PROCESS FOR BLEACHING AND SHRINK-PROOFING WOOL

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This invention relates to processes for the treatment of wool, and is more particularly concerned with an improved bleaching treatment for wool.

According to the invention, we provide a treatment of wool characterized by the fact that the wool is treated in the manner described below with a cold solution of acid chlorite until the wool turns rosy, after which the wool is bleached by means of a reducing solution. This treatment not only bleaches the wool but at the same time imports to it properties that cause it to be substantially unshrinking.

It has already been proposed to use a chlorite, such as sodium chlorite, for the purpose of bleaching wool. Unfortunately, however, numerous difficulties have been encountered, due, inter alia, to the fact that, in order to act, the chlorite must be in an acid medium but an acid chlorite bath has been found to modify the molecular constitution of the wool, which then assumes a more or less pronounced coloration ranging from pink to brown.

Attempts have been made to minimize the alteration of the wool by operating with cold solutions of acid chlorite, with a pH comprised between 4 and 5. This manner of operation, however, has not given complete satisfaction, the wool issuing from the bath not being entirely white, and still undergoing a certain shrinkage when washed. In addition, the acidity of the bath has had to be closely supervised in order to avoid any significant molecular modification which would bring about a pronounced coloration of the wool.

Other processes have been proposed which are concerned with reducing the duration of treatment by impregnating the wool with a cold solution of chlorite, followed by a hot treatment at about 90 to 95° C. with an acid bath for a very short time, e.g., a few minutes. Under these conditions, a more or less rosiness in the wool has been observed, which disappeared as a result of a subsequent reducing treatment.

This process, however, also has drawbacks, the most important of which is derived from the hot treatment in an acid bath. The duration of the passage in the acid bath must be very short and if the operation is badly timed, there is danger of causing an even more extensive alteration in the wool as a result of which the wool acquires a brown coloration which does not disappear upon subsequent treatment. On the other hand, at that temperature, the treating apparatus rapidly deteriorates for the reason that the commonly-employed materials of construction, notably the usual stainless alloys, are not resistant to acid chlorite. Finally, it is well known that solutions of acid chlorite give off, when hot, considerable quantities of chlorine dioxide (ClO₂), which is relatively poisonous, and this is an obviously-serious drawback.

The present invention makes it possible to avoid the drawbacks heretofore encountered and to obtain a white wool with minimum alteration as compared with wools treated in accordance with standard processes, which is evidenced by a moderate soda loss and by a barely perceptible decrease of dynamometric strength. Moreover, the wool treated according to the invention is partly unshrinking.

Wool is characterized by poly-peptidic chains formed by the union of a relatively large number of elementary α-amino acids. These amino acids are at least four in number and include cystine, methionine, tryptophane and tyrosine. We have found that, by the action of a solution of acid chlorite, some of these amino acid components of the wool are oxidized and become transformed into new compounds having very characteristic properties. In a cold acid medium, the solutions of chlorite cause the wool to turn pink. Under these conditions, cystine is transformed into a colorless sulphonic derivative. Methionine leads to a colorless oxidized product (very likely a sulphoxide). Tryptophane gives pink oxidation products, which may be brought to a colorless state and tyrosine appears to be unaltered.

Under the same conditions of pH and concentration, but at a temperature higher than 50° C., a different alteration of the wool is observed, the wool assuming in this case a yellow-brownish coloration. Cystine, methionine and tryptophane are oxidized in the same manner as in the cold bath, in addition, tyrosine is also attacked, leading to brown products, of the nature of polyhydroxy compounds which are greater the higher the temperature the longer the duration of the reaction or the lower the pH. The brown products are not reductible into colorless products. As a result, a wool so treated can no longer be rendered colorless by a reducing treatment or by an oxidizing treatment without risk of deteriorating.

Further, we have found that it is practically impossible to lock the oxidizable groups of the tyrosine of wool for the purpose of preventing it from becoming brown during the treatment without adversely weakening the wool fiber.

We have also found that, if the concentration of oxidizing agent, at the same pH and at the same temperature, the solutions of chlorine peroxide alone caused a more rapid brown coloration of the tyrosine component of wool.

We have, therefore, provided a process for chlorite treatment of wool which eliminates the drawbacks and disadvantages of processes heretofore known.

According to the process of the present invention, it is introduced into and submerged in a body of water and there is then gradually added to the water a dilute aqueous solution of an acid with continuous agitation of the body of water until a pH of 2-4.5, preferably 3.5, is reached. With continued agitation, there is then gradually introduced into the acidicified treating bath an aqueous chlorite solution of pH 8-9 and free from ClO₂ until the wool turns pink. Under these conditions we have observed that the pH of the chlorite solution is lowered without evolution of ClO₂ and the treating bath becomes totally colorless throughout the treatment. During this first operation, the wool turns pink as a result of the oxidation of the tryptophane. The pink wool is then rinsed with water and treated with a reducing solution which advantageously comprises either a bisulphite or a hydrosulphite, or a mixture of both.

The body of water into which the wool is immersed and the resulting treating bath are substantially at room temperature, i.e., a temperature of about 13 to 25° C., preferably 18-20° C. The treatment with the reducing solution, however, is carried out at a higher temperature and the reducing solution is advantageously at a temperature of 45 to 60° C., preferably about 50° C.

The acid employed to acidify the initial treating bath is a mineral acid, such as phosphoric acid or sulfuric acid, or an organic carboxylic acid, such as acetic acid or formic acid. In the case of acetic acid, it is advantageously used in combination with its alkali metal salt, i.e., sodium acetate, to serve as a buffer at the indicated pH. The acid is employed in the form of a dilute aqueous solution and is suitably in a concentration of about 5 to 20%, preferably about 7 to 10%, by weight. When
a buffer is used, generally 5 to 40% based on the weight of the undiluted acid is sufficient.

The chlorite introduced into the acidified bath is suitably an alkali metal chlorite, e.g. sodium chlorite, and is employed in aqueous solution of a concentration of 5 to 20%, preferably about 10%, by weight.

The reducing solution may be in the form of a bath into which the wool is immersed or it may be applied by impregnation. The reducing solution is an aqueous solution of a reducing agent such as an alkali metal bisulphite, e.g. sodium bisulphite, or an alkali metal hydroxysulphite, such as sodium hydroxysulphite, or a mixture of both bisulphite and hydroxysulphite. The reducing agent is advantageously present in the solution in a concentration of 0.2% to 1.5%, preferably 0.4% to 0.6%, by weight. After treatment with the reducing solution, the wool is thoroughly rinsed with water and dried.

Advantageously, a small amount, e.g. 0.02 to 0.1% by weight of a wetting agent is incorporated in the treating bath and in the bleaching solution. This wetting agent may be any of the known wetting agents such as a hydrophilic or oleophilic molecule adsorbed on strongly hydrophilic components. Suitable wetting agents include, for example, those sulfates and sulfonates represented by one of the following general structural formulæ:

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\begin{align*}
&\text{RCOOCH}_3\text{CH}_2\text{SO}_3\text{Na} \\
&\text{RCONHCH}_3\text{CH}_2\text{SO}_3\text{Na} \\
&\text{RCH}_2\text{SO}_3\text{Na} \\
&\text{RCH}_3\text{SO}_4\text{Na}
\end{align*}
\]

where \( R \) is an alkyl or alkenyl radical containing 12-20 carbon atoms.

Examples of suitable emulsifying agents of the character indicated are sodium stearamidoethylenesulphonate (\( \text{C}_1\text{H}_7\text{H}_2\text{CO.NH.CH}_2\text{CH}_2\text{SO}_3\text{Na} \)), sodium sulfoalkylsulphite (\( \text{C}_1\text{H}_7\text{H}_2\text{CO.CH}_2\text{CH}_2\text{SO}_3\text{Na} \)), sodium lauryl sulphate (\( \text{C}_1\text{H}_7\text{H}_2\text{CH}_2\text{SO}_3\text{Na} \)), sodium lauryl sotenate (\( \text{C}_1\text{H}_7\text{H}_2\text{CH}_2\text{SO}_3\text{Na} \)) and sodium olea-midoethyl-sulphonate (\( \text{C}_1\text{H}_7\text{H}_2\text{CO.NH.CH}_2\text{CH}_2\text{SO}_3\text{Na} \)). Examples of commercial forms of these compounds are the products sold under the trade names Igepon T, Igepon A, Igepon AP, Igepon AP Extra, Igepal C and Loral. As suitable wetting agents may also be mentioned the compounds of the alkylaryl sulphonate type sold commercially under names such as Nacconol NRSP and Santomem D, the alkyl phosphate salts, the sulphonamides and the sulfonamides as p-nitrophenyl disodium sulphisccinamate and the corresponding tetrasodium sulfoascinnamate, sold under the tradenam Aerosol. It will be understood, however, that other wetting agents may also be suitably used.

In a preferred form of the invention, hydroquinone is incorporated in the acid chloride treating bath. Hydroquinone, which is used in the amount of 0.005 to 0.05% based on the weight of the original body of water from which the bath is formed, has been found to have an activating action upon the chloride solution. When hydroquinone is used, a fully white wool is obtained as in the case when hydroquinone is absent and at the same time even the slightest tendency to deterioration of the wool is substantially eliminated. This is of particular value when the wool is to be subjected to subsequent treatments, e.g. to dyeing treatments or to an additional treatment to render it substantially fully non-shrinkable. The process of the present invention thus has particularly important advantages over known bleaching processes when it is desired to produce a highly non-shrinkable wool. Indeed, bleaching by means of chlorite as described above may advantageously be combined with an additional chlorination treatment or with a treatment with an enzyme effective to render the wool highly non-shrinkable.

For this latter purpose, a proteolytic enzyme such as papain, trypsin, etc. may be employed. It is particularly advantageous in this case to combine the reducing treat-
are placed in a stainless steel apparatus provided with a bath circulation device. 1000 liters of water are introduced, and then the quantity of acetic acid and sodium acetate necessary to bring the bath to a pH of 3.5. After 10 minutes of circulation, during which the wool uniformly absorbs the acid, there are added 2.5 kg. of sodium chloride in solution in 25 liters of water, and the mixture left under agitation for 1 hour at 20° C. The wool is then thoroughly rinsed in water and treated at 45° C. for 30 minutes in a bath containing 15 cc. per liter of a 30% solution of sodium bisulphite and 3 grams per liter of sodium hydrosulphite. Finally, the wool is thoroughly rinsed and dried.

Example 6.—100 kg. of combed wool are introduced into a stainless steel apparatus provided with bath circulation means and containing 1500 liters of water to which are successively added 0.5 kg. of a wetting agent (alkylarylsulphonate) and 5 kg. of 50% phosphoric acid in solution in 35 liters of water. After 10 minutes' agitation to distribute the acid thoroughly, 3.5 kg. of sodium chloride are introduced in solution in 35 liters of water. The reaction is continued for 1 hour at room temperature, after which the wool is rinsed and treated for 30 minutes in a bath containing 10 cc. per liter of a 30% solution of sodium bisulphite and 2 grams per liter of sodium hydrosulphite. The operation is terminated by a thorough rinsing and by drying.

Example 7.—7.7% of worsted wool are introduced into a stainless steel apparatus provided with bath circulation means. 1000 liters of water are introduced, and there are then added:

| kg. of a wetting agent (sodium lauryl sulfate) | 0.55 |
| kg. of hydroquinone                   | 0.2  |
| kg. sodium acetate                   | 1    |
| kg. acetic acid                      | 12   |
| kg. sodium chloride in 25 liters of water | 2.5 |

The reaction is allowed to proceed for one hour at ambient temperature after which the wool is rinsed and treated for 30 minutes at 45° C. in a bath containing 10 cc. per liter of a 30% solution of sodium bisulphite and 2 grams per liter of sodium hydrosulphite. Finally, the wool is thoroughly rinsed and dried.

Example 8.—50 kg. of worsted wool are introduced into a stainless steel apparatus, provided with a bath circulation device. 1000 liters of water, 0.5 kg. of a wetting agent (Na sulfoconyletholate), 3 liters of 50% phosphoric acid, in solution in 25 liters water, are added. After 10 minutes bath circulation, 1.5 kg. of sodium chloride in solution in 10 liters water are added, and the reaction is left under agitation for 1 hour to 20° C. The wool is then rinsed and treated for 30 minutes at 50° C. with a solution containing 10 cc. per liter of a 30% solution of sodium bisulphite and 2 grams per liter of sodium hyposulphite. The wool is then thoroughly rinsed and dried.

The wool is then ready for further chlorination to impart to it further unsinkable properties. In this case, it is treated with a bath of sodium hypochlorite containing 1.5% active chloride, and 8% of concentrated hydrochloric acid based on the weight of the fiber. The reaction is allowed to proceed for one hour at ambient temperature, the sodium hypochlorite being added gradually. Finally, the wool is rinsed and treated for 30 minutes at 45° C. in a bath containing 2 grams per liter of sodium hyposulphite. To finish, the wool is thoroughly rinsed and dried. The wool thus obtained is very white and fully shrink-proof.

Examples 9 and 10.—5 kg. of worsted wool are introduced into a stainless steel apparatus provided with a bath circulation device. 1000 liters of water are introduced, then 0.5 kg. of a wetting agent (alkylarylsulphonate) and 3 liters of 50% phosphoric acid diluted in 30 liters water. After 10 minutes, 2 kg. of sodium chloride in 25 liters of water are added and the reaction is left under agitation during 1 hour at 20° C. The wool is then rinsed, and treated for 30 minutes at 60° C. in a solution containing 10 cc. per liter of a 30% solution of sodium bisulphite, 2 grams per liter of sodium hydrosulphite, 5 kg. of bicarbonate of soda, and then 250 grams of papain introduced in this bath. The reaction is allowed to proceed for 30 to 60 minutes, at a temperature of 60° C., after which the wool is rinsed and dried. The reduction and the enzyme treatment may also be carried out in separate baths.

Example 10.—100 kg. of worsted wool are introduced into a stainless steel apparatus provided with a bath circulation device. 1500 liters of water are introduced, then 0.5 kg. of a wetting agent (sodium laurylsulphonate) and 5 kg. of 50% phosphoric acid diluted in 35 liters of water. After 10 minutes' agitation, there are added 3.5 kilos sodium chloride in solution in 35 liters of water. The reaction is continued for one hour at room temperature, after which the wool is rinsed and treated at 50° C. in 1,500 liters of water to which are added 15 liters of a 30% sodium bisulphite solution and 3 kg. of sodium hydrosulphite of soda. The reaction is allowed to proceed for 30 minutes, after which 6 kg. of bicarbonate of soda and 300 grams of papain are successively added, the treatment lasting one hour at 50 to 60° C. Finally, the wool is rinsed and dried. The wool subjected to the treatments described in detail in the preceding examples is white and is of a much higher grade than that which is obtained by treatment with acid bisulphite, without having the drawback inherent to the latter, i.e. wools which become yellow when stored. The white obtained by the process according to the invention is also comparable or even superior to that obtained by treatment with hydrogen peroxide, whereas it deals with the wool more gently. Thus, the loss of 9% with soda for raw wool never exceeds 15% after treatment according to the process of the invention, and even remains much lower than this latter figure when hydroquinone is used, whereas the loss with soda in the hydrogen peroxide treatment is never less than 19% for an equivalent white.

The dynamometric strength decreases very little and remains on the average greater than that of wool bleached with hydrogen peroxide.

Furthermore, the decrease in shrinkage on washing is substantial and by combining the chloride treatment with a standard chlorination or with an enzyme treatment as shown in the examples, a wool is obtained which is very white and totally unsinkable.

Finally, in accordance with the invention, the entire operation may be carried out in the same apparatus without any risk of corrosion, for the chloride treatment takes place rapidly at ambient temperature under safe conditions, since there is no emission of chlorine peroxide.

It will be understood that various changes may be made in the process as described above without departing from the scope of the invention as defined in the appended claims and it is intended, therefore, that all matter contained in the foregoing description shall be interpreted as illustrative only and not as limiting of the invention.

This application is a continuation-in-part of copending application Serial No. 357,633, filed May 26, 1933, now abandoned...

What we claim and desire to secure by Letters Patent is:

1. A process for bleaching and shrinkproofing wool with minimum alteration of the wool, which comprises introducing the wool in water, introducing progressively a dilute solution of an acid with continuous agitation until a pH of 2--4.5 is reached, containing agitation, introducing slowly an aqueous chlorite solution of pH 8--9 at a temperature below about 50° C. until the wool turns pink, whereby the pH of the chlorite solution is lowered without evolution of CI₂O₃ and the bath remains substantially colorless throughout the treatment, and treating the pink wool with a reducing solution, said introduction of the wool in water, said progressive introduc...
tion of dilute acid, said continued agitation, said slow introduction of aqueous chlorite solution of pH 8-9, and said treatment with a reducing solution being carried out seriatim.

2. A process as defined in claim 1, wherein said water is at a temperature of about 20° C. and treatment with a reducing solution is carried out at a temperature of about 50° C.

3. A process as defined in claim 1, wherein said acid is selected from the group consisting of inorganic acids.

4. A process as defined in claim 1, wherein said acid is selected from the group consisting of phosphoric acid and sulfuric acid.

5. A process as defined in claim 1, wherein said acid is selected from the group consisting of organic acids.

6. A process as defined in claim 1, wherein said acid is selected from the group consisting of acetic acid and formic acid.

7. A process as defined in claim 1, wherein said acid is added until a pH of 3.5 is reached.

8. A process as defined in claim 1, wherein said acid is employed in aqueous solution of a concentration of about 5 to 20%.

9. A process as defined in claim 1, wherein said chlorite solution has a concentration of 5 to 20%.

10. A process as defined in claim 1, wherein said reducing solution is selected from the group consisting of a bisulphite, a hydrosulphite and mixtures thereof.

11. A process for bleaching and shrinkproofing wool as defined in claim 1, wherein the reducing solution is a mixture of an alkaline bisulphite and an alkaline hydrosulphite.

12. A process for bleaching and shrinkproofing wool as defined in claim 1, wherein the acid solution of chlorite contains hydroquinone.

13. A process for bleaching and shrinkproofing wool as defined in claim 1, further comprising the step of treating the wool with at least one proteolytic enzyme.

14. A process for bleaching and shrinkproofing wool as defined in claim 1, further comprising the step of treating the wool with at least one proteolytic enzyme following the treatment with the reducing solution.

15. A process for bleaching and shrinkproofing wool as defined in claim 1, which further comprises treating the wool with a hypochlorite solution after treatment with the reducing solution and then treating the wool with a solution of alkaline hydrosulphite.

16. A process for bleaching and shrinkproofing wool as defined in claim 1, which further comprises treating the wool with a solution of alkaline hypochlorite.

17. A process for bleaching and shrinkproofing wool as defined in claim 1, wherein the reducing solution is an alkaline bisulphite.

18. A process for bleaching and shrinkproofing wool as defined in claim 1, wherein the reducing solution is an alkaline hydrosulphite.

19. A process for bleaching and shrinkproofing wool as defined in claim 18, wherein the proteolytic enzyme is papain.

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