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PROCESS FOR THE TREATMENT OF WOOL

No Drawing.

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This invention relates to a method for the treatment of wool, especially in the form of woollen fabrics or garments and the like, whereby it may be rendered substantially non-shrinkable without any appreciable or detrimental alteration of its desirable characteristics.

In the manufacture of woollen fabrics and garments it is a matter of common experience that, after being given their final form, they exhibit a tendency to shrink, especially upon being wet and dried as in the ordinary course of washing, laundering, etc. While some goods possess a greater tendency to shrink than others, which is the result of differences in the original wool, this tendency is greatly altered by the course of treatment to which they are subjected in manufacture and use. Such conditions are so numerous and so varied in character and in their relationships one to another that the ultimate results obtained present an infinite number of gradations with respect to the shrinkage characteristics of different lots of wool.

Efforts have been made to correct this difficulty by imparting to the original goods a substantial proportion of the shrinkage, so that any subsequent material alteration will be impossible. However, the processes adopted for this purpose heretofore have been so complex or so little understood that they are not amenable to control and consequently the results which are obtained by them present the objection of either progressing too far in their action upon the material treated or of not proceeding to a sufficient degree to have the desired effect.

For example, it is a well-known fact that chlorine water, obtained by saturating water with chlorine gas, has a vigorous reaction upon wool which renders it free, in large measure, from subsequent shrinkage by wetting. However, this reaction whatever may be the nature of its mechanism, is extremely rapid in its operation upon the wool, results in a very pronounced discoloration thereof, is not subject to control, and invariably leaves a degenerated structure in the fibre

which becomes weak and generally undesirable or actually unfit for use.

At the present time in current practice, chlorine water is not ordinarily used upon wool or woollen materials for this purpose, preference being given to the use of a hypochlorite or bleaching powder solution which is acidified with an excess of mineral acid, such as hydrochloric or sulfuric, for the liberation of hypochlorous acid. The latter is considered as the effective constituents and is usually referred to in terms of its equivalent in free or "available chlorine." The fabric is treated by immersing it in the hypochlorite solution as thus prepared or may be passed successively through a solution of the hypochlorite and then through a solution of the acid. In either event, it is subsequently washed free from the reagents employed and after being given a so-called "dechlorinating treatment" with a reducing agent such as bisulfite solution, it is finally dried.

Such treatment, while constituting an improvement over the use of chlorine water, is extremely rapid in its action upon the wool fibers, whereby the reactivity of the solution is rapidly reduced. Moreover, as a result of its rapidity, the different portions of the solution are reduced by the material at different rates, and the treated material is consequently of variable characteristics throughout the area of its treated surface. The product which is ordinarily obtained by such processes, therefore, is either too lightly affected or "chlorinated" so that it is not, in fact, proof against subsequent shrinkage,—or the chlorination has gone too far and resulted in the discoloration or deterioration of the fibres. In practice, both results may be evident in the same piece of goods. The value of the finished goods is accordingly diminished rather than improved by this treatment which depends for its success upon the vigilance of the operator as well as numerous factors which are not wholly known or which are at least beyond his control.

It is therefore an object of the present invention to provide a process for the treatment of wool which shall serve to render the treated

material substantially non-shrinkable under the subsequent conditions of use and wear to which it is normally subjected and which shall at the same time permit the positive control of the degree and uniformity of the hypochlorite effect to be imparted thereto.

It is a further object of the invention to provide a solution which shall be suitable for effecting this purpose through a regulatable course of reaction upon the wool.

It has been discovered, as a part of this invention, that while the desirable effect of hypochlorite solution upon wool is difficult or impossible to control in acid solution, it may be controlled in an alkaline solution and that such control is related to or a function of the hydroxyl ion concentration present. However it is not for this reason to be presumed that the hydroxyl ion is of itself the active agent in producing the effect which is obtained upon the wool fibres; it may be of importance in this connection, but it serves also as an index of the ionized condition or status of the solution as a whole, and as a determinant of the reaction requirements, to be mentioned later.

A further important element of the invention comprises a mode of controlling such concentration and also the relative concentrations of the hypochlorous acid as well as of the products of reaction, hydrolysis, and ionization which, through whatever form or agency they may operate, constitute the effective elements of the solution in imparting the desired non-shrinking properties to the wool treated therewith.

In the more general aspects of its adaptation to actual practice, the invention therefore comprises a process of subjecting wool or materials made therefrom to the action of a solution, preferably containing a readily soluble hypochlorite, which is not acidic, but which is neutral or alkaline, and in which the concentration of hydroxyl ion is adjusted to within a predetermined range of values, and maintaining the concentration within said range during a substantial portion at least of the reaction period.

By extensive experiments, substantiated by the results obtained in actual practice, it is now also discovered that the effect of hypochlorites or alkaline solutions of chlorine upon wool, reaches an optimum influence for satisfactory operation when the hydroxyl ion concentration lies between 10^{-2} and 10^{-7} molal equivalent per liter.

Within this range of hydroxyl ion concentrations, however, it is discovered that there is a preferred range of values (lying between 10^{-3} and 10^{-5} molal equiv. per liter) at which solutions possessing such values are more effective in use and generally more satisfactory in the results which may be obtained therewith.

Without attempting any theoretical expla-

nation of why this is so, since the precise nature of the modification or alteration of the wool is itself at present unknown in the art, it may be qualitatively stated that while the concentration of the hydroxyl ion in its higher values beyond the range above stated, tends to repress this action almost to the vanishing point, the presence of what may be termed free acid or hydrogen ion, even in very moderate excess, accelerates it inordinately and to such a degree that the effect produced is entirely out of control in practical operations. Intermediate these extremes, however, lies the range of values, already mentioned, within which a satisfactory product may be confidently expected.

It is an essential element of the present invention that we have discovered that an alkaline hypochlorite solution whatever its chlorine value may be brought to and maintained within the above stated range of values by adding thereto a suitably selected electrolyte (which preferably will not induce precipitation, for example, or decompose the hypochlorite) characteristically a weak acid, a salt of a weak acid and a strong base, a salt of a weak base and a strong acid, a salt of a weak base and a weak acid, or an amphoteric salt. As typical representatives of such compounds may be cited carbonic acid sodium bicarbonate, ammonium sulfate, ammonium carbonate, and sodium aluminate, respectively. A particularly satisfactory group of such compounds for use in the process under consideration may be defined as the mono-substitution products or acid salts of weak polybasic acids.

As a preferred embodiment of the invention, its application will be described with respect to the treatment of woollen garments in a solution of preferred characteristics and values, which are typical of those which have been shown to be adaptable for this purpose. For example, such a solution may comprise sodium hypochlorite containing a slight addition of sodium hydroxide, to which is added, before use, an excess of sodium bicarbonate. By excess is meant an amount greater than its molal equivalent of the free sodium hydroxide which is in the solution. The concentration may be widely varied in practice, depending upon the particular circumstances surrounding any given application, such as the nature and previous treatment of the material, but the following proportions are representative:

I { 1.85 gr. NaOCl per liter .025 mol.
 .2 gr. NaOH per liter 5×10^{-3} mol.

In such a solution, the concentration of hydroxyl ion will be substantially 5×10^{-3} mol per liter, and clearly falls within the generally desirable range of values.

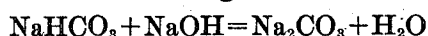
Should the hypochlorite solution be exces-

sively alkaline, as indicated, for example, by the following proportions.

II { 1.85 gr. NaOCl per liter .025 molal
20 gr. NaOH per liter .5 molal

the hydroxyl ion will be of the order of 5×10^{-1} , which is somewhat beyond the allowable range of concentrations.

If an addition of sodium bicarbonate is now made, for example to Solution II, there will be a substantially equimolal reaction of the sodium hydroxide therewith, in accordance with the following reaction:



and any excess of NaHCO_3 over that indicated will remain as such in solution. The ionization effect of these salts, per se, may be represented by the following equations which are written in terms of molal concentrations:

$$\frac{[\text{H}^+] \times [\text{CO}_3]}{\text{HCO}_3} = 6 \times 10^{-11} \quad \text{and} \quad \frac{[\text{H}^+][\text{HCO}_3]}{\text{H}_2\text{CO}_3} = 10^{-7}$$

From these and from the limitation imposed by the low solubility of H_2CO_3 , .1 mol per liter and the presence of a substantial concentration of NaHCO_3 , it will be apparent that the hydrogen ion concentration introduced by the reaction products will be equal to or below that of water itself. In other words, the addition of bicarbonate and formation of carbonate will not materially promote the acidity of the resulting solution, regardless of the absolute amounts in which they may be present.

Moreover, it goes to show that even if carbonic acid itself were added to such a solution, the hydrogen ion concentration of the saturated solution would not be materially altered thereby. Accordingly, the same will also be true of other weak acids of similar characteristics.

With respect to solutions of sodium hypochlorite such as that typified by Formula I in which the excess of NaOH or OH ion is initially within the concentration limits prescribed namely 10^{-1} to 10^{-7} , it is found that the addition of bicarbonate will tend to either increase or decrease this factor as the case may be and to cause it to approach the common logarithmic index (-4) as the molal concentration of hydroxyl ion per liter.

This tendency of sodium bicarbonate, which is also manifested in alkaline solutions of hypochlorites by the groups of electrolytes hereinbefore mentioned is termed "buffer action", and electrolytes which exhibit this phenomenon are herein referred to as "buffer electrolytes".

The result of these reactions may be summarized, in terms of their influence upon the treating solution, by saying that if the hypochlorite solution is acid, or if its hy-

droxyl ion concentration is beyond the range 10^{-1} to 10^{-7} , or in other words if it is too active or too inactive with respect to its effect upon the solution, for purposes of the regulated chlorination of wool, and a molal proportion of sodium bicarbonate, equivalent to the excess of hydroxyl or hydrogen ion present, is added thereto, the resulting solution will be brought within this range, and that if an excess of sodium bicarbonate be added beyond such an equivalent amount, the hydroxyl ion concentration will approach a value characterized by the function of 10^{-4} as a mean, which is found to promote the desirable effects of hypochlorite upon wool at a controllable rate and without accompanying or consequent reactions of a destructive character.

For example, a solution of sodium hypochlorite containing .05 mol of available chlorine per liter, which is substantially equivalent to .025 mol of the hypochlorite may contain 5×10^{-3} mol of free NaOH (Formula I). To this solution an excess (5×10^{-3} molal equivalent or more) of sodium bicarbonate may be added. When thoroughly dissolved and intimately mixed with the hypochlorite, the resulting solution, regardless of the absolute quantity of bicarbonate which may have been added above the amount stated, may be considered as automatically adjusted to within the proper range of hydroxyl ion concentration to effect a desirable anti-shrink treatment of the wool.

The woolen material, such as a woolen garment or the like, is then immersed in the solution and allowed to remain for a predetermined period of time, depending upon the degree of treatment desired, etc., which may be a matter of a few minutes only or up to an hour or more. However, ordinarily a sufficient treatment will be found to result in thirty minutes to an hour, with the solution mentioned. The exact length of time will be determined by experiment upon each lot of wool. It is then withdrawn, thoroughly washed, subjected to an acidified bisulfite solution, thoroughly rinsed with water and allowed to dry.

It will be observed that the period of reaction, or the time of treatment of the wool is appreciably extended beyond that in which an acid solution of hypochlorite completes its desired degree of reaction (a matter of seconds and on the other hand reduces the length of time which is required when the hypochlorite solution is appreciably alkaline (which is a matter of hours). Moreover, the resulting product will be found substantially devoid of the usual tendency to subsequent shrinkage under the conditions of use, wear, laundering, etc., which is ordinarily exhibited by wools which have been treated by the methods employed for this purpose heretofore. But more than this, it is found

- that the resulting product is of a higher quality both with respect to the physical and chemical characteristics of the individual fibres and to its æsthetic qualities such as color, feel, softness, uniformity of appearance and the like which are almost equally as important from the standpoint of commercial manufacture. Furthermore, there is the very significant advantage that the process may be controlled both as to the specific characteristics of the solution used and as to the rate and degree of the effect which the treatment will ultimately impart to the treated goods.
- 15 We claim:
1. A process for the treatment of woolen textiles and which comprises subjecting the same to a solution of a readily soluble alkali metal hypochlorite, said solution containing a hydroxyl-ion concentration between 10^{-3} and 10^{-5} molal equivalent per liter.
 2. A process for the treatment of woolen textiles which comprises subjecting the same to a solution of a readily soluble alkali metal hypochlorite, said solution containing a hydroxyl-ion concentration of substantially 10^{-4} molal equivalent per liter.
 3. A process for the treatment of wool in the form of woolen textiles which comprises subjecting the same to a solution of an alkali metal hypochlorite modified by the addition of an electrolyte, said electrolyte being a buffer electrolyte and substantially inert toward said hypochlorite.
 4. A process for the treatment of wool in the form of woolen textiles which comprises subjecting the same to a solution of an alkali metal hypochlorite and an electrolyte, said electrolyte being a salt of a weak acid and a strong base.
 5. A process for the treatment of wool in the form of woolen textiles comprising subjecting the same to a solution of an alkali metal hypochlorite and an electrolyte, said electrolyte being an acid salt of a weak polybasic acid.
 6. A process for the treatment of woolen textiles which comprises subjecting the same to the action of a solution of an alkali metal hypochlorite and a soluble bicarbonate.
 7. A process for the treatment of woolen textiles which comprises subjecting the same to the action of a solution of alkali metal hypochlorite and bicarbonate.
 8. A process for the treatment of woolen textiles which comprises subjecting the same to the action of a solution of sodium hypochlorite and a bicarbonate.
 9. A process for the treatment of woolen textiles which comprises subjecting the same to the action of a solution of sodium hypochlorite, sodium carbonate, and an excess of sodium bicarbonate.
 10. A solution for the treatment of wool comprising an alkali metal hypochlorite and an alkali metal bicarbonate, having a hydroxyl-ion concentration of 10^{-3} to 10^{-5} mols per liter.
 11. A solution for the treatment of wool comprising an alkali metal hypochlorite and an alkali metal bicarbonate, having a hydroxyl-ion concentration of substantially 10^{-4} mols per liter.
 12. An alkaline solution for the treatment of wool comprising an alkali metal hypochlorite, and an electrolyte, said electrolyte being a buffer electrolyte.
 13. An alkaline solution for the treatment of wool comprising an alkali metal hypochlorite, and an electrolyte, said electrolyte being a salt of a weak acid and a strong base.
 14. An alkaline solution for the treatment of wool comprising sodium hypochlorite, sodium carbonate and sodium bicarbonate.
 15. An alkaline solution for the treatment of wool comprising sodium hypochlorite, and sodium bicarbonate in excess.
- Signed by us at Boston, Massachusetts, this twenty-eighth day of May, 1924.
- LEIGHTON B. SMITH.
CHARLES E. RUBY.