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METHOD OF PERMANENTLY RESHAPING A KERATIN-CONTAINING SUBSTANCE

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The present invention relates to the treatment of keratin-containing substance and has particular reference to materials and methods employing such materials for permanently waving human hair. The method is of the cold wave type and the materials are adapted to be packaged and distributed in so-called "home cold waving kits," as well as professionally.

Hair, wool, and like epidermal materials contain a fibrous protein, viz., keratin, which is comprised of polypeptide chains joined together by cystine linkages.

Generally, in the cold permanent waving of human hair, the hair is sectioned off into about 30 to 40 individual tresses which are saturated thoroughly with a waving lotion containing a relaxing agent to modify the keratin structure of the hair so that the hair may be permanently deformed. The tresses then are wrapped upon separate curlers and resaturated with additional relaxing agent. After the resaturated hair tresses have remained on the curlers a sufficient time, e. g., 30–60 minutes, a setting solution is applied to stop the action of the relaxing agent and rebuild or restore the keratin structure of the hair whereby a permanent wave is obtained.

The present invention provides hair waving materials which are self setting, i. e., materials whose use completely eliminates the separate step of applying a setting agent to the wound tresses.

In its broadest process aspect, the present invention provides a process of treating keratin-containing substance which comprises contacting said substance with an acid sulfite keratin relaxing agent and then developing in situ on said substance a material capable of stopping the relaxing action of said acid sulfite and restoring the keratin structure of said substance.

In permanently waving human hair using the materials and methods of the present invention the hair is sectioned off into individual tresses each of which is saturated with a waving lotion comprising an acid sulfite relaxing agent and then is wound or wrapped on separate curling rods. The waving lotion wets and modifies the hair structure so that it may be deformed permanently.

Thereafter, there is developed in situ on the hair a material capable of stopping the action of the said acid sulfite and restoring the hair substantially to its original strength. To this end, urea and urease are applied to the wound tresses while the same are wet with the waving lotion. The urea and urease react to form ammonia which gradually increases the pH of the materials in contact with the hair until, over a period of time, the relaxing action of the waving lotion is stopped, whereby a permanent set is imparted to the hair.

In the present invention sulfite-type materials are utilized as the relaxing agent for modifying the keratin structure of the hair. The use of compounds having a sulfite radical for this purpose effects a number of improvements over the cold waving procedure now in most general use commercially, the mercaptan or so-called "thio" wave using thioglycolate waving lotions. In contrast with thio materials, acid sulfite materials are substantially non-odorous and they greatly reduce the hazards of irritation. The wave produced by the present invention is less susceptible to subsequent relaxation. The danger of hair breakage is substantially reduced because although the wave develops with speed comparable to that of mercaptan-type lotions, yet if the exposure of the hair to the lotion is prolonged, the hair damage so commonly experienced with mercaptan lotions does not take place.

Inasmuch as sulfite materials, like mercaptans, are reducing agents, the accepted practice of using oxidizing agents to reverse the process and rebuild the hair structure broken down by the mercaptan reducing agents has prompted the use of oxidizing agents to restore hair reduced with sulfite. However, directly contrary to the mercaptan type cold wave, the cold reaction of sulfite upon hair is not direct reduction of disulfide, and the reaction of oxidizing agents on sulfite reduced hair will not rebuild the original disulfide bonds in the keratin molecule but will irreversibly form sulphone by-products characterized by hair that is "rubbery" and waves that are limp and evanescent.

In the conventional cold waving of hair employing mercaptans or inorganic sulfhydryls, the reaction indicated by the following takes place:

(1) RELAXING (REDUCING) STEP

$$\underset{\text{Intact hair (cystine)}}{R—S—S—R} + \underset{\text{Mercaptan or inorganic sulfhydryl}}{2R'—S—H} \rightarrow \underset{\text{Relaxed hair (cysteine)}}{2R—S—H} + \underset{\text{Low molecular weight disulfide}}{R'—S—S—R'}$$

(2) REBUILDING (OXIDIZING) STEP

$$\underset{\text{Relaxed hair}}{2R—S—H} + \underset{\text{Oxidizing agent}}{(O)} \rightarrow \underset{\text{Restored hair (cystine)}}{R—S—S—R} + \underset{\text{Water}}{H_2O}$$

Wherein:

R—S—S—R represents intact hair in which the cystine linkage between two polypeptide chains is unbroken; the symbol —S—S— designates a disulfide bond of such a cystine linkage;

R'—S—H represents an organic mercaptan such as thioglycolate or an inorganic sulfhydryl;

R—S—H represents relaxed hair, the —S—H delineating the mercaptan radical in the cysteine moiety which results from the reduction of the disulfide linkage of keratin; and

R'—S—S—R' represents the organic disulfide derived by oxidation of R'—S—H.

The polypeptide structure of which hair is composed is referred to herein as "keratin" and references to "cystine," "cysteine," "disulfide bonds" are to these component groups in the keratin structure.

Thus, the first step illustrated by Equation 1 is a simple reduction of hair disulfide bonds to sulfhydryl terminal groups, which is the chemical characterization of relaxed hair indicated by RSH. It will be noted that both sulfur atoms of the disulfide bonds are converted to sulfhydryls which are readily reoxidizable. During the reaction, the reduction is effected at the expense of the added mercaptan which becomes oxidized to R' —S—S—R'.

In the second step, illustrated by Equation 2, the cysteine (relaxed hair) is oxidized, by a conventional oxidizing agent, so that the free sulfhydryl groups are rejoined to form the original disulfide bond structure of the keratin, the cystine linkage of intact hair structure. In this oxidation, as it is carried out in conventional cold waving with thioglycolate, substantially all of the sulfhydryl oxidizes symmetrically to disulfide.

Hence, the thio process is direct reduction of keratin cystine in the first step, and direct oxidation of the reduced keratin cysteine back to the original keratin cystine structure in the second step.

The chemistry of the relaxation of hair by said acid sulfite is represented by the reaction:

(3) RELAXING STEP

R—S—S—R	+ MeHSO$_3$	→	R—S—H	+ R—S—SO$_3$Me	
Intact hair (cystine)	Acid sulfite		Relaxed hair (cysteine)	Thio sulfate moiety of relaxed hair	

Wherein:

R—S—S—R and R—S—H have the same significance as in the equilibrium between intact hair and mercaptan;

Me is a cation;

HSO_3 is the acid sulfite anion; and

R—S—SO_3Me is the Me salt of a thiosulfate derivative of keratin, resulting from the action of acid sulfite on the other sulfur of the broken disulfide bond.

The acid sulfite reaction, Equation 3, illustrates what normally would be considered an "oxidation-reduction reaction" because the acid sulfite is oxidized and the disulfide bond is reduced, but it should be noted that this oxidation-reduction is internal in that it is the single large and complex keratin molecule which contains both the reduced (mercaptan or sulfhydryl) and oxidized (thiosulfate) products of the reaction.

The original disulfide bonds of intact hair are at appreciable molecular distances one from another, hence the lone mercaptan radicals (R—S—H) produced as shown are also quite distant one from another. Since these lone mercaptan radicals are part of a solid material (the relaxed hair) they have limited mobility, and very few of such lone mercaptan radicals are sufficiently near to another mercaptan radical to permit their direct reoxidation to disulfide bonds. As a result, should any oxidizing agent be applied to the hair the great majority of these mercaptan radicals will react irreversibly with the applied oxidizing agent to yield sulfone and sulfonate terminal groups instead of the reinforcing —S—S— linkages of intact hair. Thus, the reaction between hair and acid sulfite cannot be reversed by the use of an oxidizing agent. In fact, to effect rebuilding of the crystine linkages, it is essential that oxidation carefully be avoided.

One method which has been suggested for rebuilding hair relaxed by treatment with acid sulfite relaxing agents comprises applying an alkaline setting lotion to hair wet with the relaxing agent to increase substantially the pH of the materials in contact with the hair and bring about a reversal of the reaction indicated hereinabove in Equation 3 to impart a permanent set to the hair. Various materials have been suggesed for incorporation in such an alkaline setting lotion, for example, sodium carbonate, trisodium phosphate, sodium sulfite, sodium borate, lithium carbonate, dipotassium acid phosphate, and mono-, di-, and triethanolamine.

In accordance with the present invention, the hair, after having been chemically relaxed with acid sulfite lotion and physically deformed for curling, is restored to its original condition without applying directly thereto either oxidizing agents or setting lotions containing alkaline compounds. According to this invention, after the hair has been treated with a lotion which contains acid sulfite(or bisulfite) ions in an amount adequate to relax the keratin structure of the hair in a short period of time at room temperature, the hair is rebuilt by the application thereto of a mixture comprising urea and urease which gradually raises the pH of the materials in contact with the hair through the formation of ammonia until the action of the relaxing agent is stopped and the keratin structure of the hair is rebuilt or restored whereby a permanent wave is obtained.

It is essential that the urea and urease be brought into contact on the hair while the same is in the deformed curled state, i. e., before being unwound, because the rebuilding of bonds to impart the final permanent set to the wave neecssarily must take place while the hair has the desired deformation.

The acid sulfite waving solution employed in accordance with this invention to relax the hair or to split at least some of the cystine linkages present in the keratin structure of the hair preferably should have a pH within the range of about 6.0 to about 6.6. A pH as low as about 5.5 may be employed but a solution having a lower pH is not desirable since such solutions tend to evolve intolerable amounts of SO_2 gas which has a degrading and bleaching effect on the hair as well as an undesirable odor. A pH value of about 7.0 is the practical upper limit.

Acid sulfites of the alkali metals, ammonia or organic amines or suitable admixtures thereof are effective for use as the relaxing agents in the waving lotions of this invention. Thus, useful examples include sodium, potassium or ammonium acid sulfite, simple mono-, di-, or trialkyl amines such as the methyl, ethyl, propyl or butyl amines, alkanol amines such as diethanolamine, cyclic amines, such as morpholine, piperidine, and piperazine, as well as other basic acid sulfite forming organic substances such as guanidine and formamidine.

Acid sulfites are readily obtainable in a pH range below 5.5 by passing, as by bubbling, SO_2 gas through a relatively concentrated solution of a water soluble alkali metal or alkaline earth metal salt having a cation corresponding to the desired cation of the acid sulfite. The concentrated solution may then be diluted with 5 to 40% of alcohol, which brings the apparent pH into the preferred range of 6.0 to 6.6.

To restore the relaxed hair or to rebuild the cystine linkages in the keratin structure of the hair split by the action thereon of the sulfite waving lotion in accordance with this invention a mixture of materials is employed which is capable of developing in situ on the hair a material capable of substantially increasing the pH of the materials in contact with the hair. To this end, a mixture of urea and urease is applied to the hair. These materials may be applied to the hair in a water mixture although it is preferred to mix them with a quantity of the relaxing lotion and then apply the resulting mixture directly to the wound tresses. The urea and urease react to form ammonia which gradually increases substantially the pH of the materials in contact with the hair whereby the relaxing action of the waving lotion is stopped and the keratin structure of the hair is rebuilt and a permanent set is imparted to the hair.

The greater the pH difference between that of the relaxing lotion and that obtained upon reaction of the urea and urease on the hair, in the presence of the relaxing lotion, the more effective will be the rebuilding of the keratin structure of the relaxed hair. Usually about five minutes to about thirty minutes is required for the urea-urease mixture to stop the action of the relaxing agent and restore the keratin structure of the relaxed hair. The time required will depend, of course, on the efficiency of penetration of the materials into the wound tress, the type of curler used, and other factors which will be appreciated by those skilled in the art.

The urea advantageously may be incorporated with the waving lotion as manufactured or it may be supplied in a package separate from the waving lotion and added to a quantity of the waving lotion by the operator just prior to use. In the latter case, the urea may be supplied in the form of a water solution packaged in a bottle or jar or it may be in dry powder form packaged in an envelope or the like.

It is essential that the urease be kept separate from the waving lotion and the urea until just before the same is applied to the hair. The urease may be packaged in powder form in an envelope or the like. It is a further feature of this invention that the urease need not be supplied in chemically pure form or in a high potency concentrate. Thus, jack bean meal or soy bean meal, each of which contains urease, may be employed in place of chemically pure urease.

The amounts of urea and urease employed in accord-

ance with this invention are variable. It is only necessary to employ these materials in quantities such that sufficient ammonia is produced by their interaction to raise the pH of the materials in contact with the hair to a value at which, within a reasonable time, the action of the relaxing agent is stopped and the keratin structure of the hair is rebulit. It has been determnied that such a result may be obtained by an increase in the pH of the materials in contact with the hair to a pH within the range of about 8 to about 9.

In general, the urea will be employed in amounts within the range of about 5% to about 30% by weight and preferably about 15% to about 25% by weight of the waving lotion applied to the hair. The urease generally will be employed in amounts within the range of about 0.1% to about 2.0% by weight and preferably within the range of about 0.3% to about 1.5% by weight of the waving lotion and urea applied to the hair.

Various comon additives useful in hair waving lotions also may be included in the waving lotion of this invention. For example, such materials as wetting agents may be used, preferably of the non-ionic type such as the alkyl phenoxy polyethoxy alkanols, or other polyalkylene oxide derivatives, but anionic and cationic types may be used alternatively if desired, the wetting agent being present in minor quantities ranging from about 0.1 to about 3% by weight of the waving lotion. The lotion also may contain opacifying agents, such as oils or insoluble resinous materials such as polymerized methyl methacrylate together with suitable dispersing or emulsifying agents to render the lotions opaque and the lotions also may contain coloring agents, perfumes, etc. to make the product attractive. These additives, opacifiers, perfumes and colorings usually are used in minor quantities, for example, from about .001 to about 1% by weight of the waving lotion.

After-treatments may be employed as desired once the wave has been set permanently by treatment with the urea and urease. The tress is unwound and preferably rinsed with water to remove residual sulfite. The hair will be slightly alkaline after waving despite thorough washing, but it will regain its natural slight acidity in a matter of days. The reconversion to acidity desirably is accelerated by a conventional acid rinse to reduce the pH of the hair preferably below about 6.8. To insure thorough destruction of residual sulfite, such acid rinse may be oxidizing in character, but it will be understood that any oxidizing agent used with such acid rinse would be applied only as an after-treatment carried out after the wave has been fully set. A suitable acid rinse is an aqueous solution of a weak acid such as citric, tartaric, or acetic acid in water generally adjusted with a buffer to a pH in the range of 2.5 to 6.8, with or without a conventional oxidizing agent.

Treatment with urea and urease leaves the hair in a somewhat swollen state; hence, the acid rinse, or acid rinse containing oxidizing agent, which tends to reduce swelling, is preferred as an after treatment, but other after-treatments such as application of an alkaline oxidizing agent may be used. Any conventional oxidizing agent which effectively destroys residual sulfite may be used, such as an alkali metal perborate, bromate, peroxide, or other oxidizing agent known in the art.

The chemicals employed in accordance with the present invention are harmless when used in the prescribed manner and they are superior in the wave they produce. A minimum of control is required so that they are excellently adapted for home or non-professional use. For this purpose, the materials, i. e., the hair waving or relaxing lotion and the urea and urease which are cooperatively effective for purposes of first relaxing the hair, so that it will readily take the curl, and then restoring the curled hair to its original chemical structure so that the wave becomes permanent, may be made up in a "home kit," either in which all the ingredients are supplied in powder form or in which some of the compositions are in powder form and others in the form of liquids.

To indicate even more fully the nature of the present invention the following examples are set forth. These examples are presented for illustrative purposes only and they are not intended to limit the scope of the invention in any manner except as indicated in the appended claims.

PREPARATION OF KERATIN RELAXING LOTION

Example I

Sulfur dioxide gas is bubbled at room temperature into a 30% solution of ammonium carbonate in water to form an acid solution of ammonium bisulfite. An equal molar quantity of sodium bisulfite is added to the solution thus prepared and the resultant solution is diluted with water after which 10% n-propyl alcohol is added. This quantity of alcohol raises the apparent pH of the solution to approximately 6.3. Thereafter, about 0.25% of a non-ionic wetting agent, viz., an alkyl phenoxy polyethoxy ethanol, is added. About 15% of urea then is added to the mixture after which minor quantities of perfume and color are added in quantities sufficient to impart a pleasing odor and appearance to the product.

Example II

Sulfur dioxide gas is bubbled at room temperature into a 30% aqueous solution of guanidine carbonate to form an acid solution of guanidine bisulfite having a pH of about 5.8. The solution is filtered, if necessary, to remove suspended impurities. The solution then is diluted to approximately double its volume with water, after which 10% n-propyl alcohol is added. This quantity of alcohol raises the apparent pH of the solution to approximately 6.1. Thereafter, about 0.25% of a wetting agent, namely an alkyl phenoxy polyethoxy ethanol, is added. About 0.5% of a concentrated suspension of methyl methacrylate polymer, suspended in water, is added to cream and body the lotion. Minor quantities of perfume and color, sufficient to render the product attractive, then are added.

Example III

Ammonium acid sulfite is dissolved in water or may be formed in an aqueous solution from ammonium carbonate and sulfur dioxide in a manner similar to that described in Examples I and II, and diluted with ethyl alcohol to form a 15% alcoholic solution of the ammonium acid sulfite contained therein. To this is added 0.25% of a wetting agent, 0.5% of a methyl methacrylate polymer dispersion in water to impart to the solution a creamy appearance and also sufficient perfume and dye to render the product attractive. In this example, the final apparent pH of the solution is approximately 6.2.

Example IV

Guanidine acid sulfite formed as described in Examples I and II is made up into a relaxing lotion having an isopropyl alcohol content of about 30% and a wetting agent content of about 0.25%. The apparent pH is adjusted to about 7.3 with guanidine carbonate.

Example V

Guanidine acid sulfite prepared as described in Example II is made up into a solution having an apparent pH of 6.0 containing 40% of alcohol and suitable quantities of urea, a non-ionic wetting agent, a creaming agent, and minor quantities of perfume and color, as described in Examples I and II, to form an effective softening agent for relaxing the hair.

The kit also will contain urease supplied in a package separate from the urea and the relaxing or waving lotion. As indicated hereinabove, the urease is supplied in powder form packaged in an envelope or the like. In-

stead of chemically pure urease, jack bean meal or soy bean meal may be employed.

The urea may be supplied in a separate package in the kit or, as indicated in Examples I and V, it may be packaged in admixture with the relaxing lotion. In the former case, the urea may be dissolved in water and packaged in bottles or it may be in powder form packaged in envelopes.

AFTER RINSE COMPOSITIONS

Example VI

A 16% by weight solution of sodium fromate is made up in water containing additionally about 0.7% of a buffer consisting of trisodium phosphate dodecahydrate and about 7.7% of monosodium dihydrogen orthophosphate monohydrate, about 1% of a wetting agent, about 2% of an opacifier, i. e., a concentrated suspension in water of polymethyl methacrylate and perfume 0.2%. The pH of the solution is approximately 4.8. This solution is of a suitable concentration for supply with a home kit, and is normally diluted eight times with water prior to use.

Example VII

Citric acid	grams	10
Water, q. s.	ounces	16

Example VIII

	Grams
Sodium bromate	12.0
Monosodium dihydrogen orthophosphate monohydrate	10.0

These powders are mixed and sealed hermetically in a foil envelope. For use as an after rinse solution, the contents of the envelope are dissolved in one pint of water. The pH of the solution will be approximately 5.0.

A home use cold waving kit may be provided by separately packaging the waving or relaxing lotion, the urea, and the urease, the quantities of the three compositions being proportioned to effect relaxation of the hair followed by rebuilding of the hair substantially to its original strength by their sequential use. As indicated in the following examples the three compositions may be included in powder form in the kits or the kits may comprise compositions some of which are liquids and others dry powders.

Example IX

A home use cold waving kit is made up to include, in separate packages, a relaxing chemical, urea, and urease. In this kit about 5 parts of sodium acid sulfite and about 7 parts of ammonium acid sulfite are admixed and packaged as a dry powder in an envelope. About 22 parts of urea and about 1.5 parts of jack bean meal are packaged separately in envelopes. These dry powders are admixed with water or alcohol prior to application to the hair.

Example X

A home use or professional use permanent waving kit is made up to include a waving lotion containing about 4.11 parts of a 95% aqueous solution of sodium acid sulfite, about 6.60 parts of a 76% aqueous solution of ammonium acid sulfite, about 22 parts of urea, about 3 parts of a non-ionic wetting agent, and about 100 parts of water. This waving lotion is packaged in a bottle and included in a kit together with an envelope containing about 1.5 parts of jack bean meal.

Example XI

A home use or professional use permanent waving kit is made up to include two separately packaged compositions. One composition contains about 5 parts of sodium acid sulfite, about 7 grams of ammonium acid sulfite, and about 22 parts of urea. This composition is packaged in an envelope and included in a kit together with an envelope containing about 1.3 parts of jack bean meal.

While the present invention has been described with reference to particular embodiments and examples, it will be understood, of course, that many modifications, changes and substitutions may be made therein without departing from the true scope of the invention as defined in the appended claims.

Having thus described the invention, what is claimed is:

1. The method of permanently waving hair at room temperatures which comprises relaxing the hair by wetting it with a solution comprising an acid sulfite adjusted to a pH within the range of about 6.0 to 7.0, to split at least some of the cystine linkages of the keratin of the hair; deforming the hair upon a curler; and setting the wave resulting from said deformation, by restoring cystine lingages and keratin structure by applying to the curled relaxed hair non-alkaline, non-oxidizing substances comprising urea and urease in amounts sufficient to allow the gradual generation, in situ, of sufficient ammonia to increase the pH of the materials contacting the hair to about 8.0 to 9.0.

2. The method of permanently waving hair at room temperatures which comprises deforming the hair upon a curler; relaxing the hair by wetting it with a solution comprising an acid sulfite adjusted to a pH within the range of about 6.0 to 7.0 to split at least some of the cystine linkages of the keratin of the hair; and setting the wave resulting from said deformation by restoring cystine linkages and keratin structure by applying to the curled, relaxed hair, non-alkaline, non-oxidizing substances comprising urea and urease, in amounts sufficient to allow the gradual generation, in situ, of sufficient ammonia to increase the pH of the materials contacting the hair to about 8.0 to 9.0.

3. The method of permanently waving hair at room temperatures which comprises relaxing the hair by wetting it with a solution comprising an acid sulfite and urea adjusted to a pH within the range of about 6.0 to 7.0, to split at least some of the cystine linkages of the keratin of the hair, said urea being present in amount, capable, on action of urease, of releasing enough ammonia to increase the pH of materials contacting the hair to about 8.0 to 9.0; deforming the hair upon a curler; and setting the wave resulting from said deformation, by restoring cystine linkages and keratin structure, by applying, to the curled relaxed hair, a non-oxidizing, non-alkaline substance, comprising urease, in amount sufficient to allow the gradual release from the urea, of sufficient ammonia to increase the pH of the materials contacting the hair to about 8.0 to 9.0.

4. The method of permanently waving hair at room temperatures which comprises deforming the hair upon a curler; relaxing the hair by wetting it with a solution comprising an acid sulfite and urea, adjusting to a pH within the range of about 6.0 to 7.0 to split at least some of the cystine linkages of the keratin of the hair, said urea being present in amount, capable, on action of urease, of releasing enough ammonia to increase the pH of materials contacting the hair to about 8.0 to 9.0; and setting the wave resulting from the aforesaid deformation, by restoring cystine linkages and keratin structure, by applying, to the curled relaxed hair, a non-oxidizing, non-alkaline substance, comprising urease, in amount sufficient to allow the gradual release, from the urea, of sufficient ammonia to increase the pH of the materials contacting the hair to about 8.0 to 9.0.

5. A method of permanently waving hair at room temperature which comprises holding the hair in desired shape while it is in contact with (1) an acid sulfite keratin-relaxing agent in non-alkaline solution, which agent is capable of modifying the keratin structure of the hair, and (2) urea and urease, in initially non-alkaline solution to gradually release ammonia in amount capable of stopping the

relaxing action of the acid sulfite and of restoring the original keratin structure of the hair.

6. A method of permanently waving hair at room temperature which comprises holding the hair in desired shape while it is in contact with (1) an acid sulfite keratin-relaxing agent in solution, of a pH between about 5.5 and 7 which agent is capable of modifying the keratin structure of the hair by splitting at least some of the cystine linkages thereof, and (2) urea and urease in solution to gradually release ammonia in amount sufficient to raise the pH of the materials contacting the hair to about 8 to 9 and thereby to stop the hair-relaxing action of the acid sulfite and restore the original keratin structure of the hair.

7. A method of permanently reshaping hair at room temperature which comprises holding the hair in desired shape while it is in contact with an acid sulfite keratin-relaxing agent, capable of modifying the keratin structure of the hair and urea and urease capable of gradually developing ammonia in situ on the hair in amount sufficient to raise the pH of the relaxing agent to a point at which the relaxing action is stopped and the keratin structure of the hair is restored.

8. A method of permanently reshaping a keratin-containing substance which comprises holding said substance in desired shape while it is in contact with an acid sulfite keratin-relaxing agent capable of modifying the keratin

structure of said substance and urea and urease capable of gradually developing ammonia in situ on the modified keratin-containing substance in amount sufficient to stop the relaxing action of the sulfite relaxing agent and to restore the original keratin structure of said substance.

References Cited in the file of this patent

UNITED STATES PATENTS

1,716,347	Riehl	June 4, 1929
2,033,180	Bunzell	Mar. 10, 1936
2,526,614	Butterfield	Oct. 17, 1950
2,540,980	Beste	Feb. 6, 1951

FOREIGN PATENTS

1,004,940	France	Dec. 5, 1951
973,675	France	Sept. 20, 1950
552,286	Great Britain	Mar. 31, 1943
552,285	Great Britain	Mar. 31, 1943
453,700	Great Britain	of 1935
443,359	Great Britain	Feb. 20, 1936
270,698	Switzerland	Dec. 1, 1950

OTHER REFERENCES

Speakman et al.: Reactivity of the Sulphur Linkage. Part V, J. Soc. Dyers and Colourists, March 1941, pp. 73–81, esp. at pp. 78–81.