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.

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 \( R'-NH_2 \) represent the peptide and associated side chains of keratin.

The reactions take place with such readiness that the maximum possible number of linkages result. Bisulphite solutions, however, have the disadvantage that at the boiling point of water they are capable of serious destructive action on hair and at lower temperatures the rate of formation of linkages as represented by equation 2 above, is negligibly small and therefore proceeds far too slowly to be commercially useful.

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

The invention consists in treating fibrous substance containing keratin, such as wool or hair, with a solution of a reducing agent in alkaline solution to effect reduction and disruption of the constituent disulphide or cystine bond of keratin with the formation of sulphdryl groups, and then, while maintaining the substance in a form 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 oxidizing agent.

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 by disruption of the disulphide bonds of keratin, and in the following scheme:

\[
R-S-S-R + \text{reducing agent} = RSH + RSH
\]

and permanent set or form is given to the relaxed fibers according to the invention, not by the formation of S-NH bonds by interaction of sulphonie groups with amino groups as in the prior treatment referred to, but solely by direct union of sulphdryl groups themselves to form cystine bonds, brought about by the action of the oxidizing agent.

Suitable reducing agents which may be employed according to the invention are sodium sulphide, sodium hydrosulphide, cysteine hydrochloride, sodium hypophosphite, sodium thiosulphate, sodium hydrosulphite, sodium dithionate. They may be employed in the form of solutions whose concentrations may be varied in accordance with the nature of the reducing agent and its mode of use. The reducing agent may be formed in situ, for example if keratin containing fibers are moistened with alkali, e. g., baryta, hydrosulphite is formed by reaction with the fiber molecules, which may be caused to attain the required concentration by maintaining the total volume of solution low.

Reducing agents as a whole, in alkaline solutions, disrupt the disulphide bond of keratin with the formation of sulphdryl groups, although the quantity of disulphide bonds disrupted in any keratin-containing substance varies not only from one reducing agent to another, but also with the conditions of concentration, pH and temperature at which a reducing agent is employed.

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.

Although the solution of reducing agent may be of any desired alkalinity, it is found in certain cases that for the application of permanent sets...
or waves to keratin fibers, conditions are most favourable to the permanence and efficiency of the set when the reducing solution actually in contact with the hair is at or above pH 10, preferably pH 11.

At or above pH 10 reducing agents are effective, since alkalies are able to attack unstrained as well as strained disulphide bonds, sulphhydril and sulphenic acid groups being produced by hydrolysis, which latter groups are reduced by the reducing agent to sulphhydril groups. Disulphide bonds may be formed from the sulphhydril groups by the subsequent action of an oxidising agent.

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**

The hair after a preliminary shampoo is treated with a 6 per cent., sodium hydro sulphite solution brought to pH 10 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 may be applied, 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 II**

In this case, a solution of a reducing agent as specified in Example I, 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.

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. 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 crapping and blowing operations for the removal or equalising of stress in the fabrics may be replaced by such as a 10-volume hydrogen peroxide solution of reducing agents, for example a 0.6 per cent. solution of sodium sulphide. The fabrics may then be treated for the removal of the reducing agent, for example by washing, or by treatment in a solution of an oxidising agent in sufficient hydrogen peroxide solution.

Removal of reducing agents generally may be effected by treatment with an oxidising agent.

The invention may also be applied to the removal of distortion in knitted fabrics of wool arising from uneven stress in the yarn, by treating the fabric with an alkaline solution of a reducing agent and subsequent removal of the reducing agent as by treatment with an oxidising agent.

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 a reducing agent followed by removal of the reducing agent as by treatment with an oxidising agent.

1. A method of giving a desired permanent form to fibrous substances containing keratin, which comprises treating the substance with an alkaline solution of a reducing agent free from sulphite at a pH of at least 10 and a temperature appreciably below the boiling point whereby to effect reduction and disruption of the constituent disulphide or cystine bond of keratin with the formation of sulphhydril groups, and then, while maintaining the substance in a form which it is desired to render permanent, causing the formation of further cystine bonds through interaction of the sulphhydril groups by subjecting the fibers to the action of an oxidising agent comprising a per-compound.

2. A method as claimed in claim 1, wherein the reducing agent is removed from the substance prior to treatment with the oxidising agent.

3. A method of permanently waving hair which comprises treating the hair with an alkaline solution of a reducing agent free from sulphite at a pH of at least 10 and a temperature appreciably below the boiling point whereby to effect reduction and disruption of the constituent disulphide or cystine bond of keratin of the hair with the formation of sulphhydril groups and then, while maintaining the hair in a curled or waved condition, causing the formation of further cystine bonds in the hair molecules by interaction of the sulphhydril groups by subjecting the hair to the action of an oxidising agent comprising a per-compound.

4. A method as claimed in claim 3 wherein the hair in the form of strands is wound on curlers after treatment with the reducing agent and is treated with the oxidising agent while it is on the curlers.

5. A method as claimed in claim 3 wherein the reducing agent employed is an alkali metal sulphide, cystine hydrochloride, sodium hypophosphite, sodium thiosulphate, sodium hydo-sulphite and sodium dithionate.

6. A method as claimed in claim 3 wherein the reducing agent employed is an alkali metal hydrothiosulphide.

7. A method as claimed in claim 3 wherein the reducing agent employed is cystine hydrochloride.

8. A method as claimed in claim 1 wherein the per-compound is hydrogen peroxide.

9. A method as claimed in claim 1 wherein the per-compound is ammonium persulphate.

10. A method as claimed in claim 3 wherein the per-compound is hydrogen peroxide.

11. A method as claimed in claim 3 wherein the per-compound is ammonium persulphate.

12. A method as claimed in claim 3, wherein the reducing agent is removed from the hair prior to treatment with the oxidising agent.

13. A method of permanently waving hair which comprises treating the hair with a solution of an alkaline reducing agent free from sulphite at a pH of at least 10 and a temperature appreciably below the boiling point whereby to effect reduction and disruption of the constituent...
disulphide or cystine bond of keratin of the hair with the formation of sulphhydryl groups and then, while maintaining the hair in a curled or waved condition, causing the formation of further cystine bonds in the hair molecules by interaction of the sulphhydryl groups by subjecting the hair to the action of a solution of a peroxide.

14. A method of permanently waving hair which comprises treating the hair with a solution of an alkaline reducing agent free from sulphite at a pH of at least 10 and a temperature appreciably below the boiling point whereby to effect reduction and disruption of the constituent disulphide or cystine bond of keratin of the hair with the formation of sulphhydryl groups and then, while maintaining the hair in a curled or waved condition, causing the formation of further cystine bonds in the hair molecules by interaction of the sulphhydryl groups by subjecting the hair to the action of a solution of a per-salt.

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