

UNITED STATES PATENT OFFICE

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TREATMENT OF FIBERS OR FIBROUS MATERIALS CONTAINING KERATIN

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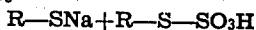
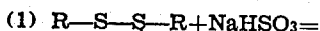
16 Claims. (Cl. 167—87.1)

This invention relates to improvements in the treatment of substances containing keratin, such as hair and wool, and is particularly concerned with treatments for the application of a permanent set to such substances or for the removal of stress from materials made from keratins such as wool and with the treatment of keratin materials in or before finishing operations.

The application is a continuation-in-part of my Patent No. 2,201,929.

Keratin-containing fibers are customarily subjected to steaming or hot water treatment in the presence of compounds which may include reducing agents at or only slightly below the boiling point for the release of strain and the application of a permanent set.

It has been proposed to treat wool or hair with a boiling bisulphite solution while tensioning the wool or hair. Such treatment at the boiling point will result in disruption of the disulphide bonds of keratin and the immediate formation of S—NH bonds as indicated by the following equations:



where R—S—S—R and R'—NH₂ represent the peptide and associated side chains of keratin. At or about the boiling point, the reactions take place with great readiness and a sufficient number of linkages to impart a permanent set to the fibers is formed in so short a time that the process is commercially useful. At lower temperatures, however, the rate of formation of linkages as represented by Equation (2) above, is so small that a permanent set is not obtained in a reasonable time, and low-temperature setting is impracticable.

The object of the present invention is to provide a treatment whereby release of strain and permanent set are obtained over a range of temperatures appreciably below the boiling point of water and especially down through temperatures to as low as room temperature where desired.

The invention consists in treating fibrous substances containing keratin, such as wool or hair, with a solution of a sulphite, or acid sulphite, such as a bisulphite or a metabisulphite, at a temperature appreciably below the boil to effect reduction and disruption of the constituent disulphide or cystine bonds of keratin with the formation of sulphydryl groups, and then while maintaining the substance in a formation which it is desired to render permanent, causing the

formation of further disulphide bonds in or between the fiber molecules by subjecting the fibrous substance to the action of an oxidising agent.

The invention further consists in treating fibrous substance containing keratin, such as wool or hair, while maintained in a formation which it is desired to render permanent, with sulphite solutions at or about pH 6 at a temperature of from 50°–70° C. whereby the disulphide or cystine bonds of keratin are disrupted and further linkages represented by R—SNH—R are formed spontaneously in or between the fiber molecules.

In all cases the invention differs essentially from the prior processes of treating keratin-containing fibers with sulphites or bisulphites at the boiling point in that release of strain in the keratin-containing fibers is brought about at much lower temperatures, for example not higher than 70° C.

The conditions for disruption of disulphide bonds of keratin are very favourable at pH 6, pH 4, and at or above pH 10. At the first pH value, the salt linkages between the peptide chains are most stable, relaxation in strained fibers is delayed, and disulphide bonds remain in a state of strain for a longer time, in which condition they are more readily reduced by acid sulphite solutions, while at pH 4, bisulphites and metabisulphites produce pronounced fiber swelling, which favours relaxation and may be further developed by employing a high content of an agent adapted to reduce ionisation of the salt and increase swelling, for example, a soluble alcohol, such as ethyl alcohol, glycerol, ethylene glycol or ethylene glycol monomethylether.

Sulphite solutions at pH 10 or above are effective owing to their alkalinity, alkalies being capable of attacking unstrained as well as strained disulphide bonds of keratin, forming sulphydryl and sulphenic acid groups by hydrolysis, which latter groups are reduced by the sulphite to sulphydryl groups.

In accordance with the invention, release of stress in keratin-containing fibers is brought about by disruption of the disulphide bonds of keratin and a permanent set or form is imparted to the fibers by linkage rebuilding which either (a) follows spontaneously in the case where sulphites at approximately pH 6 and a temperature of from 50°–70° C. are employed, or (b) is brought about by subsequent treatment of the fibers with an oxidising agent.

The mechanism of the reactions may be represented as follows, the symbols R—S—S—R and R'NH₂ representing the peptide and associated

side chains of keratin and NaHSO_3 being employed as representative of alkali metal and ammonium bisulphites.

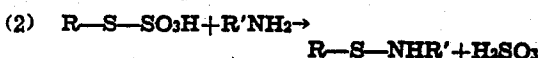
(a) When solutions at pH 6 and between 50° – 70° C. are used, disruption of the disulphide bonds of keratin first occurs as follows:



or



Linkage rebuilding then proceeds spontaneously by interaction of $\text{R-S-SO}_3\text{H}$ or $\text{R-S-SO}_3\text{Na}$ with $\text{R}'\text{NH}_2$ groups:



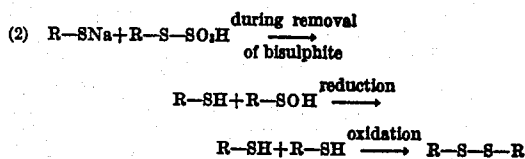
or



(b) Where a bisulphite or metabisulphite is employed as reducing agent, fiber-relaxation is first brought about by disulphide bond breakdown:



Linkage rebuilding is then induced by means of an oxidizing agent:

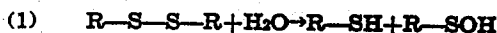


or by direct oxidation of the R-SNa and

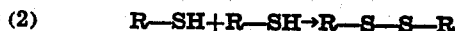


groups to R-S-S-R linkages.

(c) When an alkaline solution of sodium sulphite at or above pH 10 is used, fiber-relaxation is first brought about by the hydrolysis of the disulphide bonds by the alkali:



The R-SOH groups are then reduced to R-SH groups by the sulphite and linkage rebuilding is brought about by means of an oxidizing agent:



In the case of the R-S-NHR linkage formed when the fibrous substance is treated according to the invention with a sulphite solution at approximately pH 6 and a temperature of 50° to 70° C. (Case a), it has been pointed out above that at temperatures below the boiling point of water the rate of formation of S-NH linkages by bisulphite solutions is too slow to be commercially useful: The present invention by critical adjustment of pH as specified enables disruption of the constituent cystine bonds of keratin, followed by the spontaneous formation of SNH linkages to be obtained at the temperatures of from 50° – 70° C. at a rate which renders the process of commercial utility.

The disruption of the disulphide bond by reduction according to the invention may be employed to relieve stress in the fibers, which stress may have been caused, for example, by deforming the fibers in giving them a desired configuration, and leaves them in such a state that formation of further bonds may take place whereby the fibers will retain permanently any set or configuration which may have been given them.

Suitable sulphites and acid sulphites which may be employed according to the invention are sodium, potassium or ammonium sulphite, bisulphite and metabisulphite. Hydrosulphites, which give rise to bisulphites in solution, may also be employed.

The following are examples of convenient ways of carrying the invention into effect as applied by way of example to the permanent waving of hair.

Example I

As indicated above bisulphites and metabisulphites at pH 4 are efficient in bringing about disruption of the disulphide bond of keratin. In employing such reagents according to an example, the hair is treated with a 5 to 20 per cent. bisulphite or metabisulphite solution containing 45 per cent. ethyl alcohol for about 15 minutes at room temperature or above. The solution may be removed by rinsing in plain warm water and the hair dried. The hair in the relaxed state and having many of the disulphide bonds broken is then wound on a curler or otherwise deformed, no significant internal stress developing. The configuration given to the hair is then made permanent by treatment with a solution of an oxidizing agent such as a 10-volume hydrogen peroxide or a 10 per cent. alkali metal persulphate solution, or the treatment with an oxidizing agent may follow treatment with the ketone or aldehyde solution for instance a 60% acetone solution.

Alternatively the configuration may be made permanent by treatment with an alkali such as sodium carbonate solution, or ammonia in solution or as a gas at room temperature or above, together with or followed by oxidising agents. In this case, the alkali serves to depress swelling and promotes the action of the oxidising agent in forming disulphide bonds by oxidation of sulphhydryl groups.

The initial treatment of the hair with the bisulphite or metabisulphite solution described above may also be given after the hair has been deformed, for example on a curler, and the same subsequent treatment given for making the set permanent.

The hair may then be given the usual after treatment of permanent waving operations.

Example II

The hair after the usual preliminary shampoo is treated with a half molar solution of sodium sulphite brought to pH 11 or more by addition of sodium carbonate or sodium metasilicate. The hair may be treated with the solution before or after winding on a curler or the solution may be circulated about the hair wound on a curler. The solution is maintained in contact with the hair for about 15 minutes at room temperature or above, after which a solution of an oxidising agent is applied to the hair on the curler, for example a 10 volume hydrogen peroxide solution or 10 per cent. ammonium persulphate solution. The hair may then be subjected to the usual finishing operations of permanent waving.

Example III

In this case, a solution of a reducing agent as specified in Example I or II is employed, but instead of winding the hair on curlers it is formed into waves or curls on the head after being moistened with the solution. To facilitate manipulation of the hair, a thickening agent may be added to the solution of reducing agent, for instance agar-agar or kieselguhr in sufficient

amount to give the consistency of a paste. Suitable wetting agents may also be added. The solution is allowed to remain in contact with the hair for about 15 minutes at about room temperature or above. The formation of further bonds to give permanence to the waves or curls can then be brought about by treatment with an oxidising agent. Alternatively where the reducing agent is a bisulphite or compound capable of yielding a bisulphite, any of the following methods of making the set permanent may be adopted:

(a) By treatment with an aldehyde or ketone solution followed by treatment with an oxidising agent,

(b) By treatment with a solution of an alkali such as sodium carbonate or ammonia in the presence of an oxidising agent or followed by treatment with an oxidising agent,

(c) By exposure to an atmosphere containing volatile alkalies such as ammonia, in the presence of an oxidising agent, or followed by treatment with an oxidising agent.

When employing the solution of Example I the hair and solution may be maintained at 50°-70° C. during the 15 minutes' treatment. No subsequent step is then necessary so far as the application of a permanent set is concerned, but a solution of an oxidising agent may be employed to assist in removing the acid sulphite solution.

The hair may then be given the usual finishing treatment of permanent waving operations.

An alternative manner of carrying out the treatment of the invention according to this example, is to form the hair into waves or curls on the head and treat it with the reducing agent, the subsequent procedure being as set out above.

A further alternative is to wet the hair in the normal state with the acid sulphite solution of Example I the temperature being room temperature or above. The hair is then easily formed into waves or curls which can be made permanent by heating to about 50° C. for 15 minutes in the manner indicated above. The combing of the hair in the swollen condition may be facilitated by the use of a water soluble lubricant on the hair, for example, sulphonated castor oil.

The reagents may be applied by spraying or any other suitable means.

In the application of the invention to fabrics made of keratins such as wool, the usual crabbing and blowing operations for the removal or equalising of stress in the fabrics may be replaced by a reduction treatment in cold or warm solutions of reducing agents, for example, a 5 to 20 per cent. solution of alkali metal sulphite or bisulphite. The fabrics may then be treated for the removal of the reducing agent, for example by washing, or in the case of the bisulphite, by means of an aqueous aldehyde or ketone solution and followed by treatment with a solution of an oxidising agent such as a 10-volume hydrogen peroxide solution. Removal of reducing agents generally may be effected by treatment with an oxidising agent. Treatment with sulphite solutions at pH 6 may also be employed, the temperature being from 50° to 70° C. and the time of treatment about 15 minutes. The fabric may then be treated with a solution of a mild oxidising agent to remove the reducing agent.

Alternatively, stress may be dissipated in the fibres by heating at as low a temperature as 37° C. with the bisulphite solution containing, for example, 45 per cent. alcohol, and then treating the fibres with an oxidising agent with or without

treatment with alkaline solution at a low temperature or exposure to an atmosphere containing volatile alkalies such as ammonia.

The invention may also be applied to the removal of distortion in knitted fabrics of wool, arising from uneven stress in the yarn, by treatment of the fabric with an acid sulphite solution at about pH 6 and 50° to 70° C. or by treatment with a sulphite or bisulphite solution at 37° C. followed by treatment with an oxidising agent, a treatment with an alkali being also possible where a bisulphite is used.

Yarns for the manufacture of curl fabrics or artificial astrakhan and Persian lamb fabrics may have a permanent set given to them by treatment of the deformed yarn with an acid sulphite solution at about pH 6 and 50° to 70° C., or by treatment with a sulphite or bisulphite solution followed by treatment with an oxidising agent, a treatment with alkali in solution or as a gas being also possible where a bisulphite is used.

I claim:

1. A process of imparting a permanent configuration to hair comprising treating the hair with a soluble sulfite at a temperature which does not burn the skin while maintaining the hair in the desired configuration, and thereafter treating the hair with an oxidizing agent to oxidize the remaining sulfite.

2. A process of treating hair to impart a permanent configuration thereto comprising adjusting the hair in the configuration desired, treating the hair while thus adjusted with a solution of a sulfite at a temperature which is not injurious to the scalp, and subsequently treating the hair with an oxidizing agent to oxidize any remaining sulfite before the hair is afforded an opportunity to change its configuration.

3. A process of treating hair to impart a permanent configuration thereto comprising adjusting the hair in the configuration desired, treating the hair while thus adjusted with a solution of a sulfite at substantially normal room temperatures and subsequently oxidizing any remaining sulfite before the hair is afforded an opportunity to change its configuration.

4. A process of treating hair to impart a permanent configuration thereto comprising adjusting the hair in the configuration desired, treating the hair while thus adjusted with an aqueous solution containing about 5% of an alkali sulfite, and subsequently treating the hair with a solution containing a slight excess of hydrogen peroxide over the amount required to react with the remaining sulfite.

5. Method of imparting a permanent set of form to hair, which comprises treating the hair, at a temperature not substantially exceeding 70° C., with a solution of a soluble sulfite, and subsequently while maintaining the hair in the desired configuration subjecting the hair to the action of an oxidizing agent.

6. The process of claim 5 wherein the soluble sulfite is in the form of a solution of an acid sulfite having a pH of about 4.

7. The process of claim 5 wherein the soluble sulfite is in the form of a solution having a pH of not less than about 10.

8. The process of claim 5 wherein the solution is an acid sulfite, has a pH of about 4 and contains from 10-45% alcohol by volume.

9. The process of claim 5 wherein the said oxidizing agent is hydrogen peroxide.

10. The process of claim 5 wherein the said oxidizing agent is an alkali metal persulfate.

11. The process of claim 5 wherein the excess sulfite is removed from the hair by washing prior to the use of the oxidizing agent.

12. A process of imparting a permanent configuration to hair comprising treating the hair with a solution of an acid sulfite at about pH 4 and at a temperature not substantially exceeding 70° C., removing excess sulfite and then while maintaining the hair in the desired configuration, treating the hair with an oxidizing agent.

13. The process of claim 5 comprising treating the hair with a solution of a soluble acid sulfite at about pH 4 and at a temperature not substantially exceeding 70° C., and while maintaining the hair in the desired configuration treating the hair with a quantity of alkali to neutralize the acid and thereby depress swelling and then treating the hair with an oxidizing agent.

14. The process of claim 5 comprising treating the hair with a solution of a soluble bisulfite at

about pH 4 and at a temperature not substantially exceeding 70° C., washing to remove the excess of sulfite and subsequently while maintaining the hair in the desired configuration, treating the hair with a quantity of alkali to neutralize the acid and thereby depress swelling and thereafter treating the hair with an oxidizing agent.

15. The process of claim 12 wherein the said solution of an acid sulphite contains 10%-45% of a soluble alcohol.

16. The process of claim 5 comprising treating the hair with a solution of an acid sulphite at about pH 4 and at a temperature not substantially exceeding 70° C., washing to remove the excess of sulphite and subsequently, while maintaining the hair in the desired configuration, treating the hair with an alkali, in amount to neutralize the acid and thereby depress swelling, together with an oxidising agent.

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