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The Continuous Shrinkresist Treatment of Wool Tops using Chlorine Gas in a Conventional Suction Drum Backwash

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THE CONTINUOUS SHRINKRESIST TREATMENT OF WOOL TOPS USING CHLORINE GAS IN A CONVENTIONAL SUCTION DRUM BACKWASH

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ABSTRACT

Wool tops were shrinkresist treated successfully on a conventional suction drum backwash using chlorine gas dissolved in water. The equipment that was used was relatively unsophisticated and the release of chlorine gas into the surrounding atmosphere was negligible. The pretreatment of wool with chlorine gas dissolved in water offered several technical advantages over a pretreatment with hypochlorite/sulphuric acid. Furthermore, it was considerably cheaper. The chlorine gas pretreatment was used in conjunction with Hercosett 125, Nopcobond SWS 10 and acid colloid resins to produce shrinkresistant wool. The treatment was also carried out on loose stock on a modified suction drum machine.

At a chlorination level normally used in conventional shrinkresist treatments, namely about 2,0%, the chlorine gas generally caused considerably less modification of the fibre surface than a hypochlorite/sulphuric acid treatment. At relatively high levels of application, the lustre of wool and other keratin fibres was significantly increased.

INTRODUCTION

Although wool can be shrinkresist treated in various forms such as loose stock, tops, piece goods and garments, continuous top treatments are by far the most popular. Acording to data published by the International Wool Secretariat (IWS), more than 80% of the world production of Superwash wool was treated by continuous processes in 1976[1]. The quantity of wool treated in this manner amounted to about 15 million kg in 1981[2]. This is a remarkable achievement, especially in view of the fact that a mere decade earlier, when the process was first introduced, less than 0,5 million kg wool was shrinkresist treated in top form. It has been known for a long time that the felting shrinkage of wool can be reduced by either a chemical degradative treatment or by the application of polymer[3]. In the 1950's wool treated in this manner was generally regarded to be shrinkresistant. Since then shrinkresistance standards have become more severe, partly due to the increasing use of domestic washing machines for washing garments, including those containing wool. This has resulted in the introduction of more stringent tests for felting shrinkage, and many samples which have passed earlier tests would not pass the tests which are used at present[4].

It is much easier to shrinkresist treat wool fabrics and garments than wool tops. In the former case inter-fibre bonding prevents fibre migration during washing, whereas the directional frictional effect of individual fibres has to be reduced in the latter case. To date the only successful approach to top treatments is a two-stage process, namely an oxidative pretreatment, followed by the application of polymer.

It has been stated that the chlorine/® Hercosett process was the first commercially accepted process for the continuous shrinkresist treatment of wool tops[4]. Shortly after the introduction of the chlorine/Hercosett process (which was developed by the Commonwealth Scientific and Industrial Research Organisation (CSIRO), and the IWS), the ® Dylan process was launched by Precision Processes Ltd. Today the chlorine/Hercosett process dominates the continuous top treatment market worldwide. The development of the chlorine/Hercosett process dates back to the early 1960's, when research workers at the CSIRO in Australia found that certain chemical treatments facilitated the spreading of polymers on wool, thus improving the efficiency of the polymer treatment[5-7]. In 1967 these workers reported that wool tops could be shrinkresist treated by acid chlorination in a conventional backwash, followed by dechlorination, rinsing and the application of resin[8]. At a later stage the chlorination bowl was modified to incorporate a succession of submerged squeeze rollers and vertically opposed jets through which the pretreatment solution was circulated. In 1969 it was reported that the chlorination treatment could be carried out in a conventional horizontal pad-mangle, followed by dechlorination, rinsing and resin application in a conventional backwash[9]. In 1971 it was reported that the chlorination treatment could be carried out by means of a pad-mangle or suction drum[10]. By 1973 the shrinkresist process was carried out commercially on a five bowl suction drum backwash[11]. The main steps comprised chlorination, dechlorination, rinsing, polymer application and softener application, followed by drying the wool and curing the polymer. For the chlorination step sulphuric acid and sodium hypochlorite solutions were pumped into the first bowl to produce a chlorinating liquor at a pH of about 1,5 to 2,0. Approximately 2,0% active chlorine (on the mass of wool) was usually applied. The wool was then treated with bisulphite, rinsed and treated with about 2,0% Hercosett, followed by about 0,5% softening agent. The chlorine/Hercosett process has changed very little since those early days and at present it is still carried out in the same manner as during the early 1970's[1].

Recently a completely new approach to the shrinkresist treatment of wool was announced by Kroy Unshrinkable Wools Inc.[12-13]. A machine was developed specially for the chlorination of wool using chlorine gas dissolved in water. In the ® Kroy-Deepim machine the wool slivers are fed into a chlorine solution at an angle of not more than 10 degrees from the vertical to a depth

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of at least one metre. No suction is applied and complete penetration of the slivers by the chlorine solution is solely the result of capillary action and the progressive increase in hydrostatic pressure as the slivers are immersed deeper in the solution, thereby forcing the air out of the slivers. It has been claimed that the Kroy process offers several advantages over the conventional suction drum system, and in general the concensus of opinion is that the benefits are mainly due to the more uniform degree of chlorination[14].

A survey of the literature by the authors has revealed that the term "chlorination of wool" is used loosely to describe a wide variety of reactions, the main function of most of them being the modification of the surface of the wool fibre to reduce felting shrinkage. The chlorination of wool basically involves an oxidative attack on the scales of the fibre by a wide variety of chlorine-containing chemicals[3-4]. Some typical examples are treatments with sodium, lithium or calcium hypochlorite at pH values ranging from 1,0 to 10,0, treatments with hypochlorous acid at various pH values, and treatments with a number of chemicals which act as chlorine donors, e.g. chloroamines, chloroisocyanuric acid, etc. All the chlorination treatments referred to above are normally carried out in an aqueous medium, although some treatments have been carried out in organic solvents. As far as the use of the chlorine gas dissolved in water is concerned, the literature showed that the use of the terms "chlorine solution", "chlorine water", "aqueous chlorine solution", "free chlorine", etc., mostly do not refer to the actual use of chlorine gas dissolved in water, but rather to solutions containing acidified hypochlorite or various other chlorine containing compounds. In this report, however, the term chlorination will be used to describe the process where chlorine gas is dissolved in water for the treatment of wool, and it should not be confused with gaseous chlorination, where wool is treated with chlorine gas in an autoclave. In the latter case the wool (mainly in fabric form) is not wetted out in water, but is treated with chlorine gas in air.

As far as the Kroy process is concerned, its success could possibly be due to the novel manner in which the slivers are fed into the liquor to displace all entrapped air, or to the fact that chlorine gas dissolved in water is used for the chlorination treatment. It is also possible that both factors contribute to the very uniform degree of chlorination of the tops.

A survey of the literature on the treatment of wool with chlorine reveals that a considerable amount of information has been published on the chemistry of this reaction[4,15,16]. Relatively little has been published, however, on the use of chlorine gas in water for the shrinkresist treatment of wool. In fact, most of the available information refers to batch treatments, and with the exception of the Kroy process, practically no information has been published on the use of chlorine gas dissolved in water for the continuous shrinkresist treatment of

wool tops. In a few publications passing reference is made to the possibility that chlorine gas could be used for the shrinkresist treatment of wool slivers instead of acidified hypochlorite, but details of such treatments have never been published. In fact, the general concensus of opinion seems to be that it is not possible to chlorinate wool slivers successfully in a backwash machine using chlorine gas[12-14,17].

A study of the chemistry of acidified hypochlorite solutions and chlorine gas dissolved in water shows that the two reagents are similar, the main difference being that the hypochlorite solution contains some inorganic salts[18,19].

When chlorine gas is dissolved in water, the following equilibrium is established very rapidly:

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+Cl^- \quad \text{..(1)}$$

The pK value of hypochlorous acid (HOCl) is about 7,6 and thus it would not be in a dissociated form ($H^+ + OCl^-$) under acidic conditions (at pH values $<$ 4). In the case of equation (1) the equilibrium between dissolved Cl_2 and HOCl depends of various factors, the most important being the concentration of the chlorine and the pH of the liquor. The concentration of hypochlorous acid generally decreases when the pH of the liquor is decreased (i.e. when acid is added). Similarly, the concentration of hypochlorous acid decreases when the concentration of chloride ions (Cl^-) is increased (e.g. by adding NaCl to the solution).

Both hypochlorous acid and free chlorine impart shrinkresistance to wool, but whereas chlorine reputedly[12,20]causes more damage to the fibre, hypochlorous acid causes only minor surface modification[20-22]. For optimum results, therefore, it is highly desirable that wool be treated with solutions containing as little free chlorine as possible. Furthermore, it is clear that the concentration of free chlorine will generally be higher in the case of acidified hypochlorite solutions than in the case of chlorine gas dissolved in water. Basically this is due to the fact that the sodium hypochlorite solution contains a high percentage of sodium chloride (which is produced during its synthesis), while some more salt (Na_2SO_4) is produced when the hypochlorite is acidified with sulphuric acid in the chlorination bowl.

It is clear, therefore, that there are considerable technical and economic advantages to be gained when wool tops are treated with chlorine gas dissolved in water. The question which arises now is why has chlorine gas not been used commercially for continuous top treatments prior to the development of the Kroy technology? A survey of the literature by the authors has revealed no answer to this question. Apart from some cases where workers reported erroneously that they used chlorine or chlorine water, while they in fact used sodium hypochlorite in some form, very little reference has been made to the actual use of chlorine gas. Although it was reported that chlorine gas could

be used for the chlorination of wool tops, such claims were never supported by the publication of actual details of the process. For example, in 1967 it was reported that, apart from the hypochlorite/sulphuric acid process, chlorine gas could be dissolved in a sulphuric acid solution and used in a conventional backwash for the chlorination of wool[8]. In subsequent publications, however, those workers only described and used the hypochlorite/sulphuric acid process[9-11]. It is clear, therefore, that some apparently insoluble problems must have been encountered with the chlorine gas treatments. These could well have included the health hazards associated with undissolved or free chlorine due to the inadequacy of the techniques used at that time.

In view of the potential advantages offered by liquors comprising chlorine gas dissolved in water, SAWTRI decided to carry out an in-depth investigation into this matter and to attempt to develop a system which could be used on conventional suction drum backwash plants. This report gives some results obtained on the shrinkresist treatment of a wide variety of wools on a pilot scale machine at SAWTRI, as well as some results obtained on full-scale machinery during industrial trials, using chlorine gas dissolved in water. A comparison is also carried out between the chlorine gas process and the conventional hypochlorite process. Results obtained on the chlorine gas pretreatment followed by the application of various shrinkresist polymers are reported.

EXPERIMENTAL

Raw Materials:

Wool tops with a linear density of approximately 20 to 22 ktex and with a dichloromethane (DCM) extractable matter content of about 0,3% were used for most treatments. In some cases wool tops with a DCM content of 0,8% were used. The mean fibre diameter of the various wool tops varied from 20 to 23u. Some experiments were also carried out on mohair. A number of experiments were carried out on loose wool stock in a modified suction drum machine.

Chemicals:

Commercial grade chemicals were used in all cases. The chlorine gas was drawn from standard chlorine cylinders (70 kg) and was metered into the chlorination bowl with the aid of a flow meter. The sodium hypochlorite and sulphuric acid solutions, on the other hand, were pumped into the bowl from stock tanks via precision metering pumps.

Machines:

In the pilot scale treatments a suction drum with dimensions similar to full scale equipment, but somewhat narrower (to treat 12-15 ends) was used

for chlorination, while the dechlorination, rinse, polymer and softener treatments were carried out in subsequent bowls of a conventional (standard size) backwash. Industrial trials were carried out on full-scale machines. In most cases the processing speed was 3m/min. The process and the equipment needed for the chlorination was relatively unsophisticated and is the subject of patent application[23]. Details will be published at a later stage.

Tests:

The shrinkresist treated wool was converted into yarn which was knitted into fabric. The samples were washed for 3 hours in a Cubex machine according to IWS Test Method 185, and the percentage felting shrinkage was determined. The degree of whiteness of the wool was determined[24] on a Hunterlab D25 Colorimeter according to ASTM Method E 313-73.

RESULTS AND DISCUSSION

Initially, a comparison was carried out between the conventional sodium hypochlorite/sulphuric acid treatment and treatment with chlorine gas in water, using an acid colloid as resin. In order to highlight any possible differences between the two chlorination pretreatments a relatively low concentration of resin was employed. The results in Table 1 clearly show that for these particular wool

TABLE 1

A COMPARISON OF CHLORINE GAS AND SODIUM HYPOCHLORITE/SULPHURIC ACID AS PRETREATMENT FOR CONTINUOUS TOP SHRINKRESIST TREATMENTS

Pretreatment	% Resin*	% Shrinkage			
		Lot A (20,6 μ)	Lot B (20,8 μ)	Lot C (21,2 μ)	Lot D (22,1 μ)
1,0% NaOCl + H+	1,5	42	28	28	43
2,0% NaOCl + H+	1,5	16	10	9	14
3,0% NaOCl + H+	1,5	3	6	3	5
1,0% Cl₂	1,5	15	10	8	8
2,0% Cl₂	1,5	5	3	1	2

*Acid Colloid

lots, the chlorine gas produced considerably better results than the sodium hypochlorite/sulphuric acid treatment. Whereas 2,0% hypochlorite (active chlorine) was insufficient in most cases, treatment with 2% chlorine gas gave acceptable results in all cases. The effect of the two pretreatments on the degree of whiteness of wool is shown in Table 2. It is clear that the chlorine gas produced a significantly higher degree of whiteness than the conventional hypochlorite/sulphuric acid treatment. Furthermore, the whiteness of the wool increased when the concentration of chlorine gas increased, whereas it decreased in the case of hypochlorite.

TABLE 2

THE EFFECT OF THE CHLORINATION PRETREATMENT ON THE DEGREE OF WHITENESS OF WOOL

Treatment*	Whiteness Index**
1,0% NaOCl + H+	— 3,4
2,0% NaOCl + H+	— 3,0
3,0% NaOCl + H+	— 0,1
1,0% Cl$_2$ gas	— 5,5
2,0% Cl$_2$ gas	— 10,2

*Treated with 1,5% acid colloid in all cases
**The more negative the value the whiter the wool

A number of experiments were then carried out to establish whether the chlorine gas treatment could be carried out at higher speeds, and at elevated temperatures, as well as in the absence of wetting agent, and also to establish whether the subsequent bisulphite dechlorination treatment could be omitted. The results in Table 3 show that there was no difference between the felting shrinkage of wool treated at 15,5°C and 30°C. On the other hand, the wool treated at 5°C showed a higher degree of shrinkage. It is known[19] that chlorine hydrate crystals ($Cl_2.8H_2O$) could form at temperatures below 9,6°C, and this might have happened during the treatment which was carried out at 5°C. It is also possible, however, that the equilibrium (in equation (1)) could be shifted towards the left at lower temperatures, thus reducing the HOCl concentration. (The solubility of Cl_2 in water is 9,8g/1000g water at 10°C, and 7,1g/1000g at 20°C).

TABLE 3

THE EFFECT OF VARIATIONS IN CHLORINATING CONDITIONS (Cl₂ GAS) ON THE FELTING SHRINKAGE OF WOOL

Treatment conditions*	% Shrinkage	Whiteness Index
1,0% Cl$_2$ gas. 5°C	23,0	2,1
1,0% Cl$_2$ gas. 15,5°C	11,1	-5,5
1,0% Cl$_2$ gas. 30°C	12,0	-9,1
2,0% Cl$_2$ gas. No wetting agent. 15,5°C	1,0	-12,0
2,0% Cl$_2$ gas. No wetting agent. 30°C	4,0	-10,2
2,0% Cl$_2$ gas. 15,5°C. No bisulphite	7,1	2,3
1,4% Cl$_2$ gas. 15,5°C. 6 m/min	3,0	-10,8

*The tops were treated at a speed of 3m/min through the chlorination, dechlorination and acid colloid resin/softener bowls, using 1,5% resin.

The results in Table 3 show that it was possible to chlorinate wool in a suction drum with chlorine gas in water containing no wetting agent. In practice it was found that a good wetting out of the wool was obtained when the DCM content was less than 0,3%. Due to possible variations in the DCM contents of various wool lots, it would not be advisable, however, that the wetting agent be omitted in the case of continuous production runs. Results obtained at SAWTRI during this study indicated that the initial charge of wetting agent to the chlorination bowl (about 1g/litre) gave sufficient wetting out of the wool for at least two hours, without any further addition of wetting agent. In view of the fact that wool removes some liquor from the chlorination bowl, replenishing of the water was required during continuous runs. This was conveniently carried out with water containing some wetting agent, especially in cases where the DCM content of the wool was higher than about 0,5%.

Table 3 also shows that the bisulphite dechlorination treatment could be omitted whilst still giving an acceptable level of shrinkresistance. It is clear, however, that the wool which had not been dechlorinated was yellower than wool dechlorinated with bisulphite. In a further experiment the processing speed was increased from 3 to 6m/min without adversely affecting the shrinkresistance of the wool. At this stage it is not yet clear what the upper limit of the processing speed is for the chlorine gas treatment. It would depend, amongst others, on the maximum quantity of chlorine which can be drawn from the cylinder or tank, the efficiency of dissolving such large quantities of chlorine in water and on the rate at which the chlorinating liquor is drawn through the wool slivers.

It is well known that the pH of the liquor is very important when sodium hypochlorite and sulphuric acid are used for the chlorination pretreatment. The pH is normally maintained between 1,4 and 2,0. When it exceeds 2,0 the rate of the reaction becomes too slow, whereas pH values below 1,4 tend to produce uneven treatments. Sophisticated monitoring and metering equipment is therefore required for the conventional hypochlorite treatment. In the case of the chlorine gas treatment, on the other hand, no control of the pH is required. Figure 1 shows the pH of the chlorination liquor as a function of time, for two levels of treatment, namely 2,0% and 4,0% Cl_2. In the former case the wool was treated with 2,0% ® Hercosett 125 (a polyamide-epichlorohydrin polymer), whereas 2% ® Ultratex ESB (a silicone polymer) was used in the second case. Wool samples taken at 15 minute intervals showed that, despite the gradual decrease of the pH of the chlorination liquor, the shrinkresistance was not affected and in all cases the knitted wool fabrics shrank less than 8,0% after a three hour Cubex wash test. During industrial trials the chlorination treatment was still effective (i.e. producing even staining tests and acceptable felting shrinkage results) after runs of up to 4,5 hours, without any attention being paid to the pH of the liquor.

It is common knowledge that a considerable amount of heat is generated during the treatment of wool with sodium hypochlorite and sulphuric acid. In fact, most mills have installed chillers or cooling devices to maintain the temperature of the chlorination bowl at a temperature of about 20°C. On the other hand, the temperature of the chlorination liquor increases relatively slowly when wool is treated with chlorine gas dissolved in water. Figure 2 shows the temperature of the chlorination liquor recorded for the chlorine gas and sodium hypochlorite/sulphuric acid treatments, when no chiller or cooling device was used. It is clear that the temperature of the liquor increased at a much slower rate in the case of the chlorine gas. In the case of the sodium hypochlorite treatment the increase in temperature was due to the heat generated during the neutralisation of the alkaline hypochlorite solution with sulphuric acid, as well as the heat generated in the reaction between the chlorination liquor and the wool.

During the conventional sodium hypochlorite/sulphuric acid process there is an increase in the salt concentration in the chlorination bowl during continuous treatments. Sodium hypochlorite solutions contain about 12% (m/m) active chlorine and about 0,3-1,2% (m/m) sodium hydroxide. Furthermore, the solution contains a considerable amount of sodium chloride. Figure 3 shows the theoretical build-up of salt in the chlorination bowl for the sodium hypochlorite/sulphuric acid and chlorine gas treatments. In the calculation it was assumed that no liquor was removed from the bowl. It was also assumed that the hydrochloric acid which formed in the case of the chlorine gas was a salt. It can be seen that for the chlorine gas treatment the build-up of salt
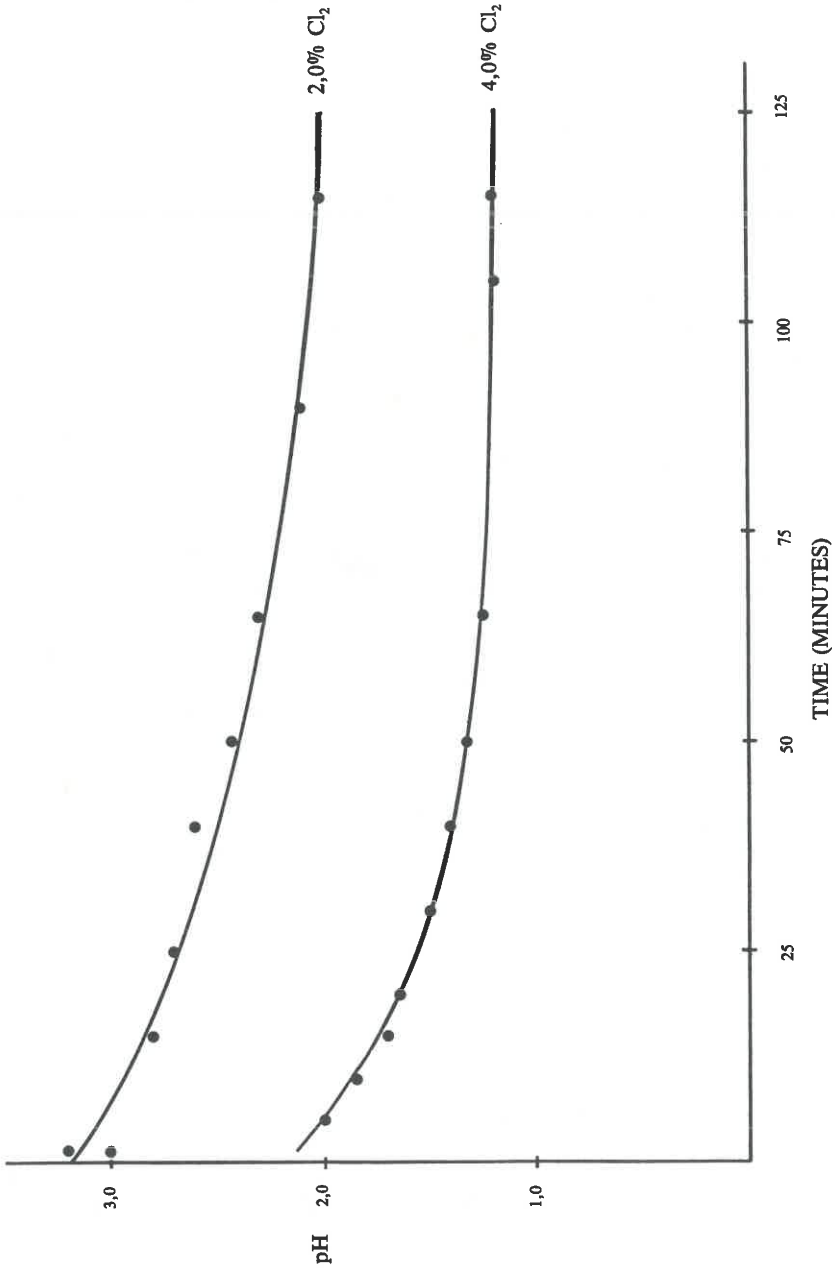
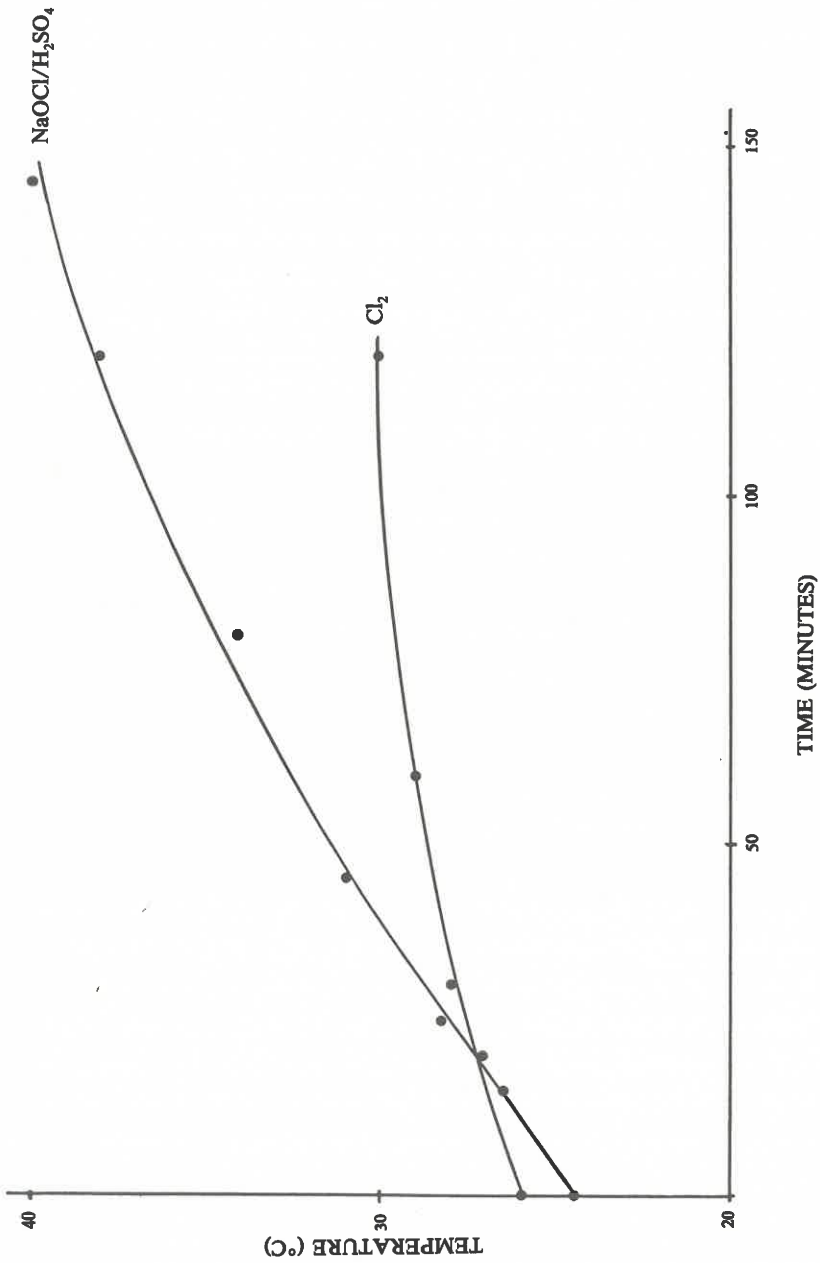Figure 1 — The pH of the chlorination liquor as a function of time

Figure 2 — *The temperature of the chlorination liquor as a function of time (no chiller was used)*
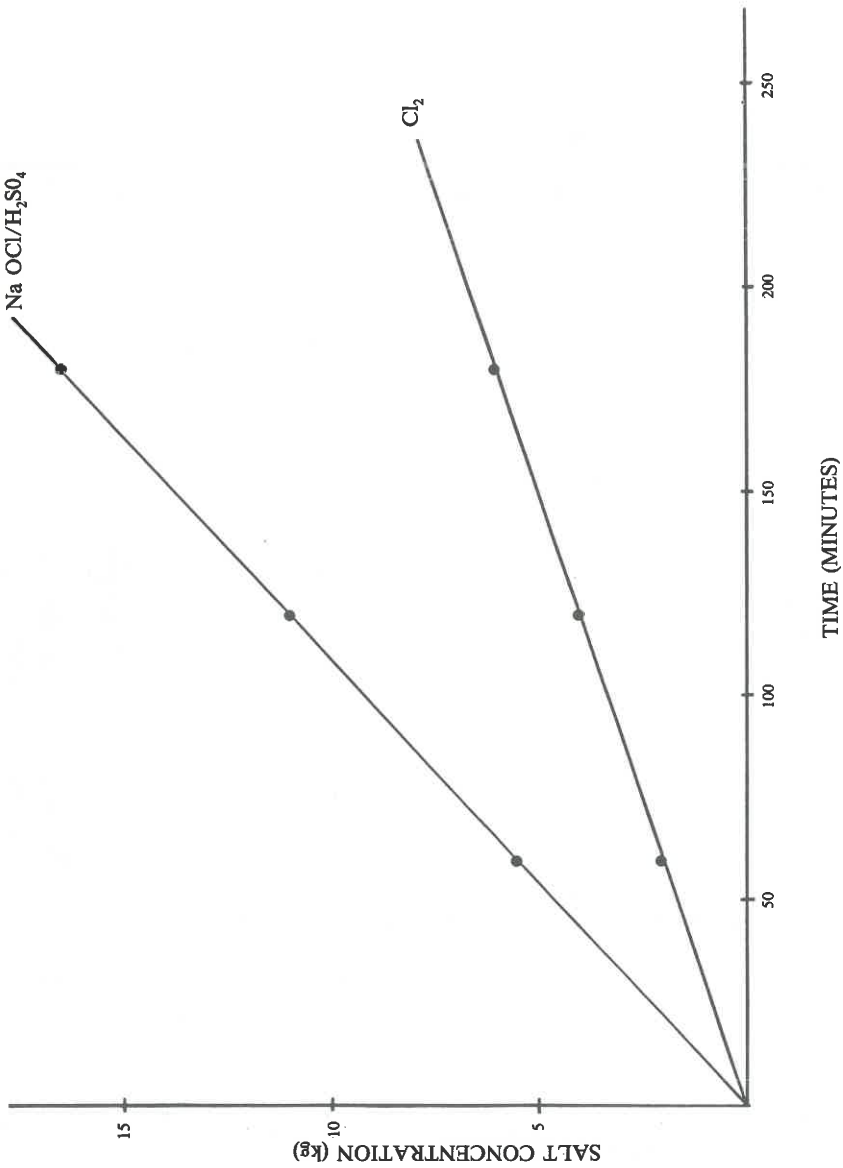
Figure 3 — Theoretical build-up of salt in chlorination liquor

Y-axis: SALT CONCENTRATION (kg)

X-axis: TIME (MINUTES)

Curves labelled: Na OCl/H$_2$SO$_4$ and Cl$_2$

was considerably slower than for the hypochlorite treatment.

The presence of salt in the chlorination bowl can adversely affect the efficiency of the chlorination treatment. Some results, given in Table 4, show that this is indeed the case. In this particular experiment three trials were carried out in water containing 0, 1,0 and 10,0% NaCl. The water in the chlorination bowl was charged with chlorine (0,4 g/L Cl_2), and the chlorine supply was then turned off. The wool tops were then continuously passed through the chlorination bowl and through bisulphite and rinse bowls, omitting the resin application. Each run lasted 6 minutes and the wool was divided into three lots (i.e. representing treatments at the beginning, middle and end of the run).

TABLE 4

THE EFFECT OF VARIOUS CONCENTRATIONS OF NaCl IN THE CHLORINATION BOWL ON FELTING SHRINKAGE

Wool treated at	NaCl concentration (%)	% Shrinkage	
		Lot E (20,6 u)	Lot F (21,8 u)
Beginning of run	0	0	2
	1	5	12
	10	6	48
Middle of run	0	5	61
	1	36	63
	10	34	68
End of run	0	65	—
	1	65	—
	10	65	—

Table 4 clearly shows that there was a marked deterioration in the felting shrinkage of the wool when the chlorination was carried out in the presence of sodium chloride. Furthermore, the felting shrinkage generally increased when the salt concentration increased. It is also interesting to note that there was a significant difference between the two wool lots. This indicates that certain wools could be more sensitive than other wools to an increase in the salt concentration in the chlorination bowl using hypochlorite.

TABLE 5

THE SHRINKRESIST TREATMENT OF WOOL WITH Cl₂/HERCOSETT 125*

Cl₂ concentration (%)	% Shrinkage			
	Lot E (20,6 μ)	Lot G (20,8 μ)	Lot H (21,7 μ)	Lot I (22,9 μ)
1,0	14	39	38	47
2,0	5	8	11	6
3,0	0	0	2	2

*2% Hercosett was applied in all cases.

In further studies various other shrinkresist polymers were evaluated in conjunction with a chlorine gas pretreatment. The results obtained on ® Hercosett 125, which is most widely used at present in conjunction with the sodium hypochlorite/sulphuric acid pretreatment, are given in Table 5. It is clear that acceptable results were obtained on a wide variety of wools when 2% chlorine gas was used, followed by the application of 2% Hercosett. No problems were encountered at any stage of the shrinkresist treatment, nor in further processing of the wools up to and including spinning.

TABLE 6

THE SHRINKRESIST TREATMENT OF WOOL* WITH Cl₂/NOPCOBOND SWS 10

Cl₂ concentration (%)	Polymer concentration (%)	% Shrinkage
1,5	2,0	19
2,0	2,0	4
2,5	2,0	1
2,0	1,0	28
2,0	1,5	7
2,0	2,0	4

Table 6 shows the results obtained on another shrinkresist polymer, namely ® Nopcobond SWS 10. Two series of treatments were carried out. In the first the concentration of polymer was fixed at 2,0%, while the level of chlorination was varied. In the second the level of chlorination was fixed at 2,0%, while the concentration of Nopcobond was varied. The results clearly show that this polymer also produced acceptable results when used together with the chlorine gas pretreatment. When the concentration of the Nopcobond was fixed at 2%, a chlorination pretreatment at the 2,0% level gave acceptable results. On the other hand, it can be seen from the table that when the concentration of chlorine was fixed at 2,0%, about 1,5% polymer was in fact sufficient to produce acceptable felting shrinkage results.

In further work extensive industrial trials were carried out on full-scale commercial machines. These were carried out on a wide variety of wools using chlorine gas only or chlorine gas and polymers such as Hercosett and Nopcobond.

In the case of the treatments involving chlorine gas only, it was found that about 4,0% Cl_2 gave acceptable felting shrinkage results in most cases.

In the case of treatments with chlorine gas and Nopcobond SWS 10, 2,0% Cl_2 gas and 2% Nopcobond were used in all trials and gave acceptable shrink resistance. Furthermore, no problems were encountered in the subsequent processing and dyeing of these wools.

TABLE 7

THE SHRINKRESIST TREATMENT OF WOOL TOPS USING Cl_2 GAS AND HERCOSETT 125 ON AN INDUSTRIAL SCALE MACHINE

Cl_2 concentration (%)	Hercosett concentration (%)	% Shrinkage
1,8	2,25	7
2,0	2,25	5
2,25	2,25	4
1,8	1,75	11
2,25	1,75	3

In the case of treatments with chlorine gas and Hercosett 125 the concentrations of chlorine and resin were varied and the results are given in Table 7. It is clear that, for this particular wool, acceptable results were obtained in all cases, except for the lowest concentration of chlorine and Hercosett. A slight increase in the concentration of either of these probably would have been sufficient to give a completely shrinkresistant product.
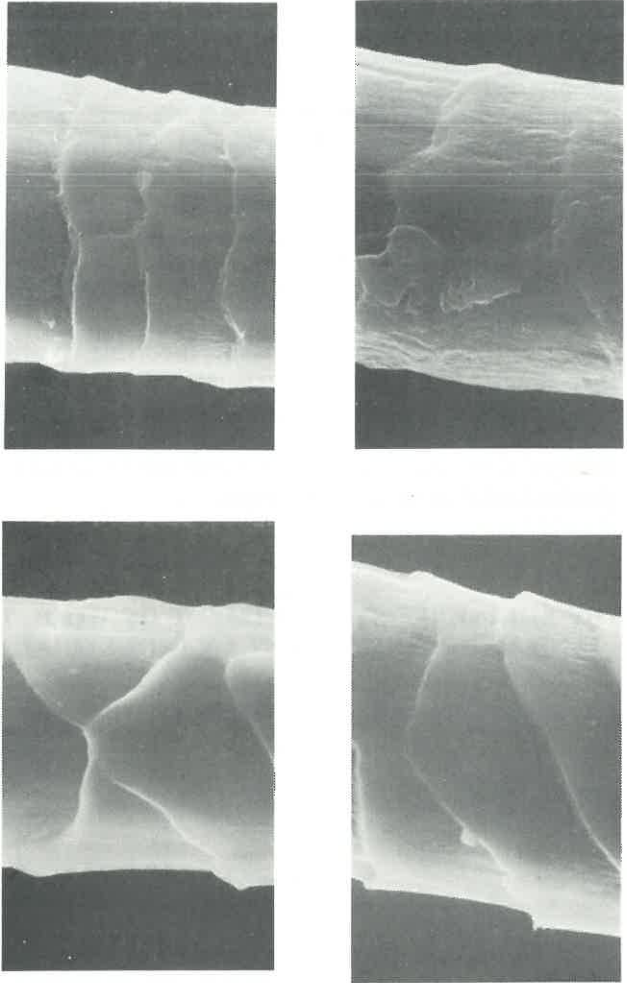
Figure 4 — SEM photographs of wool

Upper left : treated with 2,0% chlorine gas
Lower left : treated with 3,0% chlorine gas
Upper right: treated with 2,0% hypochlorite
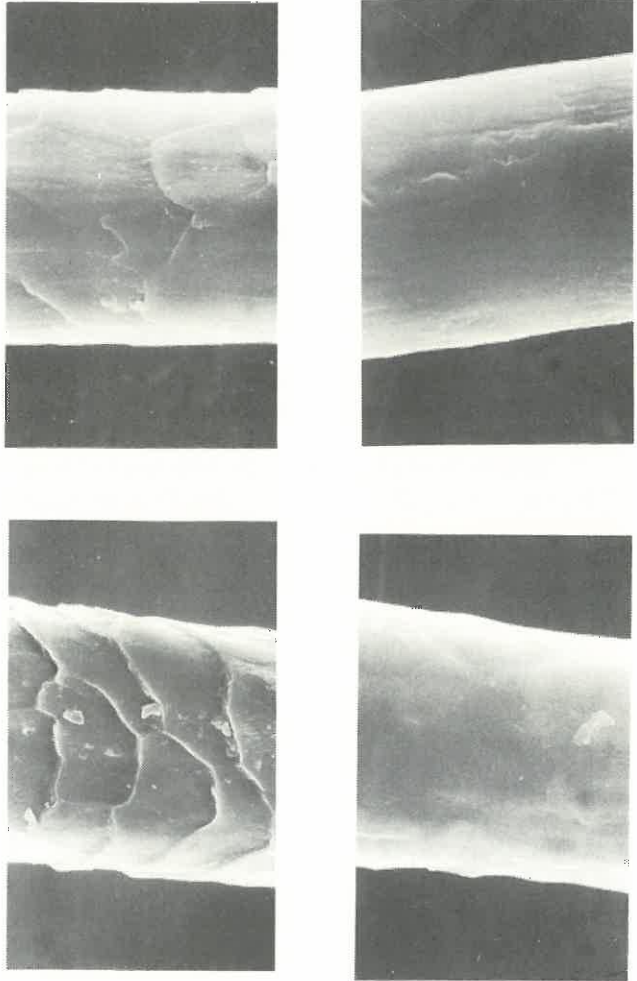Lower right: treated with 3,0% hypochlorite

Figure 5 — *SEM photographs of wool and mohair*

Upper left : Untreated wool
Lower left : Wool treated with 4,5% chlorine gas
Upper right: Untreated mohair
Lower right: Mohair treated with 4,5% chlorine gas

Apart from the treatment of wool slivers, it was also found that loose stock could be successfully shrinkresist treated using chlorine gas dissolved in water. In this particular case a pilot scale suction drum backwash was modified to facilitate the transport of the loose wool (20,6 u m.f.d, 38 mm m.f.l). The wool was treated with 2,5% Cl_2 and then dechlorinated with bisulphite and rinsed. It was then divided into two sub-lots. One was treated with 2% Hercosett in a loose stock dyeing machine, whereas the other was not treated with polymer. Both sub-lots were converted into 354 tex yarns on a DREF II spinning machine. (It was not possible to spin this very short wool on the Spinner-Twister). The yarns were then knitted into fabrics which were tested in the usual manner for 3 hours. The chlorinated wool shrank about 17% and the chlorine/Hercosett treated wool, about 3%.

Scanning electron microscope (SEM) studies were carried out on some of the shrinkresist treated wools. It was found that the treatment of wool with chlorine gas in water caused substantially less modification of the fibre surface than the treatment with sodium hypochlorite and sulphuric acid, for the same application level. Whereas most of the scales on the fibre appeared to be unaffected by the chlorine gas treatment, sodium hypochlorite caused some damage and often removed most of the scales. Some typical SEM photographs are shown in Figure 4.

Finally, it was found that the treatment of wool and other keratin fibres, such as mohair, with chlorine gas dissolved in water in a suction drum could enhance the lustre of the fibres significantly, especially when relatively high concentrations of chlorine (4% or more) were used. Some typical scanning electron microscope photographs of wool and mohair, both untreated as well as treated with 4,5% chlorine are shown in Figure 5. It is clear that the chlorine treatment removed practically all the scales from the fibres to produce highly lustrous products.

SUMMARY AND CONCLUSIONS

A series of pilot scale experiments were carried out on the continuous shrinkresist treatment of wool tops using chlorine gas dissolved in water in a conventional suction drum backwash. The process and equipment needed for the chlorination was relatively unsophisticated and is the subject of patent application. Details will be published at a later stage. An extraction system similar to that used for conventional hypochlorite treatments was used and the release of chlorine gas into the surrounding atmosphere was negligible.

Some pilot scale experiments were also carried out using the conventional hypochlorite/sulphuric acid chlorination treatment for purposes of comparison.

The chlorine gas pretreatment was used in conjunction with Hercosett 125, Nopcobond SWS 10 and acid colloid resins. Some experiments were also carried out on mohair and a number of experiments were carried out on loose

wool stock in a modified suction drum machine.

Pilot scale experiments were followed up with some industrial trials on full-scale commercial machines.

For the same application level, chlorine gas produced similar or better felting shrinkage results than the traditional hypochlorite treatment. Furthermore, chlorine gas produced less yellowing of the wool, as well as less modification of the scales of the fibre.

The temperature of the chlorination liquor increased at a considerably slower rate when chlorine gas was used than when sodium hypochlorite and sulphuric acid were used, and it appeared to stabilise at a much lower value. In fact, in most of the trials carried out at SAWTRI as well as in industry the ambient temperature varied from about 10°C to 26°C, and yet acceptable results were obtained despite the fact that no chiller was used. The efficiency of the chlorine gas treatment did not appear to be affected by the pH of the liquor and, in contrast to the hypochlorite process, the pH of the liquor did not have to be monitored or adjusted at all.

It was possible to carry out chlorination treatments for a considerably longer period with chlorine gas than with sodium hypochlorite, probably because of a much slower build-up of salt in the bowl. Implications for industry are that less frequent dropping of the bowl could reduce line stoppages so increasing output. Process control was very easy and the problems often associated with liquid metering pumps (corrosion and frequent breakdowns) were not encountered in the case of the chlorine gas treatments.

In the case of sodium hypochlorite the active chlorine content had to be determined on a daily basis due to the decomposition of the compound, whereas this procedure was obviated in the case of chlorine gas.

In conclusion, chlorine gas was used successfully in the chlorination bowl instead of sodium hypochlorite and sulphuric acid for pretreating wool in shrinkresist treatments with Hercosett 125, Nopcobond SWS 10 or an acid colloid polymer, and had both technical and economic advantages.

At relatively high concentrations (generally more than 4%), chlorine gas also increased the lustre of keratin fibres, including mohair.

cessing and Dyeing and Finishing Departments for their able assistance.

PROPRIETARY NAMES

The names of proprietary products where they appear in this report are mentioned for information only. This does not imply that SAWTRI recommends them to the exclusion of other similar products.

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