

United States Patent Office

3,062,610

Patented Nov. 6, 1962

1

3,062,610

PROCESS FOR SHRINKPROOFING WOOL

Wallace S. Russon, Chelmsford, Mass., assignor to Kroy Unshrinkable Wools, Limited, Toronto, Ontario, Canada, a corporation of Ontario, Canada
No Drawing. Filed Feb. 10, 1959, Ser. No. 792,275
8 Claims. (Cl. 8—128)

This invention relates to a process for treating wool to render it shrinkproof or non-felting.

It is well known that wool fabric will shrink in two ways when washed. Relaxation shrinkage is due to change in the position or contraction of stitches of the knitting or weaving and to relaxation of the tension of the yarn. This may be overcome by stretching to the original size; but felting due to surface friction or engagement of the scales or platelets on the individual wool fibers is permanent.

Many processes have been developed to overcome the tendency to felting by altering the platelets or surface structure of the wool by chemical treatment. Many of these processes involve treatments which chlorinate the wool and some of these processes, such as the process described in the McLauchlan Patent 2,671,006 have been successful on a continuous basis. Chlorination has no effect on shrinkage due to fiber or fabric relaxation.

Under some conditions, batch processes are preferable for treating some wool fabrics or mixtures of wool and vegetable or synthetic fibers, but these processes have been subjected to a number of difficulties and disadvantages.

Among the difficulties and disadvantages of the prior practices are yellowing of the wool, extensive scale distortion which impairs the structure of the wool and actually weakens and embrittles the fibers, damage to the wool evidenced by marked increase in alkali solubility, harshness in the hand of the wool, difficulty in obtaining uniform results, unevenness of dyeing when the treatment was of undyed wool, and changes in color when applied to dyed wool.

With these things in mind, it is an object of this invention to provide a new process of treating wool fabrics or mixtures of wool and vegetable or synthetic fibers, particularly for batch treatment but not necessarily limited thereto, which will:

- (1) Afford control of the extent of physical and chemical change of the wool;
- (2) Permit more reliable and controlled development of non-felting properties;
- (3) Minimize yellowing;
- (4) Increase the utility of the treated product;
- (5) Permit treatment of wool fabrics and other similar materials which include blends of various characters of wools, or blends of wools and other fibers;
- (6) Avoid causing harshness in the hand of the wool;
- (7) Avoid fiber damage and particularly avoid substantial increase in the alkali solubility of the wool;
- (8) Provide shrink resistance without serious color effects on properly chosen dyes and have a minimum influence on dyeing.

Other objects and advantages of the invention will become apparent as the details of the process are described.

I have found that an unusual and novel combination of chemicals produces a shrinkproof wool which is not otherwise materially altered.

According to the invention, the process is carried out in three successive stages in which the wool is subjected to treatments as follows.

1st: Pretreatment for about 10 minutes by immersion and movement within a bath containing sodium bisulfite.

2

2nd: A shrink-proofing treatment by chlorination, conducted in the bath by the addition of chemicals in three steps usually as parts of a previously prepared chlorinating solution, which parts differ in amount and are successively added to the bath at intervals over a time period totaling about 18 minutes while the bath is kept in an acid condition.

3rd: Anti-chlorination to neutralize and stop the chlorination by adding a sodium bisulfite solution directly to the chlorinating solution and moving the wool in the modified bath for about 30 minutes. Thereafter, the wool is rinsed in fresh water.

In carrying out the process, a batch of fabric is weighed and the wool content is calculated if the fabric is not all wool.

The fabric is then subjected to pretreatment by immersion and moving about in a bath containing from about 1% to about 4% on the weight of the goods of sodium bisulfite, but preferably about 2%. The treatment preferably is conducted in an acid range by adding formic acid to lower the pH of the bath to between about 3.0 and about 4.0 and is maintained at a temperature between about 56° F. and about 60° F., starting at 58° F. preferably. This temperature range is preferred as the temperature will rise to between 63° F. and 68° F. in succeeding stages of the process.

The fabric should be thoroughly cooled to 58° F. before starting the pretreatment. The water to goods ratio may be about 20 to 1 by weight and should be 30 to 1 when it is possible. The processing water should be at 58°–60° F. and not more than 60° F. at the start.

The starting bath is prepared as follows:

When the fabric is rotating, add 0.05% on the weight of the wool of a non-ionic wetting agent such as Cerfak 1400 (E. F. Houghton Co.) which is stable in the presence of the chemicals involved and at the concentration employed. (This amount can be reduced in the event that the fabric is already thoroughly wet out.) Then 1 to 4%, but preferably about 2%, on the weight of the wool of anhydrous sodium bisulfite is added and the pH of the bath is tested. The pH is adjusted to about 3.0–4.0 with formic acid. Formic acid may be added at any time to keep the pH within the 3.0 to 4.0 range, but the aim should be for 3.6 pH to 4.0 pH. Formic acid may not be necessary if the fabric is in an acid condition from a preceding finishing operation. With the chemicals in the bath and the pH between 3.0 and 4.0, the cloth is moved about or subjected to agitation in the bath from about 5 to about 15 minutes, but preferably for about 10 minutes.

Following this pretreatment, the wool is subjected to chlorination in the same bath by adding $\frac{2}{3}$ of a previously prepared hypochlorite ion containing solution made from an alkali or alkaline earth metal hypochlorite such as calcium, sodium and potassium, calcium being preferred. This solution is preferably prepared by dissolving, in a sufficient amount of water, high-test calcium hypochlorite in the amount of about 6% calculated on the weight of the wool containing approximately 70% available chlorine. When other compounds are used to supply the hypochlorite ions, they will be used in amounts to give equivalent amounts of available chlorine.

The wool is rotated in the bath or the bath is agitated for 5 or 6 minutes, but preferably about 6 minutes, to exhaust the chlorine; then $\frac{1}{2}$ of the remainder ($\frac{1}{2}$ of the whole hypochlorite solution) is added and the bath is run for 5 or 6 minutes more, but preferably about 6 minutes more.

Then the remainder of the hypochlorite solution is added and the bath is run for another 5 or 6 minutes, but preferably about 6 minutes. Thus, by the three succes-

sive additions of the hypochlorite, 4% on the weight of the goods is added by the first addition, 1% by the second and 1% by the third addition.

The first addition lowers the pH to about 3.0, or less in some instances, due to the formation of sulphuric acid and hydrochloric acid. The further additions increase the hydroxyl ions and the pH rises to 5 or 6. After each addition, the pH is quickly adjusted preferably to between 3.6 and 4.0. The aim should be to conduct the entire chlorination treatment with the pH between 3.0 and 4.0.

In lieu of adding the hypochlorite solution, the chemicals may be added in dry form directly to the bath in three additions of 4%, 1% and 1%, the process being otherwise the same as when fractions of the previously prepared solution are added.

Immediately at the end of the 18 minutes of the chlorination cycle, from about 1% to about 10% of sodium bisulfite calculated on the weight of the wool is added to stop the chlorination of the wool, but preferably from 1% to 4% approximately. The bath is not drained before this addition, but the bisulfite is added directly to the chlorinating solution.

The bath with the anti-chlor addition is run for approximately 15 to approximately 45 minutes depending on the weight of the fabric, i.e. whether a light-weight or a heavy-weight, and to some extent on the texture, and also on the concentration of the anti-chlor. At the end of that time, the machine is drained and the fabric is given a good running rinse with fresh water for at least 10 minutes and preferably for 20 to 30 minutes.

A cationic softener can be applied after the treatment, if desired.

The machine should not be stopped during the chlorination cycle and care should be exercised not to add the hypochlorite solution directly on the fabric.

The temperature of the bath throughout is between about 56° F. and about 68° F., but not more than 70° F.

The chemicals are all based on the weight of the wool disregarding and cottons or synthetic fiber in a blend.

The anti-chlor treatment (a) stops chlorination by tying any free chlorine to sodium making salt, and (b) bleaches the wool through reduction.

Although formic acid is most often used and preferred, other weak organic acids may be used, such as oxalic propionic glacial acetic, chloracetic, trichloracetic.

The following examples are illustrative of the invention as applied to particular fabrics.

Example 1

10 grams of wool fabric were pretreated for 10 minutes at 58° F. in a bath containing 0.05% Cerfak 1400 and 2% of sodium sulfite, both calculated on the weight of the goods, and enough formic acid to make the pH 4.0.

Then 6% on the weight of the goods of high-test calcium chlorite containing 70% available chlorine was dissolved in water and 2/3 of this was added to the treating bath and the goods were moved around for about 5 minutes to exhaust the chlorine. The pH was about 2.7. Then 1/2 of the remainder of the hypochlorite solution was added to the bath and stirred for about 5 minutes to exhaust the chlorine. The pH at this stage was 3.6. Then the remainder of the hypochlorite solution was added and the bath was stirred for about 5 minutes to exhaust the chlorine. The pH was 5.5, but was immediately adjusted to 4.0 with formic acid. The temperature was 60° F. The total chlorination time was 15 minutes.

The chlorination was followed by an anti-chlor treatment as above described using 10% sodium bisulfite on the weight of the wool for 20 minutes.

The fabric subjected to this treatment was white (not dyed). The white cloth was not yellowed by the treatment. The stability to machine washing was excellent. The hand was good.

The alkali solubility of the treated cloth averaged

22.5% in contrast with 19.0% untreated. This is within the 6% allowed by the Federal and commercial standards. Tensile strength (warp) of the treated woven fabric was 57.7 lbs. average in contrast with 55.5 lbs. untreated; and the tensile strength (fill) was 58.5 lbs. average treated, in contrast with 48.7 lbs. average untreated.

Example 2

In this experiment, the following fabrics were treated in a bath of the same composition as the previous example.

Grey mix spinnaker shirt fabric, knitted
Pink St. Mary's blanket, woven

The shrinkage control as tested by machine washing for 2 1/2 hours at 100° F. with soap showed the following results.

Sample	Percent Total Shrinkage After 1st Wash	Percent Total Shrinkage After 2nd Wash	Percent Shrinkage Due 2nd Wash
Spinnaker Shirt, Knitted:			
Not Treated—			
Wales.....	18.6	25.0	6.4
Courses.....	7.4	9.4	2.0
Treated—			
Wales.....	3.7	2.5	-1.2
Courses.....	-3.7	-3.7	0.0
Pink Woven Blanket Cloth:			
Not Treated—			
Warp.....	19.0	21.4	2.4
Filling.....	21.4	27.4	6.0
Treated—			
Warp.....	1.2	1.2	0.0
Filling.....	4.2	3.7	-0.5

In an experiment duplicating the procedure of Example 1 except for increasing the time to 18 minutes in the chlorination step at three intervals of 6 minutes each, it was found that the most rapid chlorine exhaustion occurs during the first and second minutes after the hypochlorite is added. The exhaustion rate then tapers until the sixth minute where approximately 75% of the available chlorine is exhausted or utilized.

Since this 75% exhaustion produces a satisfactory treatment, there is nothing to be gained by running to complete chlorine exhaustion which might actually be detrimental to the wool since the longer contact in chlorine solution would allow the chlorine to penetrate deeper into the fibers and cause damage. A good chlorination treatment alters the surface scale structure of the wool, but does not penetrate into the fiber itself to an appreciable extent.

A dry run of the treatment with no wool present showed that much of the chlorine in the first addition of the hypochlorite during the chlorination step was tied up probably as sodium chloride and was not available for action on the wool. The next two additions of the hypochlorite produced a sharp increase in the available chlorine showing that an overbalance of the system had been caused. This excess chlorine reacts on the wool imparting shrinkage resistance to nullify the felting shrinkage potential of the wool.

Example 3

A sample of undyed coat cloah was treated for 10 minutes in a bath having a water ratio of 30:1 at temperatures of 58°-64° F. from start to finish and containing 2% sodium bisulfite and also 0.05% Cerfak 1400 wetting agent. The bath was kept at a pH of 3.5-4.0.

In the second stage, a 6% calcium hypochlorite solution prepared as before was added as previously described in three steps over an 18 minute chlorination period. The bath was maintained at a pH of between 3. and 4. with formic acid.

In the third stage, anti-chlor consisting of 10% O.W.G.

5

sodium bisulfite was added and the bath was run for 30 minutes.

Then the sample was rinsed in cold water for 15 minutes.

In a washing test, total shrinkage showed in percent:

	After 1st Wash	After 2nd Wash	Percent Felting in 2nd Wash
Warp-----	3	4	1
Fill-----	-1	-1	0

Alkaline solubility showed:

Untreated Percent Absolute Average Value	Percent Increase Due to Treatment
35.14	4.79

Stain test was satisfactory and hand and color were soft and white.

From these observations, it is also clear that by use of readily available chemicals wool fabrics can be made fully shrink-resistant, with little change in appearance. There is no less in tensile strength, and the wool does not stiffen in a drying or simulated semi-decating procedure. White wool comes out whiter and there is only a slight color change of some acid dyed wools.

The cost is low. The process can be completed in less than 1½ hours and is easily adjustable by merely changing the amount of hypochlorite while holding the bisulfite and pH constant.

Other tests have shown that with conditions the same as Example 3 except for percentage of calcium hypochlorite and the chlorination time, 4½% calciumhypochlorite on the weight of the wool and a chlorination period of only 12 minutes produced satisfactory results with knitted underwear fabric containing 50% cotton and 50% wool. This is considered to be due to a lesser felting potential in the blended fabric.

With heavyweight wools, the hypochlorite might conceivably have to be increased to 7 or 8%. Concentrations below 4% tend to undertreat while concentrations over 8% tend to overtreat. Therefore, I prefer to operate between those limits and preferably at about 6%.

Within the foregoing examples and limits, it will be observed that since the calcium hypochlorite contains 70% available chlorine, 4% on the weight of the wool means that 2.8% chlorine on the weight of the wool is present during the chlorination stage; and likewise at 8%, there will be 5.6% chlorine on the weight of the wool.

In a bath of 30:1 water to wool ratio, there will be available chlorine present from about 0.093% to about 0.186% on the weight of the solution, while in a 20:1 water to wool ratio, there will be chlorine present from about 0.14% to about 0.28% on the weight of the solution.

These amounts of chlorine in the solution during chlorination can be supplied by other chemicals, as mentioned, by additions in amounts calculated in advance to supply the desired chlorine.

In experiments on coat fabric in which the sodium bisulfite pretreatment was omitted and the hypochlorite was reduced to 4% on the weight of the goods, the degree of shrink resistance was found satisfactory, but the alkali solubility increase was 8.2% as opposed to 4.79% increase when the bisulfite pretreatment was used with a 6% on the weight of the goods hypochlorite solution. Moreover, the 4% treated sample was yellow and harsh whereas the 6% with the bisulfite treatment was white and soft.

From these observations, it is clear that the pretreat-

6

ment with bisulfite is clearly advantageous and a marked improvement over prior art practices.

What is claimed is:

1. A method for imparting shrink-resistance to wool containing fibrous textile materials which comprises agitating said material in an aqueous bath containing as essential ingredients from about 20 to about 30 parts water to one part wool by weight and between about 1% and about 4% on the weight of the wool of sodium bisulfite, at a pH between about 3 and about 4, from about 5 to about 15 minutes to impregnate said wool with an anti-chlor solution, adding to said bath between about 2½% and about 5½% on the weight of the wool of a hypochlorite selected from the group consisting of hypochlorous acid, the alkali metal hypochlorites, and the alkaline earth metal hypochlorites, maintaining said bath at a pH between about 3 and about 4 and agitating said material in said bath for a further 5 to 6 minutes, then adding to said bath an additional ½% to 1½% on the weight of the wool of a hypochlorite as above identified and agitating said material in said bath for a further 5 to 6 minutes, then adding to said bath an additional ½% to 1½% on the weight of the wool of a hypochlorite as above identified and again agitating said material for 5 to 6 minutes and then stopping the chlorination.

2. The method claimed in claim 1 in which the chlorination is stopped by adding to the bath a solution containing from about 1% to about 10% on the weight of the wool of an anti-chlorinating agent and agitating the bath for from about 15 to about 45 minutes.

3. A method for imparting shrink-resistance to wool containing fibrous textile materials which comprises agitating the material in an aqueous bath containing as essential ingredients from about 20 to about 30 parts water to one part wool by weight and between 1% and 4% on the weight of the wool of sodium bisulfite at a pH between about 3 and about 4 from about 5 to about 15 minutes to impregnate said wool with an anti-chlor solution, then adding to said bath a hypochlorite selected from the group consisting of hypochlorous acid, the alkali and the alkaline earth metal hypochlorites which in solution will supply available chlorine in amount between about 0.093% and about 0.28% on the weight of the solution, such addition being made in three approximately equal time intervals of from about 5 to about 6 minutes each with the first addition being of about twice the quantity as the second and third, combined, and then stopping the chlorination.

4. The method claimed in claim 3 in which the chlorination is stopped by adding to the bath a solution containing from about 1% to about 10% on the weight of the wool of an anti-chlorinating agent and agitating the bath for from about 15 to about 45 minutes.

5. A method for imparting shrink-resistance to wool containing fibrous textile materials which comprises agitating the material in an aqueous bath containing as essential ingredients about 20 parts water to one part wool by weight and between 1% and 4% on the weight of the wool of sodium bisulfite at a pH between about 3 and about 4 from about 5 to about 15 minutes to impregnate said wool with an anti-chlor solution, then adding to said bath a hypochlorite selected from the group consisting of hypochlorous acid, the alkali and the alkaline earth metal hypochlorites which in solution will supply available chlorine in amount between about 0.14% to about 0.28% on the weight of the solution, such addition being made in three approximately equal time intervals of from about 5 to about 6 minutes each with the first addition being of about twice the quantity as the second and third combined, and then stopping the chlorination.

6. A method for imparting shrink-resistance to wool containing fibrous textile materials which comprises agitating the material in an aqueous bath containing as essential ingredients about 30 parts water to one part wool by weight and between 1% and 4% on the weight of the

7

wool of sodium bisulfite at a pH between about 3 and about 4 from about 5 to about 15 minutes to impregnate said wool with an anti-chlor solution, then adding to said bath a hypochlorite selected from the group consisting of hypochlorous acid, the alkali and the alkaline earth metal hypochlorites which in solution will supply available chlorine in amount between about 0.093% to about 0.186% on the weight of the solution, such addition being made in three approximately equal time intervals of from about 5 to about 6 minutes each with the first addition being of about twice the quantity as the second and third combined, and then stopping the chlorination.

7. A method for imparting shrink-resistance to wool containing fibrous textile materials which comprises agitating the material in an aqueous bath containing as essential ingredients from about 20 to about 30 parts water to one part wool by weight and between 1% and 4% on the weight of the wool of sodium bisulfite at a pH between about 3 and about 4 from about 5 to about 15 minutes to impregnate said wool with an anti-chlor solution, then adding to said bath a hypochlorite selected from the group consisting of hypochlorous acid, the alkali and the alkaline earth metal hypochlorites which in solution will supply available chlorine in amount of about 0.14% to about 0.21% on the weight of the solution, such addition being made in three approximately equal

8

time intervals of from about 5 to about 6 minutes each with the first addition being of about twice the quantity as the second and third combined, and then stopping the chlorination.

8. The method claimed in claim 7 in which the chlorination is stopped by adding to the bath a solution containing from about 1% to about 10% on the weight of the wool of an anti-chlorinating agent and agitating the bath for from about 15 to about 45 minutes.

References Cited in the file of this patent

UNITED STATES PATENTS

1,639,704	Richter et al. -----	Aug. 23, 1927
1,781,415	Smith et al. -----	Nov. 11, 1930
1,883,193	Wells -----	Oct. 18, 1932
2,017,985	Opfermann et al. -----	Oct. 22, 1935
2,178,649	Schuber -----	Nov. 7, 1939
2,307,137	Kennedy -----	Jan. 5, 1943
2,351,718	Speakman -----	June 20, 1944
2,671,006	McLauchlan -----	Mar. 2, 1954

OTHER REFERENCES

Moncrieff: Wool Shrinkage and Its Prevention, The National Trade Press Ltd., London, 1953, pages 283 and 340.