory grade. The percentages given are expressed on the mass of the wool except where indicated otherwise.

Shrinkresist treatments

Initially a *batch* chlorination and polymer application process was

employed. Subsequently a *continuous* chlorination, followed by a *batch* polymer application process was used.

(A) Batch Chlorination with Hypochlorite at pH 2,0:

This treatment was carried out on a laboratory winch, using a wool to liquor ratio of 1:40. The solution comprised

3,5% HCl

4% Melafix CH (Ciba-Geigy)

1,3% active chlorine (as sodium hypochlorite)

The temperature was increased from 20°C to 35°C over 15 minutes. When at least 85 *per cent* of the chlorine was exhausted, the wool was dechlorinated by the addition of one *per cent* sodium metabisulphite. After 5 minutes the polymer was added to the bath.

Batch Polymer Application:

The polymer dispersion containing 0,27 *per cent* PAE (Hercosett 70, Hercules Inc.) and 2,38 *per cent* polyacrylate was added to the bath and 10 minutes later the pH was adjusted to 5,5 with sodium bicarbonate. Five minutes later the pH was adjusted to 7,5 with sodium carbonate. Treatment was continued for a further 10 minutes after which the bath was dropped. The fabric was rinsed, air dried and cured for 15 minutes at 90°C.

(B) Continuous Chlorination with DCCA:

Further studies were carried out using a *continuous* chlorination process developed at SAWTRI⁽⁶⁻⁹⁾, followed by a *batch* application of the polymer. Pieces of fabric (25 metres) were treated in a pad mangle at room temperature (26°C) with 0,8 *per cent*, 1,2 *per cent* and 1,6 *per cent* active chlorine (as Basolan DC, B.A.S.F.). The solution contained 12,5 *per cent* acetic acid (vol/vol), 1,25 *per cent* sulphuric acid (vol/vol) and 0,5 *per cent* Tergitol Speedwet (Union Carbide) (mass/vol.). The fabric was dechlorinated with 3 *per cent* sodium metabisulphite and 3 *per cent* sodium bicarbonate.

Samples were cut always from the same position in the different fabrics, starting from the end of the fabric. Only the last five metres of each fabric was used for further studies.

Batch Polymer Application:

Preliminary experiments were carried out to establish to what extent an untreated fabric would felt in the Linitest apparatus when agitated in the absence of polymer in an aqueous medium containing one *per cent* Tergitol Speedwet. The sample holders contained various quantities of water (450, 400, 360, 240 and 120 ml). The wool to liquor ratio was 1:40. The samples were treated for 30 minutes at room temperature and the area shrinkage was then determined. No significant shrinkage was observed and 280 ml of liquor was used in the Linitest apparatus for all further studies. Two fabrics (15 x 15 cm) were treated simultaneously in each container.

The various polymers were applied to the wool fabrics at 35°C. After 30 minutes the fabrics were removed, air dried and cured at 90°C for 15 minutes.

Preparation of PAE-polyacrylate dispersions:

Various PAE-polyacrylate dispersions were used in this study. They were all prepared in a similar way by stirring the polyacrylate with an emulsifying agent (Lissapol NX (I.C.I.), 20 *per cent* on mass of acrylate) and then slowly adding this dispersion to a solution of PAE containing emulsifying agent (20 *per cent* on mass of PAE). These dispersions did not coagulate within 24 hours and will be referred to as *stable* dispersions. In some cases where the emulsifying agent (Lissapol NX) was omitted, the resultant dispersions normally coagulated within one hour. These will be referred to as *unstable* dispersions.

Various polyacrylates were used in this study. The Primal polyacrylates were supplied by Messrs. Rohm and Haas and Revertex A275 by Messrs. Revertex Ltd. The total area shrinkage of the fabrics was determined according to IWS Test Method 185, by washing in a Cubex apparatus for 3 hours at 40°C.

RESULTS AND DISCUSSION

(A) Batch chlorination and polymer treatment:

This treatment generally gave unsatisfactory results. The concentration of active chlorine used initially, namely 1.3 *per cent*, was increased to 2.0 *per cent*, but this did not decrease the degree of shrinkage of the fabrics to an acceptable level. Some typical results are shown in Table I. The results show that the addition of certain polyacrylates such as Revertex A275, Primal B15 and Primal AC55 to the PAE reduced the degree of shrinkage of

T A B L E I

**THE PERCENTAGE AREA SHRINKAGE OF BATCH CHLORINATED*
AND POLYMER TREATED WOOL**

TREATMENT	AREA SHRINKAGE (%)
0,27% PAE + 2,38% Primal E485	55
0,27% PAE + 2,38% Primal B15	18
0,27% PAE + 2,38% Primal HA24	61
0,27% PAE + 2,38% Primal B85	64
0,27% PAE + 2,38% Primal AC55	37
0,27% PAE + 2,38% Primal E358	57
0,27% PAE + 2,38% Revertex A275	17
0,27% PAE	54

*2% active chlorine

the chlorinated wool, compared with the PAE only treatment. On the other hand, several other polyacrylates had no effect at all on the shrinkage of the fabrics. Attempts were made to modify this shrinkresist process and to decrease further the degree of shrinkage of the fabrics. Other sources of chlorine, such as DCCA, were used. The temperature of the polymer treatment was increased to 45°C, and the time of reaction to 60 minutes. These modifications, however, did not have a significant effect on the shrinkage of the fabrics. It was decided, therefore, to use the method developed at SAWTRI for the continuous chlorination of wool, employing DCCA at low pH values, and to subsequently exhaust the various polymers onto the wool in a batch process.

(B) Continuous chlorination-batch polymer application:

Because only relatively small pieces of the fabric could be treated with polymer in the Linitest apparatus, some preliminary washing experiments were carried out to study the effect of the sample size on the percentage area shrinkage of the chlorinated wool. Small fabrics (15 x 15 cm), as well as the standard size samples (30 x 30 cm) were washed together in a Cubex apparatus at 40°C. The percentage area shrinkage of the fabrics was determined after specific washing times. (Figure 1) The results show that the rate of shrinkage of the smaller fabrics was slightly lower than that of the standard size ones. Both followed the same pattern and it was, therefore,

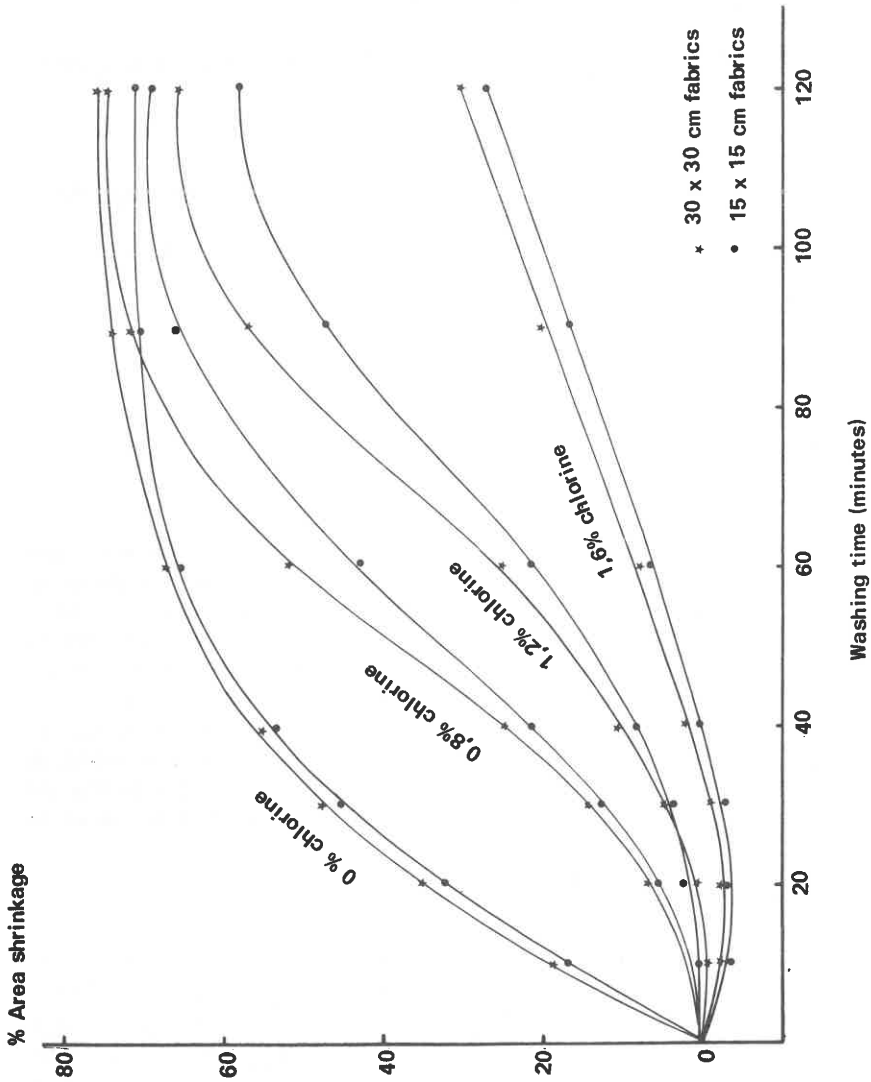


Fig 1 The effect of fabric size on the percentage area shrinkage of wool

TABLE II

**THE EFFECT OF THE STABILITY OF THE POLYMER DISPERSION ON
THE DEGREE OF SHRINKAGE OF WOOL**

POLYMER TREATMENT *	AREA SHRINKAGE (%)		
	0,8% CHLORINE	1,2% CHLORINE	1,6% CHLORINE
PAE + Revertex A275, stabilised	57	56	7
PAE + Revertex A275, not stabilised	70	65	17
PAE only	69	68	21
PAE + Primal E485, stabilised	67	65	18
PAE + Primal E485, not stabilised	70	66	19
PAE only	68	67	19
PAE + Primal B15, stabilised	71	47	9
PAE + Primal B15, not stabilised	68	56	9
PAE only	68	62	17

* 0,27% PAE and 2,38% polyacrylate were used

decided to use the small (15 x 15 cm) fabrics for further investigations.

Several factors which could possibly affect the shrinkresist treatment of the wool with the various polymers were studied. Attention was paid firstly to the stability of the various dispersions. The percentage area shrinkage after washing the fabrics treated with *stable* as well as *unstable* dispersions is shown in Table II. The results do not show large differences between the stable and unstable dispersion. In a few cases the stable dispersion seemed to be marginally better than the unstable dispersion. The results show furthermore that the use of the Revertex A275 or Primal B15 dispersion together with the PAE resulted in a lower degree of shrinkage than when the fabrics were treated with PAE only. In the case of Primal E485, however, the addition of this polyacrylate to the PAE had no effect on the degree of shrinkage of the fabrics.

The effect of different concentrations of PAE on the shrinkage of wool which had been treated with 0,8, 1,2 and 1,6 *per cent* chlorine was then studied. The results obtained are shown in Fig 2. It can be seen that the area shrinkage of the fabrics decreased as the concentration of PAE was increased. The importance of the level of chlorination is also demonstrated by the graphs. At lower levels of chlorination, more PAE is required to reduce the shrinkage of the fabric to the same level than at higher levels of chlorination. To reduce the shrinkage of the fabrics to five *per cent*, approximately 0,3 *per cent* PAE was required for wool treated with 1,6 *per cent*

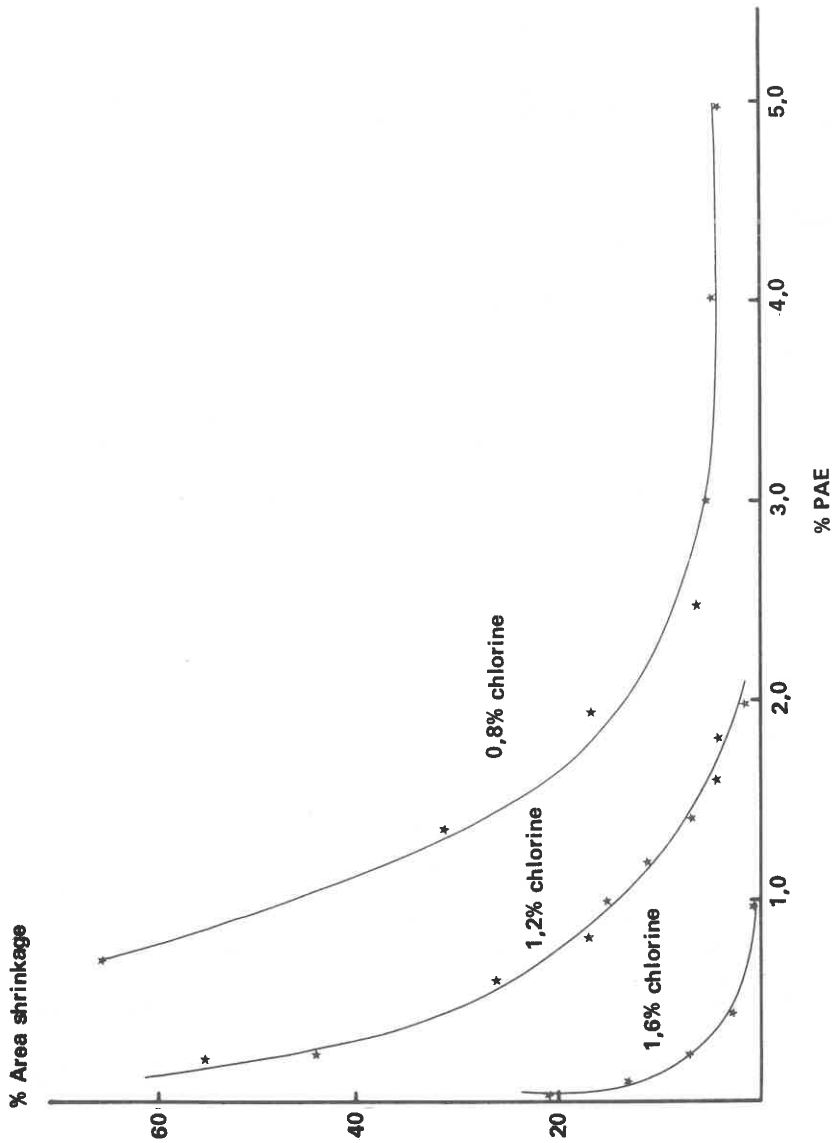


Fig 2 The percentage area shrinkage of wool treated with different concentrations of active chlorine and PAE polymer

chlorine, whereas 3,0 per cent PAE was required when the fabric was treated with 0,8 per cent chlorine. These values merely serve to indicate trends and should not be considered as absolute values, since smaller than standard size samples were treated and washed.

TABLE III

THE EFFECT OF VARIOUS CONCENTRATIONS OF PAE AND REVERTEX A275 ON THE DEGREE OF SHRINKAGE OF CHLORINATED WOOL

CHLORINATION LEVEL (% ACTIVE CHLORINE)	POLYMER TREATMENT		% AREA SHRINKAGE	
	PAE (%)	PAE + REVERTEX A275 (%)	PAE	PAE + REVERTEX A275
0,8	0,7	0,7 + 1,95	66	1
	0,5	0,5 + 2,15	68	1
	0,3	0,3 + 2,35	71	32
	0,1	0,1 + 2,55	72	72
1,2	0,4	0,4 + 2,25	13	1
	0,3	0,3 + 2,35	44	18
	0,2	0,2 + 2,45	44	33
	0,1	0,1 + 2,55	54	50
1,6	0,2	0,2 + 2,45	6	1
	0,1	0,1 + 2,55	12	11
	0,05	0,05 + 2,60	15	20
	0,01	0,01 + 2,64	20	18

Finally, some of the fabrics were treated with dispersions of Revertex A275 and PAE. The results obtained are shown in Table III. It can be seen that, in certain cases, the addition of a polyacrylate dispersion to the PAE did reduce the shrinkage of the fabric, when compared with the treatment with PAE only. For each level of chlorination, however, there seemed to be a certain *minimum level* of PAE required in the dispersion to reduce the area shrinkage of the fabrics to less than five per cent. Once the concentration of the PAE decreased below this value, the shrinkage of the fabrics increased significantly, despite the fact that a high concentration of polyacrylate was still present in the solution. This minimum level of PAE increased as the level of chlorination decreased from approximately 0,2 per cent PAE for 1,6 per cent chlorine, to 0,4 per cent PAE for 1,2 per cent

chlorine and 0,5 *per cent* for 0,8 *per cent* chlorine. This shows, once again, that the level of chlorination of the wool is very critical and that it determines the minimum quantity of PAE which must be used in the polyacrylate dispersion for the successful shrinkresist treatment of the fabrics.

Finally, it must be emphasised that the method of *chlorination* employed in the last part of this study involved a continuous treatment in the nip, where the reaction was probably restricted to the fibre surface and which was therefore more effective than the batch exhaustion process where longer liquor ratios and more diluted solutions were used. It seems therefore that, in the case of batch treatments, higher concentrations of chlorine will be required, together with more PAE in the polyacrylate dispersion than is commonly accepted.

SUMMARY

The shrinkresist treatment of woven wool fabrics by a *batch chlorination* process, followed by a batch application of PAE-polyacrylate dispersions, generally produced unsatisfactory results. No clear picture could be formed about the various factors involved in this shrinkresist treatment and consequently most of the studies were carried out on a *continuous chlorination* process followed by a batch exhaustion of the various polymers.

In agreement with other research workers it was found that the addition of certain polyacrylate dispersions to relatively *low* concentrations of PAE resulted in a lower percentage area shrinkage than when the PAE polymer only was used. Some polyacrylates, however, had no effect at all on the degree of shrinkage of the fabrics. The stability of the dispersion seemed to have only a marginal effect on the degree of shrinkage of the fabric, the stable dispersions giving slightly better results than the unstable dispersions.

The effect of different concentrations of PAE on the shrinkage of wool treated with different concentrations of chlorine was also studied. It was found that increasing amounts of PAE had to be used when the level of chlorination was decreased. In certain cases the addition of a polyacrylate dispersion to the PAE reduced the shrinkage of the fabrics. When the concentration of PAE became too low, however; the addition of polyacrylate did not reduce the shrinkage of the fabrics significantly. For each level of chlorination there seemed to be a certain *minimum level* of PAE below which the addition of polyacrylate did not have any effect. This minimum level of PAE increased with decreasing levels of chlorination.

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THE USE OF PROPRIETARY NAMES

The fact that products with proprietary names have been used in this investigation in no way implies that there are not others as good or even better.

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