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PROCESS OF RENDERING WOOL UNSHRINKABLE

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This invention described herein may be manufactured and used by or for the Government for governmental purposes, without the payment to us of any royalty thereon.

This invention relates in general to chlorination processes and more particularly has reference to a process for rendering wool and similar substances unshrinkable.

It is well known that materials fabricated from wool and similar animal fibres have the undesirable property of shrinking when subjected to conditions such as are incurred in washing the material. The desirability of a practical and efficient method of rendering the wool or similar substance non-shrinkable is obvious.

Previous to this time, the processes generally followed for treating the wool to prevent the shrinking thereof when subjected to conditions such as those encountered in washing have involved the chlorination of the same in an aqueous medium. In the processes heretofore employed, substances such as acidified solutions of bleaching powder and hydrochlorous acid solutions have been used as chlorinating agents.

These treatments heretofore practiced, have been attended with numerous disadvantages, the foremost among which is that the wool or other material is usually damaged while undergoing treatment. When, for example, wool is treated with an aqueous solution of bleaching powder, acidified with strong mineral acids, under the conditions necessary for commercial practice, it is difficult, if not impossible, to avoid the presence of free chlorine in the bath. Free chlorine, as is well known, causes damage to wool even when present in very small quantities. It will be appreciated, therefore, that a reagent containing a minimum amount of free chlorine is desirable.

If hypochlorous acid solutions in the absence of free chlorine are employed, better results are obtained than if the chlorination is effected with solutions of bleaching powder acidified with strong mineral acids. The preparation of pure hypochlorous acid solutions, however, requires such exceeding care to avoid the presence of free chlorine as to render the process employing the same impractical. Also, such solutions are unstable and undergo decomposition with a consequent deterioration in the chlorinating power of the solution.

It will be appreciated, therefore, that any process for effecting the chlorination of wool and similar materials to render the same unshrinkable, which avoids the disadvantages inherent in the

processes heretofore developed, is of decided value.

An object of this invention is to provide a process for rendering wool unshrinkable.

Another object of this invention is to provide a process for rendering wool unshrinkable, in which chlorine may be fixed in the wool in either large or small quantities.

Another object of this invention is to provide a process for treating wool, in which chlorine may be fixed therein without damage to the wool.

Yet another object of this invention is to provide unshrinkable wool and similar materials.

A further object of this invention is to provide a process for rendering wool unshrinkable, in which chlorine may be fixed in the wool for a substantial time.

A still further object of this invention is to provide a method for chlorinating wool and like material by subjecting the material to the action of an organic chlorinating agent.

With the above and other objects in view, the invention consists in the method and product to be hereinafter set forth and claimed, with the understanding that the several necessary substances and compounds employed in our invention and the several steps may be widely varied with respect to proportions and relations without departing from the spirit of the invention or the scope of the claims.

In order to more clearly set forth the invention, specific procedures and compounds will be described in detail, but we wish it to be clearly understood that the scope of the invention is not to be limited to the particular steps and compounds herein set forth.

This invention consists in general of treating wool with an organic chlorinating agent so as to render the same unshrinkable. The process consists in treating the wool with a suitable stable hypochlorite or a stable hypochlorite in solution with a diluent. After treatment, the material may be dechlorinated.

The introduction of less than 1% of chlorine into woollen fabric is sufficient to prevent shrinking of the material when subjected to normal washing. In order to render wool unshrinkable when washed at high temperatures, however, it is necessary to introduce higher percents of chlorine into the same.

By the process hereinafter described, we are able to introduce either small or large quantities of chlorine into the wool, to suit the particular requirements for which the cloth is intended.

We have found that certain organic hypochlo-

rites are very efficient chlorinating agents for permanently fixing chlorine on wool without damage to the same. We have found particularly that tertiary alkyl hypochlorites are very effective for this purpose. As an example of our invention, we have immersed woolen material in sufficient tertiary butyl hypochlorite to cover the same, for one-half hour at a temperature of 40° C. and found after washing with carbon tetrachloride that the chlorinated cloth contained about 1½% of active chlorine fixed therein. The chlorine content may be determined by titration of the iodine liberated by a known weight of chlorinated wool from an acidified solution of potassium iodide, and the same calculated on the basis of one chlorine atom as the equivalent of two atoms of iodine.

The speed of the chlorinating reaction may be controlled by allowing the moisture in wool under treatment to come to equilibrium with that in an atmosphere of a definitely controlled relative humidity previous to carrying on the process. In carrying on the foregoing process, the moisture in the material was allowed to come to equilibrium with an atmosphere having a controlled relative humidity of 81% at 25° C. This may be accomplished by suspending the wool over a saturated solution of ammonium sulphate in an enclosed chamber for approximately twenty-four hours, or until the moisture in the material has come into equilibrium with the humidity of the atmosphere therein at the desired temperature. Of course, any other method of controlling the moisture content of the fabric may be employed. The speed of the chlorinating reaction may be increased by raising the moisture content of the material, or decreased by lowering the moisture content.

The following specific examples are set forth as illustrative of the effect that the moisture content of the wool has on the speed and extent of a chlorinating reaction carried on in accordance with this invention.

Relative humidity	Time, hours	Temperature, ° C.	Active chlorine in the wool
Percent 67	2	40	Percent 2.4
81	½	40	1.6
81	1½	40	5.3

It will be seen from the foregoing tabulation that as high as 5% of active chlorine may be introduced into woolen material. This may be accomplished without causing any appreciable damage to the material.

If it is desired, the material may first be impregnated with an acid buffer, such as, for example, sodium acetate. This treatment accelerates the chlorination reaction and allows a greater amount of chlorine to be introduced into the wool or similar material without any damage thereto.

In carrying on the process with sodium acetate, the wool or other material under treatment is immersed in a 1% solution of sodium acetate to incorporate the same therein to the extent of 1½ times the weight of the material. The quantity of the solution in the material may be regulated by wringing or other methods. After this treatment, the material is dried, leaving an amount of the acid buffer in the material, equal to 1½% by weight of the material. The moisture content of the dry impregnated wool may then

be regulated by allowing it to come to equilibrium with the moisture in an atmosphere having a relative humidity of 81% at 25° C. After this treatment, the humidified wool is immersed in a solution of tertiary butyl hypochlorite at 34° C. for four hours.

The following specific examples will serve to illustrate the effect of impregnating with sodium acetate previous to the chlorinating reaction on the speed and extent of the reaction when subsequently exposed to a chlorinating agent.

Sodium acetate impregnation	Relative humidity	Time, hours	Temperature, ° C.	Active chlorine in the wool
Percent 1½ 0	Percent 81 81	1 2½	34 34	Percent 3.8 2.6

The following tabulation will serve to illustrate the effect of temperature and time on the speed and extent of the reaction.

Relative humidity	Time, hours	Temperature, ° C.	Active chlorine in the wool
Percent 75	18	24	Percent 3.5
67	2	40	2.4
81	½	40	5.3

By first impregnating with an acid buffer, it may be possible to fix as high as 8% of active chlorine, by weight, in the wool without causing any appreciable damage thereto.

It will be appreciated that it is not necessary to introduce such a high amount of chlorine into wool in order to render the same unshrinkable. Smaller amounts of active chlorine may be fixed in the material under treatment by decreasing the moisture content of the wool, the temperature, time of chlorination, and by diluting the chlorinating agent with a diluent, such, for example, as carbon tetrachloride.

Also, it is to be understood that the invention is in nowise limited to the sole use of tertiary butyl hypochlorite as a chlorinating agent, as other organic hypochlorites, such as, for example, tertiary amyl hypochlorite, may be employed to advantage without damaging the material under treatment. In fact, it is deemed that any stable organic hypochlorite or other compounds having the characteristic properties thereof, may be used.

If, for example, tertiary amyl hypochlorite is employed, the material under treatment may be immersed in the same at a temperature of 34° C. for two hours, sufficient solution being used to cover the same. The material, if desired, may then be removed and washed with any suitable inert solvent, such, for example, as carbon tetrachloride. By this method, as high as 4% of active chlorine may be fixed in the wool. The foregoing reaction may be accelerated and a larger amount of chlorine introduced into the material without damage thereto by first impregnating it with an acid buffer such as sodium acetate, as previously described with reference to the use of tertiary butyl hypochlorite.

In carrying on a treatment of this character with tertiary amyl hypochlorite, the same procedure as already set forth in the use of tertiary butyl hypochlorite is followed, previous to immersion in the chlorinating bath. The humidified fabric is then immersed in tertiary amyl hypo-

chlorite and maintained at 34° C. for one hour. In following this treatment, as high as 5% of active chlorine by weight, may be fixed in the wool without any appreciable damage thereto.

In treating to render the material unshrinkable, subsequent usage should be considered to determine the process most suitable for effecting the desired results, that is, whether the material will be later subjected to what may be termed normal or low temperature washing, or to high temperature washing where shrinkage of wool and similar material is most likely to occur.

In the first instance, where the material will be normally washed, it has been found that a solution of tertiary butyl hypochlorite in a diluent, such as carbon tetrachloride, may be advantageously employed. In this instance, the material under treatment may be immersed in a 50% solution by weight, of tertiary butyl hypochlorite in carbon tetrachloride at a temperature of 40° C. for one-half hour.

It is deemed desirable to use only enough solution to cover the wool or woollen material, so as to render the process as commercially practical as possible. The material thus chlorinated is removed from the bath and may be washed with a relatively inert solvent and, if desired, may be subsequently subjected to a dechlorinating process after washing. Also, the chlorinated material may be treated directly with a dechlorinating agent with the elimination of the step of washing, or if so desired, the material may be removed from the chlorinating bath and dried in any desired manner without further treatment.

In treating wool for rendering the same unshrinkable even when subjected to subsequent washing at high temperatures, it may be desirable to first impregnate the same with an acid buffer such as sodium acetate and subject the same to an atmosphere of a controlled relative humidity in order to obtain a definite moisture content. After the above mentioned preliminary treatment which has been hereinbefore described in detail, the material to be treated is immersed in the chlorinating bath.

In following this treatment, the wool or other material, having previously been impregnated with sodium acetate and humidified as described with reference to the hereinbefore mentioned processes, is immersed in a solution of a tertiary alkyl hypochlorite at 34° for one hour, and after removal from the bath, may be treated as hereinbefore described, or dried in any desired manner without further treatment. The wool or other material under treatment, if subjected to any one of the foregoing processes may, after chlorination, be subjected to a dechlorinating bath, which may consist of sodium bisulphite, sodium thio-sulphate or any similar dechlorinating solutions. An immersion over a period of approximately five minutes in a one to five percent solution of a dechlorinating agent, such, for example, as sodium bisulphite will remove a large part of the active chlorine.

If deemed desirable, the wool after removal from the chlorinating bath may be washed with a relatively inert solvent such as water or carbon tetrachloride. If dechlorination is employed, the washing step precedes the dechlorination, but if desired it may be effected subsequent thereto.

To illustrate the wide variation to which the described processes may be subjected without any detrimental effect on the results, the following example is given.

Wool or similar material may be treated with

about 1½% of sodium acetate solution as described elsewhere in this specification. After this treatment, the material may have its moisture content regulated to desired value. A suitable moisture content may be obtained by subjecting the material to an atmosphere of 81% relative humidity at 25° C. It has been found that after a preliminary treatment as described above, desirable results can be obtained by subjecting the material for one and one-half hours at a temperature of 46° C. to the action of a solution of tertiary butyl hypochlorite in carbon tetrachloride, containing about 6% by weight of tertiary butyl hypochlorite. After chlorination, the material may or may not be subjected to any of the subsequent treatments hereinbefore described.

It has been found that approximately 1½% of active chlorine may be fixed in the material by the foregoing procedure.

The results obtained employing either of the two chlorinating compounds herein described are so similar that it is possible to substitute the tertiary butyl hypochlorite for the tertiary amyl hypochlorite mentioned in the examples of practice described, or to substitute tertiary amyl hypochlorite for the tertiary butyl hypochlorite mentioned in the described examples of practice.

For purposes of illustration, the acid buffer solution has been described as being of a specific concentration. It should be understood, however, that the concentration may be varied over a wide range and yet the solution will be effective for its intended purpose. The variation is also applicable to the quantity of solution taken up in the material.

Also, relative humidities of rather definite and specific percentages have been mentioned. In this instance, we wish it to be understood that the chlorination may be carried on either without first subjecting the material to a conditioning atmosphere or by subjecting it to atmospheres of widely varying moisture contents.

It will be appreciated that the present invention provides a wool or similar substance which may be subjected to conditions encountered in washing without the disadvantage of shrinking.

There is accomplished by this invention, improved processes for the chlorination of wool and similar materials to render the same unshrinkable without causing appreciable damage thereto by treating with an organic hypochlorite of suitable stability. Also, the chlorine may be fixed on the material in either large or small quantities.

While in describing our process, we have specifically mentioned two tertiary alkyl hypochlorites, we wish it to be clearly understood that other tertiary alkyl hypochlorites having chlorinating properties similar to those herein described in detail may be employed.

In the foregoing description, the processes and product have been mentioned in connection with wool and similar materials. The process is, of course, applicable to other fibers of animal and other origins which may be rendered non-shrinkable by chlorination.

While we have described the preferred embodiment of our invention, we wish it to be understood that we do not confine ourselves to the precise steps or ingredients set forth herein by way of illustration, as it is apparent that many changes and variations may be made therein by those skilled in the art, without departing from the spirit of the invention or exceeding the scope of the appended claims.

We claim:

1. A process of rendering wool unshrinkable, comprising chlorinating the wool with tertiary butyl hypochlorite.
2. A process of rendering wool unshrinkable, comprising chlorinating the wool with tertiary amyl hypochlorite.
3. A process of rendering wool unshrinkable comprising chlorinating the wool with tertiary butyl hypochlorite, and subsequently treating the same with a dechlorinating agent.
4. A process of rendering wool unshrinkable comprising chlorinating the wool with tertiary amyl hypochlorite, and subsequently treating the same with a dechlorinating agent.
5. A process of rendering wool and similar material unshrinkable, comprising treating it with tertiary butyl hypochlorite in a diluent.
6. A process of rendering wool and similar material unshrinkable, comprising treating it with tertiary amyl hypochlorite in a diluent.
7. A process of rendering wool unshrinkable, comprising treating it with an acid buffer and subsequently chlorinating it with tertiary butyl hypochlorite.
8. A process of rendering wool unshrinkable, comprising treating it with an acid buffer and subsequently chlorinating it with tertiary amyl hypochlorite.
9. A process of rendering wool and similar material unshrinkable, comprising subjecting the material containing its normal water content under usual atmospheric conditions, to chlorination with tertiary butyl hypochlorite.
10. A process of rendering wool and similar material unshrinkable, comprising subjecting the material containing its normal water content under usual atmospheric conditions, to chlorination with tertiary amyl hypochlorite.
11. A process of rendering wool unshrinkable, comprising establishing a definite moisture content in the wool, and chlorinating the same with tertiary butyl hypochlorite.
12. A process of rendering wool unshrinkable, comprising establishing a definite moisture content in the wool, and chlorinating the same with tertiary amyl hypochlorite.
13. A process of rendering wool unshrinkable, comprising treating the wool in 1% solution of sodium acetate, to the extent of 1½ times the weight of the wool, subsequently drying whereby 1½% of sodium acetate is deposited on the wool, treating it with tertiary butyl hypochlorite, and subsequently washing with a relatively inert solvent.
14. A process of rendering wool unshrinkable, comprising treating the wool in 1% solution of sodium acetate to the extent of 1½ times the weight of the wool, subsequently drying whereby 1½% of sodium acetate is deposited on the wool, treating it with tertiary butyl hypochlorite in a diluent and subsequently washing with a relatively inert solvent.
15. A process of rendering wool unshrinkable, comprising treating the wool with a solution of sodium acetate to the extent of about 1½ times the weight of the wool, subsequently drying whereby the sodium acetate is deposited in the wool, treating it with tertiary butyl hypochlorite in carbon tetrachloride, and subsequently washing with a relatively inert solvent.
16. A process of rendering wool unshrinkable, comprising treating it with an acid buffer, subjecting the wool to an atmosphere of a definitely controlled relative humidity, treating it with predetermined parts by weight of tertiary butyl hypochlorite and carbon tetrachloride, and subsequently washing it with a relatively inert solvent.
17. A process of rendering wool unshrinkable comprising treating it with an acid buffer, establishing a definite moisture content in the wool, subjecting the wool to treatment with tertiary butyl hypochlorite, and subsequently treating the material with a dechlorinating agent.
18. A process of rendering wool unshrinkable comprising treating it with an acid buffer, establishing a definite moisture content in the wool, subjecting the wool to treatment with tertiary amyl hypochlorite, and subsequently treating the material with a dechlorinating agent.
19. A process of rendering wool unshrinkable comprising treating it with an acid buffer, establishing a definite moisture content in the wool, subjecting the wool to treatment with tertiary butyl hypochlorite, washing the material with a relatively inert solvent, and subsequently treating it with a dechlorinating agent.
20. A process of rendering wool unshrinkable comprising treating it with an acid buffer, establishing a definite moisture content in the wool, subjecting the wool to treatment with tertiary amyl hypochlorite, washing the material with a relatively inert solvent, and subsequently treating it with a dechlorinating agent.
21. A process of rendering wool and similar material unshrinkable comprising establishing a definite moisture content in the wool, chlorinating the wool with a tertiary hypochlorite of the alkyl series consisting of tertiary amyl hypochlorite and tertiary butyl hypochlorite and then dechlorinating to remove the free chlorine.
22. A process of rendering wool unshrinkable comprising chlorinating the wool with a tertiary alkyl hypochlorite of the group consisting of the tertiary amyl hypochlorite and tertiary butyl hypochlorite.
23. A process of rendering wool unshrinkable comprising chlorinating the wool with a tertiary alkyl hypochlorite of the group consisting of tertiary amyl hypochlorite and tertiary butyl hypochlorite and then treating with a dechlorinating agent.
24. A process of rendering wool unshrinkable comprising treating it with an acid buffer and subsequently chlorinating it with a tertiary alkyl hypochlorite of the group consisting of tertiary amyl hypochlorite and tertiary butyl hypochlorite.
25. A process of rendering wool unshrinkable which comprises establishing a moisture content in the wool equivalent to that which would be obtained by allowing the wool to reach a stabilized moisture content in an atmosphere of 67% or upward relative humidity at 25° C., and then chlorinating the wool with a stable hypochlorite of the group consisting of tertiary butyl hypochlorite and tertiary amyl hypochlorite.
26. The invention as defined in claim 25, wherein the moisture content of the wool is equivalent to that obtained by allowing the wool to reach a stabilized moisture content in an atmosphere of substantially 81% at 25° C.

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