

⑫ **EUROPEAN PATENT APPLICATION**

⑳ Application number: **82305728.6**

㉑ Int. Cl.³: **D 06 M 3/08, D 06 M 15/54**

㉒ Date of filing: **28.10.82**

㉓ Priority: **28.10.81 ZA 817466**

㉔ Applicant: **SOUTH AFRICAN INVENTIONS
DEVELOPMENT CORPORATION, Administration
Building Scientia, Pretoria, Transvaal (ZA)**

㉕ Date of publication of application: **01.06.83
Bulletin 83/22**

㉖ Inventor: **Barkhuysen, Francois Albertus, of 6 Hatting
Road, Summerstrand Port Elizabeth (ZA)**
Inventor: **Van Rensburg, Nicolaas Jacobus Janse,
42 Louis Botha Crescent, Summerstrand Port Elizabeth
(ZA)**

㉗ Designated Contracting States: **DE FR GB IT**

㉘ Representative: **Lewin, John Harvey et al, Elkington and
Fife High Holborn House 52/54 High Holborn, London
WC1V 6SH (GB)**

㉙ **Shrink-resist treatment of wool.**

㉚ A method for the shrinkresist treatment of wool including the steps of chlorinating the wool with an acidified hypochlorite; dechlorinating the product; acidifying the product; and applying an acid colloid solution of suitable methylolmelamine resin to the product.

The chlorination is preferably carried out in a suction drum in such a manner that the level of active chlorine on the wool is in excess of 2% (m/m).

SHRINK-RESIST TREATMENT OF WOOL

THIS invention relates to the shrinkresist treatment of wool, particularly wool tops.

In this specification the term 'wool' will be used as also including wools blended with
5 other fibres.

Although there are numerous effective processes available for the shrinkresist treatment of wool fabrics, this is not the case with wool tops. This is mainly due to the
10 fact that the requirements for top treatments are much more demanding than those for fabric treatments.

One of the known processes for the shrinkresist treatment of wool tops was developed by
15 SAWTRI and was first described in SAWTRI

Technical Report No. 259 (August, 1975)
and CSIR Technical Brochure T1.13.10
(October, 1975).

The aforesaid process of SAWTRI (which
5 will hereafter be referred to as the
SAWTRI-process) and which constitutes the
subject matter of S A patent No 74/2248, as
well as several corresponding overseas pa-
tents, such as, for example, U S patent
10 3,994,681, entails the chlorination of wool
tops with a solution of the potassium or
sodium salt of dichloroisocyanurate (also
known as DCCA) in the presence of acetic
acid at pH 1,3 to 2,2 in a pad mangle;
15 dechlorination of the product in a solution
of sodium bisulphite/sodium bicarbonate;
rinsing in water; acidification of the

product in dilute acid; applying an acid
colloid solution of a suitable methylol-
melamine resin containing a polyethylene
softening agent to the product; drying the
5 treated wool tops; and curing the resin in
a drier.

Although the SAWTRI process proved to be
successful for the treatment of a wide
range of different wools, it has been found
10 not to be so in instances where the type of
wool requires chlorination at levels higher
than the approximately 2% (m/m) active
chlorine which is more or less the optimum
level possible with the SAWTRI process.

15 It is accordingly an object of this inven-
tion to provide an improvement to the SAWTRI

process with which the aforesaid shortcoming will be overcome or at least minimised.

According to the invention a method for the shrinkresist treatment of wool includes the
5 steps of chlorinating the wool with an acidified hypochlorite; dechlorinating the product; acidifying the product; and applying an acid colloid solution of a suitable methylolmelamine resin to the
10 product.

Preferably the dechlorinated product is rinsed before it is acidified.

Alternatively the rinsing and acidification steps may be combined into a single
15 step.

The chlorinated product may also be rinsed prior to the dechlorination step.

Preferably the method according to the invention comprises the SAWTRI process where-
5 in the conventional chlorinating agent i.e. DCCA and acetic acid, is replaced by acidified hypochlorite.

Further according to the invention the chlorination of the wool is carried out in a
10 manner to give an active chlorine treatment level in excess of 2,0% (m/m) of wool.

Still further according to the invention the chlorination of the wool is carried out in a suction drum.

Preferably the method includes the steps of chlorinating wool tops in a suction drum using an aqueous solution of a suitable hypochlorite which has been acidified to a pH of 1,2 to 2,2; dechlorination of the product with sodium bisulphite/sodium bicarbonate solution; rinsing the product in water; acidifying the product with dilute acetic acid; applying an acid colloid solution of a suitable methylol-melamine resin containing a suitable softening agent to the product; drying the product; and curing the resin at a temperature in the order of between 80° and 120° C.

15 Preferably the chlorinating agent comprises a solution of sodium hypochlorite which has been acidified with sulphuric acid.

Applicant has found that with the method according to the invention a level of chlorination (i.e. the amount of chlorine exhausted onto the wool) of up to 5,0% (m/m)

5 active chlorine is possible, depending on the type of wool being treated.

The acid colloid may be prepared by well-known processes from commercially available methylolmelamine resins, such as, for example, those normally used for the crease resist treatment of cotton fabrics. The softening agents may be commercial products such as, for example, those of the polyethylene type; Crosoft SW; etc. which are
15 compatible with the acid colloid resin and which do not cause precipitation or coagu-

lation of the resin bath. The ratio of acid colloid resin to softening agent is preferably in the order of about 2:1.

The method according to the invention is preferably carried out on a continuous basis employing a suction drum and a series of bowls such as those used in conventional backwashing machines in which case the method entails the following steps:

- 10 (i) Supplying sodium hypochlorite and sulphuric acid from storage tanks to the suction drum via metering pumps: the rate of addition being determined by the level of chlori-
15 nation required and the quantity of wool to be treated in a given time;

- (ii) Optionally passing the product into
a rinse bowl and rinsing with water;
- (iii) Passing the product to a dechlorina-
tion bowl containing an aqueous so-
lution of between 0,1 and 3,0% (m/v)
sodium bisulphite and between 0,1
and 3,0% (m/v) sodium carbonate and/
or bicarbonate to remove any residual
chlorine left on the wool;
- (iv) Passing the product into a rinse
bowl and rinsing with water to
remove any salts and other products
carried over from the preceding bowls;
- (v) Passing the product through a bowl
containing a dilute acid solution

(e.g. 2% CH_3COOH) to adjust its pH to a value which would prevent precipitation of the acid colloid resin;

(vi) Passing the product through a
5 bowl containing the acid colloid
resin and a suitable softening
agent in concentrations which would
give a final add-on of resin solids
onto the wool varying between 0,5%
10 and 3,0% resin; and

(vii) Drying the treated wool and curing
the resin at a temperature which
depends on the treatment speed, and
the specific drier being used
15 (typically a temperature of between
80° C and 120° C when the speed varies

between 1m/min and 15m/min).

It will be appreciated that, if required, suction drums may be employed instead of the aforesaid bowls. Also, where only a three-
5 bowl backwash system is available, the rinsing and acidification steps may be combined.

One embodiment of a method according to the invention will now be described by means of
10 the following example:

Example:

Alcopol 650 (Allied Colloids Ltd), a wetting agent which is resistant towards oxidising agents, is added to a
15 suction drum charged with water so that

the concentration of the solution in the drum with respect to the Alcopol is 0,1% (m/v).

Sodium hypochlorite and sulphuric acid are
5 then pumped into the bowl of the drum until the active chlorine content of the solution is 0,3 g/l and the pH 1,5.

Twelve wool tops are then continuously passed through the bowl of the suction drum
10 at a speed of 3 metre/minute and sodium hypochlorite is simultaneously pumped into the drum at a rate which effectively gives 3% active chlorine on the mass of the wool being treated and at the same time sulphuric
15 acid is pumped into the bowl of the drum to maintain the pH of the solution at approxi-

mately 1,5. The wool is then passed through squeeze rollers to remove the excess liquor, optionally rinsed in water, and then enters the dechlorination bowl where it is immersed in the (0,1 to 3,0% (m/v)) sodium bisulphite/ (0,1 to 3,0% (m/v)) sodium carbonate and/or bicarbonate solution. Thereafter the wool passes through squeeze rollers and into the rinse bowl where it is rinsed, followed by squeezing, after which it enters the acid bowl containing 2% (v/v) acetic acid. The wool then passes through a further set of squeeze rollers into the resin bowl containing an aqueous solution of 2,0% (m/v) acid colloid prepared from Cassurit HML (Hoechst Ltd) and 1,0% (m/v) Polythem N-40 (Textile Chemicals Ltd) as softening agent. The wool then passes

through squeeze rollers whereafter it is dried and the resin cured at 118°C. After conditioning, the tops can be processed further into yarn.

5 In table I some typical results obtained with the shrinkresist treatment of the present invention are compared with those obtained with the conventional SAWTRI process.

10 These results clearly reflect the improvement possible with the method of the present invention when compared with results obtained with the conventional SAWTRI process.

15 As can be noted, in the case of wool Lot HT it was necessary to increase the active

chlorine concentration to at least 3,5% before the treated product was able to pass the IWS TM 185 test. This concentration is significantly higher than the levels normally required for a wool of this diameter and a comprehensive study was carried out on this particular wool, varying the level of chlorination as well as the resin addon level. The results, given in Table II, show that for this particular wool the effect of chlorine concentration was much more pronounced than that of resin concentration. It is also clear that at least 3,5% chlorine and 1,2% resin were required for an acceptable degree of shrinkresistance. This is a very high level of treatment and it was

thought that it could have had an adverse effect on the strength of the wool.

Bundle breaking strength tests were therefore carried out on some of the

5 samples. The results, however, showed practically no difference between the untreated and shrinkresist treated wools (Table III). In some further studies the wool samples were dyed and the mass loss
10 after dyeing was determined. The results, given in Table IV, show an increase in mass loss when the level of chlorination was increased. The results also show that the resin offered some protection to the fibre
15 during dyeing, and that the mass loss decreased when the resin add-on level was increased.

As will be noted from Table V, it was found that the formaldehyde release of wool treated with the method according to the invention was well within the internationally acceptable limits and that the released formaldehyde level was less for increased curing temperatures and that backwashing of the treated wool reduced the level to below 100 $\mu\text{g/g}$ of wool in each instance.

It will be appreciated that the scope of the invention also extends to wool which has been shrinkresist treated by the method according to the invention as well as to yarns, and/or rovings and/or fabrics including such treated wool.

It will be appreciated further that there are many variations in detail possible with a method for the shrinkresist treatment of wool according to the invention, and the
5 products thereof, without departing from the scope of the appended claims.

TABLE I

THE FELTING SHRINKAGE OF DIFFERENT SHRINKRESIST TREATED WOOL

	WOOL TYPE NO.	FIBRE DIA- METER μ	PERCENT CL ₂	PERCENT RESIN	PERCENT SHRINKAGE
CONVEN-	LOT 220	21,1	1,5	1,9	24,0
TIONAL	LOT 220	21,1	2,0	1,8	22,0
SAWTRI	LOT HT	22,9	1,5	1,8	23,2
PROCESS	LOT HT	22,9	2,0	1,8	22,1
METHOD	LOT 220	21,1	2,50	1,8	3,0
ACCOR-	LOT HT	22,9	2,50	1,6	20,4
DING TO	LOT HT	22,9	3,00	1,6	12,2
THIS IN-	LOT HT	22,9	3,50	1,6	6,2
VENTION	LOT HT	22,9	4,00	1,6	0,0

THE EFFECT OF DIFFERENT LEVELS OF CHLORINE AND RESIN ON THE
FELTING SHRINKAGE OF WOOL LOT NO. HT
-A

PERCENT CHLORINE	PERCENT RESIN	PERCENT AREA SHRINKAGE
1.5	0.8	53.0
1.5	1.2	43.2
1.5	1.6	50.1
1.5	2.0	54.5
2.0	0.8	42.6
2.0	1.2	53.9
2.0	1.6	49.7
2.0	2.0	27.2
2.5	0.8	25.9
2.5	1.2	37.7
2.5	1.6	22.9
2.5	2.0	20.4
3.0	0.8	10.0
3.0	1.2	17.2
3.0	1.6	12.2
3.0	2.0	9.1
3.5	0.8	11.6
3.5	1.2	8.3
3.5	1.6	6.2
3.5	2.0	4.8
4.0	0.8	7.4
4.0	1.2	7.7
4.0	1.6	-0.7
4.0	2.0	5.0
UNTREATED CONTROL		55.7

TABLE III

THE BUNDLE BREAKING STRENGTH OF TREATED WOOL LOT NO. HT

TREATMENT	BUNDLE BREAKING STRENGTH (cN/TEX)	EXTENSION %
3.5 PERCENT CHLORINE/0.8 PERCENT RESIN	11.8	20.9
3.5 PERCENT CHLORINE/1.2 PERCENT RESIN	12.6	21.2
3.5 PERCENT CHLORINE/2.0 PERCENT RESIN	12.2	19.3
4.0 PERCENT CHLORINE/0.8 PERCENT RESIN	12.3	20.4
4.0 PERCENT CHLORINE/1.2 PERCENT RESIN	12.3	21.7
4.0 PERCENT CHLORINE/2.0 PERCENT RESIN	12.8	20.9
UNTREATED CONTROL	12.4	23.5

TABLE IV

THE MASS LOSS OF TREATED WOOL LOT NO. HT AFTER DYEING

TREATMENT PERCENT CHANGE IN MASS

PERCENT CL₂

PERCENT RESIN

1.5	1.2	-0.6
2.0	1.2	-1.9
2.5	1.2	-2.8
3.0	1.2	-3.7
3.5	1.2	-3.5
4.0	1.2	-4.0

4.0	0.0	-4.6
4.0	0.8	-4.1
4.0	1.2	-4.0
4.0	2.0	-3.5

UNTREATED CONTROL

1.5

TABLE V

THE FORMALDEHYDE RELEASE OF WOOL TREATED WITH THE METHOD
ACCORDING TO THE INVENTION

TREATMENT		FORMALDEHYDE ($\mu\text{g/g}$ WOOL)			
RESIN	DRY °C	CURE °C	AFTER TREATMENT	AFTER WASHING	
1.0 PERCENT CASSURIT HML	20C	-	643	38	
1.0 PERCENT CASSURIT HML	80C	-	673	44	
1.0 PERCENT CASSURIT HML	80C	100C	681	85	
1.0 PERCENT CASSURIT HML	80C	120C	425	60	
1.0 PERCENT CASSURIT MLP	20C	-	624	57	
1.0 PERCENT CASSURIT MLP	80C	-	679	62	
1.0 PERCENT CASSURIT MLP	80C	100C	742	80	
1.0 PERCENT CASSURIT MLP	80C	120C	573	76	
UNTREATED WOOL		LESS THAN 20			

CLAIMS:

1. A method for the shrinkresist treatment of wool including the steps of chlorinating the wool with an acidified hypochlorite;
5 dechlorinating the product; acidifying the product; and applying an acid colloid solution of a suitable methylolmelamine resin to the product.
- 10 2. The method of claim 1 wherein the dechlorinated product is rinsed before it is acidified.

3. The method of claim 1 wherein the acidification step is combined with a rinsing step.
4. The method of any one of claims 1 to 3 wherein the chlorinated product is rinsed before the dechlorination step.
5. The method of any one of the preceding claims which differs from the conventional SAWTRI process in that the chlorinating agent, i.e. DCCA and acetic acid, is replaced by acidified hypochlorite.
6. The method of anyone of the preceding claims wherein the chlorination of the wool is carried out in

a manner to give an active chlorine treatment level in excess of 2,0% (m/m) of wool.

5 7. The method of any one of the preceding claims wherein the chlorination of the wool is carried out in a suction drum.

10 8. A method for the shrinkresist treatment of wool including the steps of chlorinating wool tops in a suction drum using an aqueous solution of a suitable hypochlorite which has been acidified to a pH of 1,2 to 2,2; dechlorination of the
15 product with sodium bisulphite/
sodium carbonate and/or bicarbonate

5 solution; acidifying the product
 with dilute acetic acid; applying
 an acid colloid solution of a
 suitable methylolmelamine resin
 containing a suitable softening
 agent to the product; drying the
 product; and curing the resin at a
 temperature in the order of 80°C
 to 120°C.

10 9. The method of claim 8 wherein the
 dechlorinated product is rinsed be-
 fore it is acidified.

 10. The method of claim 8 wherein the
 acidification step is combined with
 a rinsing step.

15 11. The method of anyone of claims 8-10
 wherein the chlorinated wool is rin-

sed with water prior to the dechlorination step.

12. The method of any one of the preceding claims where the chlorinating agent is a solution of sodium hypochlorite which has been acidified with sulphuric acid.
13. The method of any one of the preceding claims wherein the acid colloid comprises an aqueous solution of between 0,5 and 2,0% (m/v) of a suitable resin such as Cassurit HML or Cassurit MLP or Aerotex M3 together with between 0,25 and 1% (m/v) of a suitable softening agent such as, for example, Polythem N40, Crosoft SW etc..

14. A method for the shrinkresist treatment of wool on a continuous basis employing a suction drum and a series of conventional back washing bowls and/or suction drums including the steps of:

(i) Supplying sodium hypochlorite and sulphuric acid from storage tanks to the suction drum via metering pumps; the rate of addition being determined by the level of chlorination required and the quantity of wool to be treated in a given time;

(ii) Optionally rinsing the product with water;

- 5 (iii) Passing the product to a
dechlorination bowl con-
taining an aqueous solu-
tion of between 0,1 and 3,0%
(m/v) sodium bisulphite
and between 0,1 and 3,0%
(m/v) sodium bicarbonate
and/or carbonate to remove
any residual chlorine left
10 on the wool;
- 15 (iv) Passing the product into a
rinse bowl and rinsing it
with water to remove any
salts and other products
carried over from the
preceding bowls;
- (v) Passing the product through

a bowl containing a dilute acid solution (e.g. 2% CH_3COOH) to adjust its pH to a value which would prevent precipitation of the acid colloid resin;

- (vi) Passing the product through a bowl containing the acid colloid resin and a suitable softening agent in concentrations which would give a final add-on of resin solids onto the wool varying between 0,5% and 3,0% resin; and

(vii) Drying the treated wool
and curing the resin at
a temperature which depends
on the treatment speed, and
the specific drier being
used (typically a tempera-
ture in the order of 80 °C
to 120 °C when the speed
varies between 1m/min and
15m/min);

10 15. A method of shrinkresist treating
wool substantially as herein des-
cribed with reference to the exam-
ple.

15 16. The product of the method of any
one of the preceding claims.

17. Yarns and/or roving and/or fabrics
containing the product of claim 16.