

[54] HAIR CONDITIONING AND COMPOSITION THEREFOR

4,038,995 8/1977 Edelberg 132/7
4,197,865 4/1980 Jacquet 132/7
4,214,596 7/1980 Kaplan 132/7

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[57] ABSTRACT

[21] Appl. No.: 236,127

A hair conditioning composition particularly useful in conjunction with hair waving having a pH value of about 4–9 and containing water having dissolved therein about 0.05–5 weight percent quaternary nitrogen-containing conditioning polymer having a molecular weight of about 10,000–10,000,000, and about 0.5–10 weight percent of a water-soluble disulfide-containing polycarboxylic acid or salt thereof, as well as methods for its use and preparation are disclosed.

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[52] U.S. Cl. 132/7; 424/72

[58] Field of Search 132/7; 424/70–72

[56] References Cited

U.S. PATENT DOCUMENTS

3,693,633 9/1972 Kalopissi 132/7
3,760,819 9/1973 Vogt 132/7
3,957,065 5/1976 Busch 132/7

16 Claims, No Drawings

HAIR CONDITIONING AND COMPOSITION THEREFOR

DESCRIPTION

1. Technical Field

This invention relates to conditioning hair, and particularly to compositions and processes for selectively conditioning hair whose configuration is to be altered.

2. Background Art

Permanent hair waving is usually carried out by subjecting the hair to reagents containing a free —SH group or thiol. These materials are also called mercaptans. In this treatment, the hair is usually first wound on rollers and then saturated with the thiol. The thiol waving agent acts to break the disulfide bonds within the hair fiber forming thiol groups in the hair protein and disulfide bonds between two thiol waving agent molecules. When a sufficient number of hair disulfide bonds have been broken, the hair is realigned to pair previously unpaired hair protein thiol groups opposite each other. At this point, the hair is rinsed, removing the unreacted thiol waving agent and disulfide reaction product formed from it, and then saturated with an oxidizing agent, or neutralizer, such as hydrogen peroxide or a bromate salt, to reform disulfide bonds between the newly paired hair protein thiols and to give the hair a configuration or wave. This process may be used to add curl or straighten the hair.

Salts of thioglycolic acid, such as ammonium thioglycolate, and thioglycolic acid esters, such as glycerol thioglycolate, are typically utilized as the thiol waving agent. Other thiol-containing reagents such as thiolactic acid, beta-mercaptopropionic acid, beta-mercaptobutyric acid, mercaptosuccinic acid and the like are also known in the art to be effective.

As the above waving process is usually carried out, the hair is wet with water or a disulfide bond breaking agent prior to its being wrapped on the rollers. In some instances, the thiol-containing waving lotion is used as the wetting agent, or prewrap, as it is known in the art.

This latter treatment begins the hair disulfide bond breaking process, and hastens the overall process. However, as the hair is difficult to wrap while wearing the gloves normally used with thiol waving agents, beauticians frequently use their bare fingers for this step, and continual contact of the skin with thiol-containing reagents may cause skin irritation to some individuals.

The problems of using bare fingers to wrap hair on rollers after treatment with a disulfide bond-breaking reagent was largely solved by the invention of the co-assigned U.S. Pat. No. 4,214,596 to Kaplan et al. That patent describes the use of a bisulfite ion-containing composition in a prewrap which is mild to skin and non-irritating.

One problem which U.S. Pat. No. 4,214,596 did not solve was the under waving and over waving (under and over processing) which may occur during waving on different parts of a single hair fiber or in different areas of the hair mass due to the physical and chemical condition of the hair itself. For example, hair which has been waved, bleached, or bleached and waved is more porous than is hair which has not undergone these chemical treatments, such as portions of the hair fiber near the root which has grown out since the last bleaching or waving. Similarly, even hair having no previous history of bleaching or waving is more porous near the tip end than near the root end simply because hair near

the tip has been brushed more, or has been subjected to more weathering.

As a consequence of these porosity differences, the hair tends to take-up more waving agent in some areas, and less waving agent in others. Over waving or processing tends to occur in the more porous portions of the hair while under waving or processing tends to occur in the less porous areas. These trends are exactly the inverse of what is desired since the hair which usually needs the waving treatment the most gets the least waving, and vice versa.

Aside from changes in porosity, hair which has been bleached and/or waved is also believed to have a different chemical make-up than does virgin, unchemically-treated, hair. In addition, older hair which has been brushed more often tends to have a rougher cuticle or outer layer than does hair which is newer, closer to the scalp, and therefore brushed fewer times. This observed roughness is believed to be due to several factors including: (1) the physical abrasion of portions of the cuticle caused simply by repeated contact with hair brush bristles; and (2) the physical damage done to the tip ends when a brush or comb is pulled through the tips at the end of the brushing or combing stroke.

Conditioning agents for hair have been known in the art for several years. Typically, these conditioning agents are relatively small molecules having a single quaternary nitrogen atom bonded to at least one 8-20 carbon atom chain with the remaining nitrogen bonds being taken up by ethyl, methyl or benzyl groups. These conditioners are used after a shampoo as put-on, rinse-out compositions; put-on, leave-on compositions also being known. At least one commercial waving preparation is said to use a relatively small molecule quaternary conditioning agent in the prewrap composition.

A disadvantage of the relatively small molecule quaternary conditioning agents is that they are substantially washed out of the hair after a single shampoo and therefore do not provide a lasting effect. In addition, the relatively small molecule quaternary conditioners provide little, if any, set control to the hair, and tend to leave the hair limp, with little body.

U.S. Pat. No. 3,912,808 to Sokol teaches the use of a polymeric quaternary nitrogen-containing polymer in a composition used for changing the configuration of hair; i.e., a waving lotion. When such polymeric quaternary nitrogen compounds are used as the conditioning agents, it is known that the hair will remain conditioned through several shampoos. However, use of this conditioning agent in a prewrap can lead to hair which is too slippery to wind on rollers. The smaller quaternary molecule conditioning agents also produce some slipperiness on the hair, but not so much slipperiness as to interfere with manipulating the hair, as during rolling of the hair in a waving process.

Water-soluble dithiopolycarboxylic acids and their salts, such as diammonium dithiodiglycolate, are known to be useful in waving lotion of hair waving preparations to effect some protection from over waving. However, these disulfides are not known to be useful in prewrap preparations. It is known to use a less soluble ester of such disulfides in a prewrap composition in conjunction with a relatively small molecule, quaternary nitrogen conditioning agent. However, the conditioning effect, if any, of the relatively small molecule quaternary nitrogen compound when used with the

less-soluble disulfide ester is, as stated above, substantially lost after shampooing.

It would therefore be beneficial if the over waving protection provided by water-soluble disulfides could be combined with the long lasting conditioning properties of a polymeric quaternary nitrogen-containing conditioning agent without the hair slipperiness which is associated with such polymers. Such a composition could be used as a prewrap and allow the proper winding of the hair on rollers, while imparting its conditioning effect through several shampoos and protecting the hair from over waving.

The difficulties associated with manipulation of slippery hair when the configuration of the hair is to be changed are not unique to hair waving. Rather, the provision of a lasting conditioning effect to hair without undue slipperiness is general to hair configurational change processes, such as water setting, where wet or damp hair is manipulated subsequent to the application of the conditioning composition.

SUMMARY OF THE INVENTION

According to the present invention, a unique hair conditioning composition is prepared. This composition contains water having dissolved therein about 0.05 to about 5 weight percent of a quaternary nitrogen-containing polymer having a molecular weight between about 10,000 and about 10,000,000, and about 0.5 to about 10 weight percent of a water-soluble disulfide-containing polycarboxylic acid or salt thereof. The composition of this invention has a pH value between about 4 and about 9 measured at 80° F. (26.7° C.).

In addition, a process for treating hair whose configuration is to be changed subsequent to the application of a conditioning composition of this invention is disclosed. According to this process, a composition of this invention is applied to the hair, distributed substantially evenly therethrough, and the configuration of the hair thereafter altered while the hair is at least partially damp.

The compositions and processes of this invention possess many advantages and benefits.

One advantage of the compositions and processes of this invention is that the hair is selectively conditioned by absorbing more conditioning agent at porous areas needing conditioning the most, and less conditioner at portions of the hair requiring less conditioning.

Another benefit of the instant compositions and processes when used in waving is that the amount of waving tends to be leveled along the hair shaft by protecting porous areas from over processing while permitting enough waving of less porous portions of the fiber. This allows the beautician or home user added leeway in choice of product strength and treatment duration for hair which is between the porosity extremes of virgin hair and bleached and waved hair.

Yet another advantage of the compositions and processes disclosed herein is that their conditioning and over-waving protection lasts through several shampoo treatments, and thus the compositions may be applied days before waving is performed.

Still another advantage of the present invention is that when a composition is applied prior to changing the hair configuration, the hair is easily wrapped on rollers without the usual slippery feel associated with polymeric quaternary nitrogen conditioning agents. In addition, when used as a permanent wave prewrap, the beautician need not wear gloves during wrapping be-

cause the compositions of this invention are not irritating to the hands.

Yet another benefit of the present invention is that the compositions may be used as a put-on, leave-on product or as a put-on, rinse-out product and in either use add a long term conditioning benefit to the hair.

An additional benefit of this invention is that the tensile strength of waved hair treated with its compositions tends to be greater than that for hair which has only been waved, and not treated with the compositions disclosed herein.

Still other benefits and advantages of the instant invention will be apparent to those skilled in the art from the disclosure which follows.

DETAILED DESCRIPTION OF THE INVENTION

The compositions of the present invention are broadly useful for conditioning human hair. These compositions are particularly useful for conditioning hair whose configuration is to be changed subsequent to the application of the conditioning composition since configuration changes typically require manipulation of the hair, and use of the compositions of this invention provides hair which is conditioned but not too slippery to manipulate.

As used herein, changing or altering the configuration of hair is meant to include both straightening and curling processes which are carried out while the hair is wet, or at least damp. Illustrations of hair configuration changing processes include, but are not limited to, hair waving using a thiol-containing reagent and water setting.

Since the problems associated with hair waving typically include those found in other hair configurational change processes, as well as those intrinsic to waving, the discussion hereinbelow will be primarily centered upon the application of the instant invention to hair waving. It should be understood however, that use of the compositions of the present invention is not limited to hair waving processes, and includes use on tinted hair, on bleached and/or previously waved hair, or as a pre-treatment prior to oxidative color or bleaching treatments, or whenever conditioning is desired.

The unique compositions of this invention are prepared by dissolving both a water-soluble, disulfide-containing polycarboxylic acid or salt thereof and a quaternary nitrogen-containing polymer in water. The words "dissolving" and "solution" in their various grammatical forms, are meant herein to include the formation of true solutions as well as the formation of substantially clear, non-settling dispersions. High molecular weight polymers rarely form true solutions in water and tend, at best to form non-settling, substantially clear dispersions. Some lower molecular weight polymers may form true solutions.

The preferred water-soluble disulfide-containing polycarboxylic acids, also called dithiopolycarboxylic acids, useful herein are typically symmetrical in structure on either side of the disulfide bond, although asymmetrical compounds may also be used. These disulfides are typically formed by the oxidation of two molecules of mercapto-monocarboxylic acid. The preferred disulfide-containing polycarboxylic acids of this invention are illustrated by dithiodiglycolic acid, 3,3'-dithiodipropionic acid, cystine, dithiodilactic acid, dithiodisuccinic acid and the like; dithiodiglycolic acid being especially preferred.

The disulfide-containing polycarboxylic acids may be present in the compositions of this invention at about 0.5 to about 10 weight percent of the total composition when it is put on the head. In preferred practice, the water-soluble disulfide-containing polycarboxylic acid is present at about 1 to about 5 weight percent of the total composition.

The dithiopolycarboxylic acids may be added to the water as the free acids and the pH value of the resulting solution thereafter adjusted, if necessary, as discussed hereinafter. Preferably, however, the dithiopolycarboxylic acids are used as their water-soluble salts; the preferred cations being alkali metal ions such as sodium or potassium, or more preferably the ammonium ion. Cosmetically acceptable substituted ammonium ions such as the alkanolammonium ions, illustrated by the monoethanolammonium, di-isopropanolammonium and triethanolammonium ions, are also useful cations. The above described amounts of dithiopolycarboxylic acid in the compositions of this invention are calculated as the acid, rather than as a salt thereof.

A wide variety of water-soluble quaternary nitrogen-containing polymers are useful herein. Broadly, such polymers are useful in the range of about 0.05 to about 5 weight percent of the compositions. Preferably, these polymers are present in the range of about 0.1 to about 2 weight percent, and more preferably these polymers are useful in the range of about 0.1 to about 1 weight percent. The molecular weights of the polymers useful herein are broadly between about 10,000 and about 10,000,000, and preferably between about 100,000 and about 4,000,000, with various useful polymers having a generally more narrow molecular weight range.

The preferred polymeric cationic polymers include those prepared from polydiallyldimethylammonium salts as is described in U.S. Pat. No. 3,288,770 and No. 3,412,091. These polymers may be prepared by polymerizing diallyldimethylammonium chloride or bromide, or other suitable diallyldimethylammonium salts, using a free radical generating polymerization catalyst, such as a peroxide or hydroperoxide, then employing a suitable anion exchange resin. The resulting polymers are polydiallyldimethylammonium salts, such as polydiallyldimethylammonium chloride. The homopolymer so produced has been given the name Quaternium-40 in the *CTFA Cosmetic Ingredient Dictionary (CTFA Dictionary)*, 2nd ed., 1977, published by the Cosmetic Toiletry and Fragrance Association, Inc.

The copolymer formed using acrylamide and a diallyldimethylammonium salt is also useful herein. The *CTFA Dictionary* name for the diallyldimethylammonium salt copolymerized with acrylamide is Quaternium-41.

Both Quaternium-40 and Quaternium-41 are commercially available under the respective designations MERQUAT-100 and MERQUAT-550 from Merck & Company, Inc. The polymer of the product designated MERQUAT-100 is said by the manufacturer to have a molecular weight of about 100,000 to about 1,000,000, while the polymer of the product designated MERQUAT-550 is said by the manufacturer to have a molecular weight of about 1,000,000 to about 10,000,000. MERQUAT-100 is sold as a 40 weight percent aqueous solution of the polymer, and has a Brookfield viscosity at 25° C. in the range of about 8,000-12,000 centipoises (cps). MERQUAT-550 is sold as an 8 weight percent aqueous solution of polymer, and has a Brookfield viscosity at 25° C. in the range of about 7,500-15,000 cps.

Another preferred quaternary nitrogen-containing polymer useful herein is a cationic guar. This material has 3-trimethyl-ammonium-2-hydroxypropyl groups bonded to the mannopyranosyl and galactopyranosyl units which make up the guar chains; chloride ion being the anion usually associated with the polymer. The name adopted by the Cosmetics, Toiletries and Fragrances Association for this material, although not appearing in the above *CTFA Dictionary*, is Guar Hydroxypropyltrimonium Chloride. A suitable cationic guar is supplied under the designation COSMEDIA GUAR C 261 by Henkel, Inc., while a similar material is sold under the designation JAGUAR C-13-S by Stein, Hall & Company, Inc.

A copolymer prepared from about 80 weight percent N-vinyl pyrrolidone and about 20 weight percent N,N-dimethyl-aminoethyl methacrylate, quaternized with dimethyl sulfate is also preferred herein. This material is named Quaternium-23 in the *CTFA Dictionary*.

Quaternium-23 is available from GAF Corporation under the designation GAFQUAT-755 and GAFQUAT-734. The polymer designated GAFQUAT-734, has an average molecular weight of less than about 100,000, while that designated GAFQUAT-755 has a molecular weight of greater than 1,000,000.

Yet another preferred polymer useful herein is a copolymer prepared from acrylamide and N,N-dimethylaminoethyl methacrylate, quaternized with dimethyl sulfate. Viscosities of 1 weight percent aqueous solutions of these polymers typically have Brookfield viscosities of about 35 to about 1200 cps.

These copolymers are named in the *CTFA Dictionary* as Quaternium-39, and are available under the designation RETEN from Hercules, Inc. Commercially available polymers include those designated RETEN SPX 1104, SPX 1105 and SPX 1106.

The copolymers designated RETEN SPX 1104, SPX 1105 and SPX 1106 are stated by their manufacturer as being highly cationic, and are reported to have Brookfield viscosities of 35-50 cps, 100-400 cps and 600-800 cps, respectively, for 1 percent by weight solutions in water at 25° C. RETEN SPX 1104 is most preferred of this type of polymer for use herein. Copolymers designated RETEN 210 and 220 having viscosities in the range of about 600 to about 1200 cps, under the above conditions, are also suitable.

The most preferred water-soluble polymer for use herein is a quaternary nitrogen-containing hydroxyethyl cellulose having a backbone chain of anhydroglucose units with pendant substituent groups bearing a full positive charge spaced along the anhydroglucose backbone. The pendant substituent group are spaced about the anhydroglucose units along the chain, thereby making the substituent groups themselves pendant and spaced along the chain. These hydroxyethyl cellulose derivatives contain a plurality of quaternary nitrogen-containing groups with each anhydroglucose unit having from zero to three quaternary nitrogen-containing groups. These materials are typically prepared by reacting hydroxyethyl cellulose with epichlorohydrin followed by reaction with a tertiary amine; the preferred tertiary amine being trimethylamine. The preparation of these quaternary nitrogen-containing polymers is described in U.S. Pat. No. 3,472,840.

These cationic, hydroxyethyl cellulose derivatives are named Quaternium-19 in the *CTFA Dictionary*, and are commercially available under the designation POLYMER JR from the Union Carbide Corporation. The

presently available materials include POLYMER JR-125, POLYMER JR-400 and POLYMER JR-30M. The molecular weights of these polymers are reported to be between about 300,000 and about 1,000,000, with polymers of a given designation having narrower average molecular weights. For instance, POLYMER JR-30M is reported to have an average molecular weight between about 700,000 and 1,000,000, while POLYMER JR-125 is reported to have an average molecular weight between about 300,000 and about 400,000, and nearer to 300,000 than to 400,000. A two percent by weight aqueous solution of POLYMER JR-125 is reported to have a Brookfield viscosity at a 30 r.p.m. spindle speed of 75-175 cps (No. 1 spindle), while a one percent solution of POLYMER JR-30M is reported to have a Brookfield viscosity of 1,000-2,500 cps (No. 3 spindle) under the same measurement conditions.

Of these polymers, POLYMER JR-400 is most preferred. A two weight percent aqueous solution of POLYMER JR-400 at 25° C. reportedly has a Brookfield viscosity of 300-500 cps (No. 2 spindle), again at 30 r.p.m. The average molecular weight of POLYMER JR-400 is said to be between about 300,000 and about 400,000, nearer to 400,000 than 300,000, and above that of POLYMER JR-125.

As used, the compositions of this invention suitably have a pH value of from about 4 to about 9. When used generally as a conditioner, the compositions preferably have a pH value of from about 5 to about 8, while when used as a prewrap before a waving process, the pH value is more preferably from about 6.5 to about 8.

The mechanisms by which the composition and process of the instant invention provide their unique and lasting selective conditioning and over waving protection results are not known. While not wishing to be bound by any one set of theories or hypotheses, it is thought, however, that the composite mode of action of the compositions of this invention may be as follows.

First, it is believed that treating hair to be waved with a solution of a dithiopolycarboxylic acid before the thiol-containing waving lotion is applied can allow more of the over-waving protective dithiopolycarboxylic acid, or its salt, to be taken up by the hair than when the dithiopolycarboxylic acid is used in the waving lotion. This is because there can be no competition for binding sites within the hair fiber between the dithiopolycarboxylic acid and the thiol-containing waving agent when the former is applied before the latter.

Second, as the accompanying Example 4 demonstrates, the useful conditioning, quaternary nitrogen-containing polymer binds more to hair with a previous history of bleaching and/or waving than to virgin hair, and it is bleached and/or waved hair which is most susceptible to over waving. Consequently, a further possible mode by which selective protection from over waving is afforded by the compositions of this invention may be due to the formation of a physical barrier to penetration of the hair fiber by the thiol-containing waving agent caused by selective polymer binding to those portions of the hair which have a previous history of bleaching and/or waving or are otherwise relatively porous.

Third, the dithiopolycarboxylic acid or its salts are found to have a synergistic effect on the conditioning caused by the quaternary nitrogen-containing polymer. Thus, while it is known that the polymers useful herein will condition hair, hair treated with the polymer alone tends to be too slippery when wet or damp to wind

effectively on rollers. However, it has now been found that when quaternary nitrogen-containing polymers are combined with the dithiopolycarboxylic acid or its salts, as taught herein, the wet or damp hair is still conditioned, but it is not so slippery that it will not wind properly on rollers. The conditioning effect is also found to last through several shampoo treatments. Additionally, hair treated with the compositions of this invention has more body than hair treated with either an equal amount of the quaternary polymer or the dithiopolycarboxylic acid alone. This is shown in Example 3, hereinafter.

In addition to the water, dithiopolycarboxylic acid or salts thereof and quaternary nitrogen-containing polymer, additional ingredients may also be present in the compositions of this invention. These additional ingredients may be selected from preservatives, perfume, one or more surfactants, nonionic surfactants being preferred, colorants, and additional conditioning agents, such as benzalkonium chloride.

An illustration of the use of the conditioning compositions of this invention on hair whose configuration is to be changed is as follows. The hair is usually first shampooed and left wet or damp. It is then treated with a composition of this invention by applying the composition to the hair and distributing the composition substantially evenly therethrough. The configuration of the hair is thereafter altered while the hair is wet or at least partially damp from the application of the conditioning composition. The configuration of the hair can be altered by winding upon rollers, or the like, with no other treatment, or by further treatment with a waving or straightening agent as is known in the art, and then dried.

Additional steps are carried out when hair is to be waved substantially immediately after treatment with the composition of this invention, e.g., while the hair is still at least partially damp after application. In this embodiment, the hair is divided into a plurality of sections and a composition of this invention is applied to a section, distributed substantially evenly therethrough, and the treated section wound on a roller. These steps are then repeated on each of the remaining hair sections until all of the hair to be waved is wound on rollers. Because of the mildness of the compositions of this invention, no gloves need be worn during the wrapping step. The hair is thereafter waved by conventional techniques.

Best Modes For Carrying Out The Invention

Example 1: Prewrap Composition

Components	Weight percent of the Composition
(1) Water (deionized)	91.02
(2) Quaternary Nitrogen-containing Polymer (Note 1)	0.25
(3) Dithiopolycarboxylic acid salt (Note 2)	8.0
(4) Surfactant (Note 3)	0.5
(5) Preservative	0.115
(6) Perfume	0.04
(7) Ammonium hydroxide (28% NH ₃)	0.075

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