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PROCESS AND COMPOSITION FOR TREATING KERATINOUS MATERIAL

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The present invention relates to compositions particularly useful for treating keratin-containing materials, such as hair and wool, and to processes employing such compositions for treating keratin materials to alter their chemical and physical properties.

Wool, hair, fur and like epidermal materials are characterized by the presence therein of the fibrous protein, keratin. Keratin is comprised of polypeptide chains joined together by cystine linkages. In recent years there have been proposed many processes for changing the chemical and physical properties of naturally-occurring keratin-containing materials by chemical treatment involving splitting of the cystine linkages of the keratin. Processes for the permanent waving of human hair or for straightening human hair, for example, fall in this category, and the invention will be described with particular reference to hair waving, although it will be understood that it is applicable generally to the treatment of keratin-containing materials and to articles fabricated therefrom.

In the permanent waving of human hair it is well recognized that some of the cystine linkages present in the keratin structure must be split in order to permit the development of a wave undulation. To this end, the hair is usually treated with a suitable reducing agent while it is held under stress in a coiled or curled condition. The splitting of cystine linkages permits a reorientation of the polypeptide chains to relieve the stress and this accounts for the development of the wave undulation. Thereafter it is essential that the action of the reducing agent be arrested and that linkages in the keratin structure be rebuilt, otherwise the wave undulation will not be permanent.

The preferred reagents for keratin cystine linkage attack have been compounds in the mercaptan family or compounds having a sulfite radical. In the first classification, thioglycollates enjoy a wide application, and in the second classification, alkali metal sulfites and amine sulfites are extensively used. In the so-called "cold" permanent waving process an aqueous solution of ammonium thioglycollate has been a preferred selection as the processing solution. After the usual shampooing operation, the hair is treated with this preparation and is then wrapped around a rod of small diameter. After a suitable processing period, which varies with the condition and texture of the hair, a wave undulation develops.

Despite the excellent acceptance of the cold permanent waving process, certain fundamental

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defects in this treatment are well recognized. One such defect is the large incidence of waving failures which are a result of the difficulty associated with forcing an oxidizing agent uniformly through a wrapped tress which is already saturated with cold waving solution. Also, the action of the reducing solution is difficult to control and overprocessing of the hair is quite common. Further, these defects include the fear that sulfhydryl compounds might be absorbed through the skin and induce systemic reactions in the human body.

An object of the present invention is to provide improved processes for altering the chemical and physical properties of keratin materials through rupture of cystine linkages therein. Another object of the invention is to provide compositions, useful in treating keratin materials in processes of this character, which do not necessitate subsequent application of a separate oxidizing solution to the keratin material. Another object is to provide improved cold permanent waving processes and hair treating lotions for use in such processes.

The compositions of the present invention have the desired reducing properties when applied to keratin containing material but are inherently auto-oxidizing and self-limiting in their effect. As reduction by these compositions proceeds, a second reaction which destroys the reducing power of the solution takes place. These compositions permit the formation of hair waving lotions, for example, which will give an optimum reducing effect but which need not be followed by the usual separate oxidizing treatment and which at the same time minimize the incidence of waving failures, the hazards of skin irritation and toxic effects, and the hazard of overprocessing.

The invention involves treatment of the keratin material with a material which functions as an oxidation catalyst in the environment provided by the keratin and the reducing agent.

In accordance with one aspect of the invention, the substantive properties of keratin are made use of to permit pretreatment of hair, for example, with a suitable catalytic agent to form an association with the hair which is sufficiently stable to resist normal rinsing operations and to remain effective during subsequent steps of the waving treatment. For this purpose, we may use, for example, an aqueous solution of magnanese chloride containing 200 parts per million of manganese. The treated hair can then be subjected to the action of a suitable reducing agent, or

may be dried before application of the reducing agent. Under the influence of the catalytic agent and atmospheric oxygen, the reducing capacity of the reducing agent is gradually lessened and the liquid in contact with the hair is gradually converted to an oxidizing medium which brings about rebuilding of cystine linkages.

In accordance with another aspect of the invention, the reagent for controlling the effect of the reducing agent may be combined with the reducing agent. When this combination is applied to the keratin, as in hair waving, the reduction proceeds to a desired extent before it is overcome by the oxidation reaction characteristic of my novel composition. This oxidation destroys the reducing power of the solution and promotes rebuilding of cystine linkages in the keratin structure. This linkage rebuilding renders the physical changes which have been effected in the keratin structure permanent for all practical purposes.

The following examples illustrate various applications of the invention to the permanent waving of hair:

The hair is shampooed in the usual way and excess water squeezed out. Then from 4 to 32 ounces of a liquid solution of manganese chloride and a wetting agent is poured through the hair. The concentration of the manganese may be from 50 parts per million (0.005%) in 32 ounces to 1,000 parts per million (0.1%) in 4 ounces. A suitable wetting agent is aerosol AY which may be present in an amount from 0.1% to 1.0%. The manganese solution may then be removed from the hair either by rinsing or by squeezing it out, after which the hair is partially towel dried, sectioned, blocked and wrapped on cold waving rods in the usual way. An aqueous waving lotion is then applied to the wrapped tresses. This lotion may comprise:

Ammonium thioglycollate	0.7 normal
Ammonium hydroxide	0.7 normal

This lotion has a pH of about 9.3.

The waving lotion is allowed to remain in the wrapped tresses until a curl pattern is developed. The skilled operator will readily determine the length of this period in accordance with the condition and type of the hair and the strength of the lotion. Two hours would be an adequate period of time for the 0.7 normal lotion described. Finally, the curls are unwound and the hair is fluffed, rinsed in tepid water and styled as desired.

The action of the atmospheric oxygen on the hair and on the lotion can be accelerated by removing excess lotion from the hair after the lotion has been in contact with the hair long enough to cause a curl pattern to be developed. Removal of excess lotion facilitates access of atmospheric air to the hair and increases the diffusion rate of oxygen into the liquid phase of the system, whereby conversion of the liquid to an oxidizing medium is promoted at a more rapid rate, thus shortening the time required for the waving process. Any convenient means for dehydrating may be employed; for example, a towel may be used to remove excess liquid from the hair. A more effective method of dehydrating the hair is through the application of absorbent pads to the individual tresses. Also, the usual hair drying devices commonly found in beauty shops may be employed for this purpose. It will be understood that this step of removing excess liquid may be employed, if desired, in the process of the foregoing example

and also may be employed in the processes described in the following examples.

The following example is given as illustrative of a hair waving process in which the manganese is incorporated in the shampoo and a dehydrating step is employed.

Shampoo the hair, making three applications of fresh shampoo containing manganous chloride in amount sufficient to give a concentration of manganese between 500 and 2,000 mg. per liter (0.05–0.2%). Approximately 4 ounces of shampoo should be used. During this operation manganese is deposited on or in the hair due to the substantive properties of the keratin. Thereafter the hair is rinsed and then is sectioned, blocked, wrapped, treated with waving lotion, dried, rinsed and styled as described above.

The following example illustrates a hair waving process employing a novel composition of the present invention. The hair is shampooed with an ordinary shampoo material, rinsed thoroughly, and then sectioned, blocked and wrapped on cold waving rods. The wrapped tresses are then treated with an aqueous waving lotion comprising the following:

Ammonium thioglycollate	0.7 normal
Ammonium hydroxide	0.7 normal
Hydrated manganous chloride	parts per million 720
Aerosol AY (wetting agent)	per cent 0.6

This lotion has a pH of about 9.3.

After the curl pattern has developed properly the tresses are pressed with a dry towel to remove excess liquid. Thereafter absorbent pads are placed over each curl to remove excess liquid and admit air to "fix" the wave. The absorbent pads may be of any suitable absorbent material, such, for example, as blotting paper, fabrics, or a material prepared from bleached cotton fibers which have been converted into unwoven fabric of the type and in the manner set forth in United States Patent No. 2,277,049. As the liquid is removed from between the hair fibres, air gains entrance and serves, in the presence of the metal catalyst, to nullify the effect of the reducing solution. After about fifteen minutes, the absorbent pads are removed, the curls are unwound and the hair is fluffed and rinsed in tepid water and styled as desired.

In the processes of the foregoing examples a waving solution containing thioglycollate is employed. Instead of this solution, a solution in which the active reducing agent is a sulphite can be used. Such a solution may contain—

	Parts
Sodium sulphite	11.34
Water	200
Ammonium carbonate	13

The ammonium carbonate acts as a buffer to maintain the pH at about 9. The solution may contain cobalt chloride in concentration of about 100 parts per million.

The preferred catalytic agent for the thioglycollate waving solution is manganese, which may be present in the form of a solution of one of its water soluble salts. For the sulphite waving solution, the preferred catalytic agent is cobalt.

We have also found that copper, iron, and to a somewhat lesser extent nickel, are effective. These metals are employed in a form to make the metallic ions available, for example in the form of water-soluble salts.

The period of time for which the lotion con-

taining a catalytic agent is permitted to remain in the wrapped curls may be varied and this period will depend to some extent upon the relative concentrations of the catalytic agent and the reducing agent as well as upon the type of reducing agent. For solutions to be used in the beauty parlor, this lotion may be formulated to remain in contact with the hair for a period from a few minutes up to about half an hour. For home use this period may be increased.

The proportion of manganese or manganese compound in the waving lotion should be such as to give a manganese concentration of from about 25 parts per million (0.0025%) to 500 parts per million (0.05%) by weight. This range will vary somewhat depending upon the reducing agent included. With thioglycollates we prefer to use proportions of manganese salts such as to give a concentration of manganese from 100 parts per million to 300 parts per million.

In the system described, manganese appears to function as an oxidation catalyst. In place of a normally slow oxidation of the reducing agent on exposure to air, a rapid oxidation takes place. From a chemical standpoint, the ammonium thioglycollate is converted to diammonium dithioglycollate. As long as air is available this chemical change is stable and a hydrolytic reversion of the diammonium dithioglycollate to ammonium thioglycollate does not take place.

Although it is true that ammonium thioglycollate solutions oxidize upon exposure to air, the rate of this reaction with reduced intact keratin fibres is such that it cannot be relied upon to destroy the reducing power of the solution. In fact, event after prolonged exposure, the equilibrium obtained in accordance with the law of mass action allows for the presence of appreciable quantities of the sulfhydryl compound.

The present invention goes a long way toward solving the difficulties associated with the cold waving process. Any cold waving lotion accidentally spilled on the scalp will be rapidly oxidized due to the catalytic effect of the manganese, cobalt or other metal. On the other hand, hair in the coiled state undergoing waving will process in the desired manner because the diffusion rate of oxygen into the liquid phase of the system is limited by the surface of the curl exposed to the atmosphere. In other words, these conditions are desirably different from those holding when the lotion is spilled and spreads into a thin film on the scalp.

Our invention is also applicable to keratolytic treatments such as depilation of human hair and corn removal.

From the standpoint of overprocessing, the manganese-treated hair prevents the usual progressive reduction action from continuing for too long a period. The diffusion of oxygen into the coiled tress, although slow, is adequate to accomplish a desirable slowing up of the waving action as the desired curl strength is approached.

We claim:

1. A method of permanently changing the configuration of human hair upon the head without appreciable damage to the hair structure, which comprises imparting the desired configuration to the hair, subjecting the hair to treatment with a keratin reducing agent in the presence of an oxidation catalyst, said oxidation catalyst being present in the hair at least from the commencement of said treatment, until the desired configuration is obtained and then exposing the hair

to atmospheric oxygen to oxidize the reducing agent by the action of the atmospheric oxygen in the presence of the oxidation catalyst and thereby fix the desired configuration.

2. A method of permanently changing the configuration of human hair upon the head without appreciable damage to the hair structure, which comprises imparting the desired configuration to the hair, subjecting the hair to treatment with a keratin reducing agent in the presence of a metallic oxidation catalyst, said oxidation catalyst being present in the hair at least from the commencement of said treatment, until the desired configuration is obtained and then exposing the hair to atmospheric oxygen to oxidize the reducing agent by the action of the atmospheric oxygen in the presence of the oxidation catalyst and thereby fix the desired configuration.

3. A method of permanently changing the configuration of human hair upon the head without appreciable damage to the hair structure, which comprises treating the hair with an aqueous solution containing not over 0.2% of a metallic oxidation catalyst, expressed as free metal, imparting the desired configuration to the hair, then treating the hair with a keratin reducing agent at a pH above about 9 until the desired configuration is obtained, and then exposing the hair to atmospheric oxygen to oxidize the reducing agent by the action of the atmospheric oxygen in the presence of the oxidation catalyst and thereby fix the configuration.

4. A method of permanently changing the configuration of human hair upon the head without appreciable damage to the hair structure, which comprises imparting the desired configuration to the hair, treating the hair with an aqueous solution containing a keratin reducing agent and not more than 0.05% of a metallic oxidation catalyst, expressed as free metal, at a pH value above about 9, until the desired configuration is obtained, and then exposing the hair to atmospheric oxygen to oxidize the reducing agent by the action of the atmospheric oxygen in the presence of the oxidation catalyst and thereby fix the configuration.

5. The method of claim 1, in which the keratin reducing agent employed is an alkaline thioglycolate, at a pH value above about 9.

6. The method of claim 3 in which the metallic oxidation catalyst is a water soluble manganese salt and the keratin reducing agent employed is an aqueous solution containing ammonium thioglycolate.

7. The method of claim 3 in which the oxidation catalyst employed is a water soluble iron salt and the keratin reducing agent is an aqueous solution containing ammonium thioglycolate.

8. The method of claim 3 in which the oxidation catalyst employed is a water soluble cobalt salt and the keratin reducing agent is an aqueous solution containing ammonium thioglycolate.

9. The method of claim 4 in which the oxidation catalyst employed is a water soluble manganese salt and the keratin reducing agent an aqueous solution containing ammonium thioglycolate.

10. The method of claim 4 in which the oxidation catalyst employed is a water soluble iron salt and the keratin reducing agent an aqueous solution containing ammonium thioglycolate.

11. The method of claim 4 in which the oxidation catalyst employed is a water soluble cobalt

salt and the keratin reducing agent an aqueous solution containing ammonium thioglycolate.

12. A permanent waving composition for changing the configuration of human hair upon the head without appreciable damage to the hair structure, comprising a keratin reducing agent in an effective hair waving concentration and not more than about 0.05% of a metallic oxidation catalyst, expressed as free metal, said composition having a pH value above about 9, whereby oxidation of the keratin reducing agent may be effected after the configuration of the hair has been permanently changed by treatment therewith, by exposure of the hair to atmospheric oxygen without use of additional oxidizing agents.

13. The product of claim 12 in which the oxidation catalyst is a water soluble manganese salt.

14. The product of claim 12 in which the oxidation catalyst is a water soluble iron salt.

15. The product of claim 12 in which the oxidation catalyst is a water soluble cobalt salt.

16. The product of claim 12 in which the oxidation catalyst is a water soluble manganese salt and the keratin reducing agent an aqueous solution containing ammonium thioglycolate.

17. The product of claim 12 in which the oxidation catalyst is a water soluble iron salt and the keratin reducing agent an aqueous solution containing ammonium thioglycolate.

18. The product of claim 12 in which the oxidation catalyst is a water soluble cobalt salt and the keratin reducing agent an aqueous solution containing ammonium thioglycolate.

19. The method of claim 1 in which the keratin reducing agent employed is a mercaptan.

20. The product of claim 12 in which the keratin reducing agent employed is a mercaptan.

21. The product of claim 12 in which the oxidation catalyst is a water soluble manganese salt and the keratin reducing agent is an aqueous solution containing ammonium thioglycolate in a concentration of about 0.7 normal.

22. The product of claim 12 in which the oxidation catalyst is a water soluble iron salt and the keratin reducing agent is an aqueous solution containing ammonium thioglycolate in a concentration of about 0.7 normal.

23. The product of claim 12 in which the oxidation catalyst is a water soluble cobalt salt and the

keratin reducing agent is an aqueous solution containing ammonium thioglycolate in a concentration of about 0.7 normal.

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