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(54) Permanent waving composition

(57) A permanent waving composition which imparts to the hair a substantially increased curl rentention, as well as substantially improved hair manageability and improved hair feel and appearance, is attained by the incorporation into the waving composition of a strong hydrogen bonding amino acid and a water soluble or emulsifiable silicone-based compound. By employing these two additives, a synergistic effect is achieved. Preferably, the strong hydrogen bonding amino acids are derived from hydrolyzed silk protein.

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SPECIFICATION

Permanent waving composition

This invention relates to the art of permanent waving of hair, and more particularly to novel compositions therefor which impart substantially increased lasting or staying ability to the permanently waved hair.

In view of the unique composition of hair fibers and the various changes in styles and fashion, the waving of hair has long been of particular interest. In order to best understand the various methods in which hair fibers can be styled or waved, it is important to remember that normal hair has three major bonds that hold the configuration of the hair and are responsible for the strength of the hair. These three bonds are salt linkages, hydrogen bonds, and disulfide bonds.

As is well known, hair is a protein produced from units known as "amino acids". A high proportion of these are diamino and dicarboxylic "amino acids", and thus the hair fiber is amphoteric in character. Since the number of free acid and basic groups are approximately equal, the hair's mechanical properties, such as its strength, are at their maximum at neutrality (pH 7). For example, the fiber becomes easier to stretch as the pH increases or decreases from pH 7. The cohesion of hair is also demonstrated by the minimum swelling in water at neutrality.

Because they are so numerous, the hydrogen bonds, involving the amino hydrogen and carbonyl oxygen of the amide linkages, are most important. Water, particularly in the monomolecular state, as occurs with moisture in the air (humidity), can weaken these bonds, be becoming a part of a hydrogen bonding structure. However, some of these hydrogen bonds are protected by hydrophobic bonds and will remain even when the hair is wet with water. More powerful hydrogen bond breakers, like high concentration of lithium bromide and urea are required for complete breakage of all hydrogen bonds.

As long as the hair fiber is dry, the strength of the hair fiber is not reduced. For example, a straight hair, wet with water and held by mechanical force in a curly configuration while drying will remain in a curly shape due to the formed hydrogen bonds and salt linkages, and it will not return to its straight shape so long as it remains dry. However, unless mechanically restrained, upon being wet with water, the hair will lose its curly configuration and become straight.

Furthermore, when hair is set by the use of water alone, the hair will gradually lose its curly shape through the absorption of atmospheric moisture and the resulting rearrangement of the hydrogen bonds. This is due to the fact that in water, the dominant bond is disulfide bond, while in the dry state, the dominant bonds are the salt linkages and the hydrogen bonds.

In regard to the disulfide bonds, hair is composed of a unique protein material called "keratin", which is distinguished by the fact that it contains a very significant amount of an amino acid (cystine) which contains the element sulfur in addition to the elements nitrogen, oxygen, carbon and hydrogen. In the natural synthesis of hair, the element sulfur covalently links adjacent polypeptide chains (K) through two sulfur atoms (S-S) to give keratin protein (K-S-S-K). Only by chemical action can this covalent linkage be broken.

Similarly, it is well established that in order to permanently wave hair, this disulfide linkage must be broken. In this regard, many prior art compositions have been developed for the "cold permanent waving" of hair. Typically, these prior art systems treat the hair with a reducing agent which breaks the disulfide (cystine) linkages in the hair while the hair is wound around a curling rod.

It is believed that certain hydrogen bonds are protected by the cystine bond and are only broken by water when the cystine bond is split into two cysteine moieties. By the same rationale, these hydrogen bonds are re-formed in the new configuration and protected by the newly formed cystine bonds created in the neutralization step of permanent waving. In effect, these protected hydrogen bonds supplement the disulfide bonds in creating permanency to the new curl configuration.

In general, 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. The chemistry involved in the reaction of the mercaptan with the cystine disulfide bonds in the hair fiber is illustrated by the following chemical equation:

$$KSSK + 2RSH \rightleftharpoons 2\ KSH + RSSR$$

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. Then, the hair is saturated with an oxidizing agent, or neutralizer, such as hydrogen peroxide or

bromate salt, to reform disulfide bonds between the newly paired hair protein thiols, thereby giving the hair a new configuration or wave, or adding curl to the hair. By rebonding the sites of the reduced keratin in their new curled configuration, a permanent set which is impervious to water is established.

The rebonding of the reduced sites accomplished by the action of the chemical oxidizing agent is illustrated by the following chemical reaction:

$$2\ KSH + H_2O_2 \rightarrow KSSK + 2H_2O.$$

In spite of the substantial effort that has occurred in the development of various permanent waving compositions of this general nature, there has been a general inability to improve the holding power or curl configuration retention of "cold permanent waving" formulations. The typical problem encountered with the use of mercaptan reducing agents for the permanent waving of hair is that the permanency of the curl will not last until it is cut off. Instead, the curl relaxes slowly from the normal wear and tear of every day hair care. In the normal grooming process of shampooing, combing, drying and brushing the hair, the fibers are constantly being put under tension and exposed to forces that oppose the new disulfide and hydrogen bonds that were created in the new curl configuration.

In addition to longer curl retention, the industry has also sought to increase the luster, sheen, gloss and manageability of the hair, as well as provide a permanently waved head of hair which is soft, supple, and possesses a natural feel. However, these goals have not been fully attained.

It is, therefore, an object of the present invention to provide a "cold permanent waving" formulation which can impart to the permanently waved head of hair a substantially increased lasting and curl retention ability and may also impart a high luster, gloss, sheen and improved manageability, as well as a full-bodied appearance which is easily managed and feels soft and silky.

It has been found that by incorporating into generally conventional cold permanent waving compositions two specific hair enhancing additives, namely a strong hydrogen bonding amino acid compound, preferably a hydrolyzed silk protein, and a water soluble or emulsifiable silicone-based compound, it is possible to impart substantially increased lasting and curl retention ability to the permanently waved hair.

Thus in accordance with the invention there is provided a waving composition for use in the cold permanent waving of hair, said composition being characterised in that there are incorporated therein as additional additives (A) a strong hydrogen bonding amino acid compound and (B) a water soluble or emulsifiable silicone-based compound in amounts sufficient to provide enhanced curl retention.

The strong hydrogen bonding amino acid compound (additive A) is generally present in the composition in an amount of from 0.001 to 10% by weight/volume, preferably 0.1 to 2.0% wt/vol. Similarly the silicone-based compound (additive B) is generally present in an amount of from 0.001 to 10% wt/vol, preferably 0.1 to 2.0% wt/vol.

It has been found that the strong hydrogen bonding amino acid compound, especially hydrolyzed silk protein, contributes substantially to the permanent waving of the hair and is believed to interact with the permanent wave composition to impart to the overall composition a substantially increased curl or wave staying power or long-lasting ability. Furthermore, the increased curl or wave longevity, as well as hair manageability, is further enhanced and substantially improved by the use of the water soluble or emulsifiable silicone-based compound therewith, since it has surprisingly been found that an interactive, synergistic result is attained when the water soluble or emulsifiable silicon-based compound is used in combination with the amino acid compound such as a hydrolyzed silk protein.

The use of these additives A and B, in addition to the generally conventional permanent waving compounds, have produced an overall cold permanent waving formulation which provides both luster, sheen, manageability and soft and silky feeling hair, as well as allowing the head of hair to retain the permanent waved configuration for a substantially increased time period. Thus the commonly experienced problem of curl relaxation following the application of a cold permanent wave can be substantially eliminated or reduced and a firm and a permanent wave achieved.

Another advantage of the present invention is that the conventional method of permanently waving human hair on the head is employed without deviation. In this way, the present invention is easily employed, without requiring special steps to be learned.

Hydrogen bonds, especially those between an amide nitrogen and an adjacent carbonyl oxygen make a major contribution to the strength of the fiber. Dry fibers are more difficult to elongate than fibers immersed in water. The explanation assumed is that hydrogen bonds are weakened in the presence of water and therefore offer less resistance to the unfolding of polypeptide chains. The magnitude of the contribution of hydrogen bonds to the strength of wet keratin fibers is in the order of about 35%. There is persuasive evidence that hydrogen bonds—not

disulfide bonds alone—are involved in present-day hair waving practices. One of the primary objectives of this invention is to increase the percentage of hydrogen bonds in the hair fiber, especially those unavailable or resistant to water.

Silk is a protein fiber unique and different from hair or wool in that its composition is high in strong hydrogen bonding amino acids, namely glycine, alanine, serine and tyrosine, and contains practically no sulfur containing cystine. These four amino acids comprise over 80% of the silk fiber and it is their strong hydrogen bond cross linkages that hold the fiber together making it resistant even to boiling water.

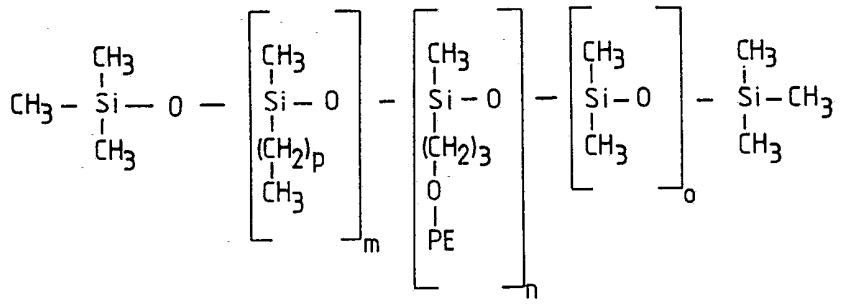
Silk can be hydrolyzed to its individual amino acids by acid, alkaline or enzymatic processes. It is commercially available and listed in the CTFA Dictionary as Silk Amino Acids. The hydrolysate contains seventeen amino acids with a mean molecular weight of 90. This means that the molecules are able to penetrate the cuticle in undamaged hair and enter the matrix in the cortex area of the hair fiber.

This invention is based on the discovery that one can substantially improve the permanent waving of hair and extend the period of time that a new wave configuration is retained in the hair by incorporating in the waving lotion some of these strong hydrogen bonding amino acids. The precise nature of this holding action is not completely understood but it is believed that these amino acids are entrapped by the closing of the sulfur bond in the new wave configuration making additional hydrogen bonds unavailable to water and thus complementing the disulfide bonds in maintaining the permanency of the curl.

This theory is offered only as a possible explanation and is not intended to further limit or define the present invention. It is recognized that other mechanisms may contribute to the permanency of the set in the present invention. For example, a layer of a polysiloxane on the hair surface may provide a hydrophobic barrier that reduces the rate of absorption of atmospheric moisture and thus reduces the rate of hydrogen bond rearrangement and loss of permanency.

In addition to the increased staying power, another object of this invention is to provide increased lubricity to the hair fiber for increased slip. In this way, little or no tension is applied to the hair during the subsequent combing and brushing of a freshly made permanent wave. It is particularly desirable to incorporate this lubricity action in the permanent wave lotion where its action can be effective when the hair is in a softened and easily stretched condition.

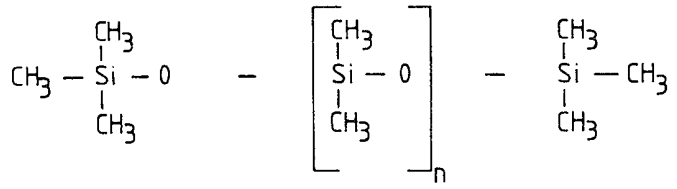
In order to attain this goal, the present invention also incorporates a water soluble or emulsifiable silicone-based compound, in addition to the Silk Amino Acids. In the preferred embodiment, dimethicone copolyol ordimethylsiloxane-glycol copolymer comprises the silicone-based compound. The preferred dimethicone copolymol is nonionic and water soluble, and comprises a polymer of dimethylsiloxane with polyoxyethylene and/or polyoxypropylene side chains. The following represents the general formula for dimethicone copolyol:



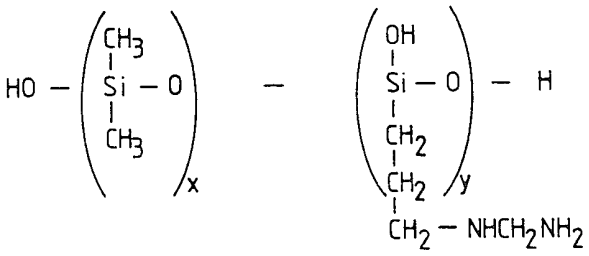
WHERE PE = $(C_2H_4O-)_x$ $(C_3H_6O-)_yH$

The incorporation of a silicone-based compound provides the hair with lubricity for increased slip and easy combing action. Furthermore, the silicone-based compound provides a synergistic effect, increasing the action of the other constituents used in the hair treatment composition.

Although the use of dimethicone copolyol is preferred, other water soluble or emulsifiable silicone-based compounds can be employed, without departing from the scope of the present invention. One other alternative compound is dimethicone, which is a mixture of fully methylated linear siloxane polymers end blocked with trimethylsiloxy units. Empirically, the formula for dimethicone is $(C_2H_6OSi) \times C_4H_{12}Si$, with the following being representative of its general formula:

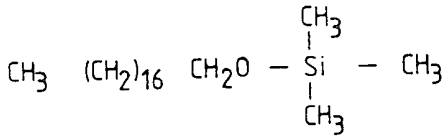


In addition, amodimethicone can be employed as the silicone-based compound. Amodimethicone is a silicone polymer end blocked with amino functional groups. Its formula is represented as follows:



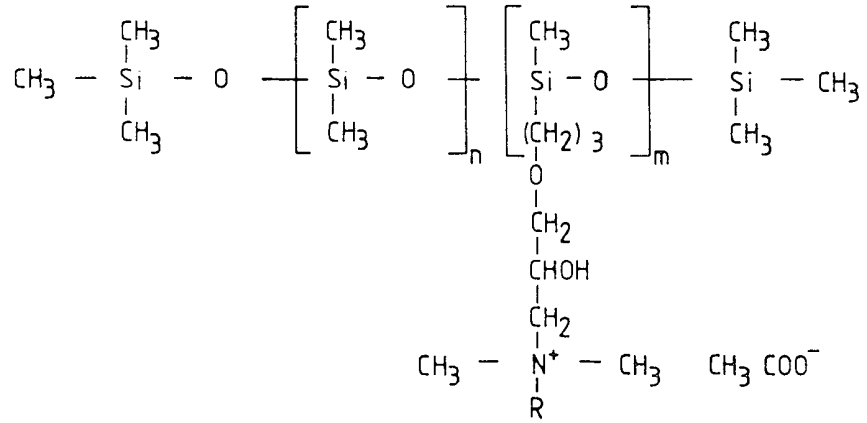
where x has a value of 4 or more

Another silicone compound which can be employed is stearoxytrimethylsilane which is an organo-silicon compound having the empirical formula of $C_{21}H_{46}OSi$. Its formula generally conforms to the following:

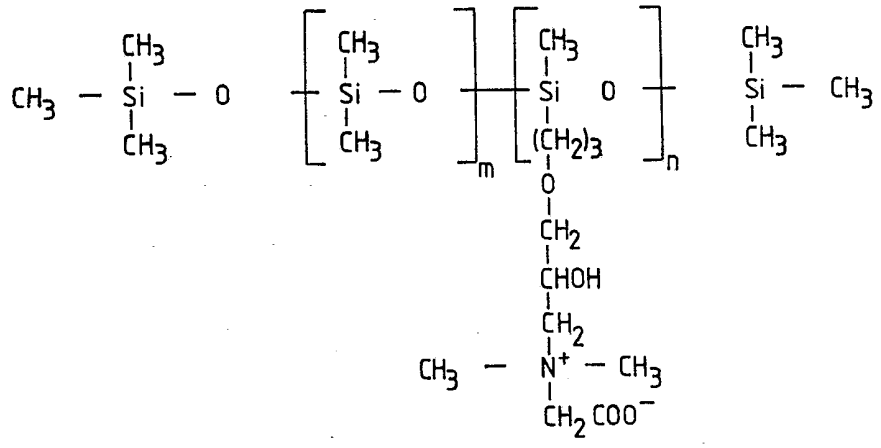


In addition, stearoxy dimethicone can be employed, which is a polymer of dimethylpolysiloxane end blocked with stearoxy groups.

Furthermore, the silicone compound employed in the permanent wave lotion can be a quaternized silicone compound or a betaine silicone compound. A typical quaternized silicone compound is polysiloxane polydimethyl dialkylammonium acetate copolymer, having the following general formula:



The betaine silicone compounds are typified by polysiloxane polyalkyl betaine copolymer having the following general formula:



In a preferred embodiment of the invention, the present waving composition can comprise:

A. from 2% to 10% by weight/volume of ammonium thioglycolate;
B. from 0.5 to 2% by weight/volume of a wetting agent;
C. from 0.1 to 2% by weight/volume of hydrolyzed silk protein;
D. from 0.1 to 2% by weight/volume of a water soluble or emulsifiable silicone-based compound; and
E. water forming the balance of the composition, with the final composition having its pH adjusted to a value in the range from 6 to 10.

Advantageously this composition may further comprise from 2 to 10% by weight/volume of ammonium dithiodiglycolate.

In another preferred embodiment, the waving composition can comprise:

A. from 2 to 30% by weight/volume of glyceryl monothioglycolate;
B. from 0.5 to 2% by weight/volume of a wetting agent;
C. from 0.1 to 2% by weight/volume of hydrolyzed silk protein;
D. From 0.1 to 2% by weight/volume of a water soluble or emulsifiable silicone-based compound; and
E. water forming the balance, with the pH of the final composition being adjusted to a value in the range from 6 to 8.5.

Advantageously the foregoing composition may further comprise from 2 to 30% by weight/volume of diglyceryl dithiodiglycolate.

In the foregoing permanent waving compositions of the invention, the pH value can be adjusted to the required value by the use of one or more alkanolamines, ammonia and carbonates of ammonia.

The following Tables set forth permanent waving compositions in accordance with the invention unless otherwise stated.

In Tables I—IV, compositions of four permanent wave lotions made in accordance with this invention are detailed, with the ranges of each constitute clearly indicated therein. It has been found that these four compositions are substantially equivalent in their efficacy, with each composition providing substantially equivalent enhanced curl retention, hair manageability, and hair appearance improvement.

TABLE I

	PERCENT BY WGT/VOLUME
Ammonium Thioglycolate	2.0 - 10.0%
Wetting Agent	0.5 - 2.0%
Hydrolyzed Silk Protein (Silk Amino Acids)	0.1 - 2.0%
Silicone-Based Compound	0.1 - 2.0%
Ammonium Dithiodiglycolate	2.0 - 10%
Water	qs to 100%
pH adjusted to	6.0 - 10.0

(pH adjustments may be made with alkanolamines, ammonia or the carbonates of ammonia).

TABLE II

	PERCENT BY WGT/VOLUME
Glyceryl Monothioglycolate	2.0 - 30.0%
Wetting Agent	0.5 - 2.0%
Hydrolyzed Silk Protein (Silk Amino Acids)	0.1 - 2.0%
Silicone-Based Compound	0.1 - 2.0%
Diglycerol dithiodiglycolate	2.0 - 30%
Water	qs to 100%
pH adjusted to	6.0 - 8.5

(pH adjustments may be made with alkanolamines, ammonia or the carbonates of ammonia).

TABLE III

	PERCENT BY WGT/VOLUME
Ammonium Thioglycolate	2.0 - 10.0%
Wetting Agent	0.5 - 2.0%
Hydrolyzed Silk Protein (Silk Amino Acids)	0.1 - 2.0%
Silicone-Based Compound	0.1 - 2.0%
Water	qs to 100%
pH adjusted to	6.0 - 10.0

(pH adjustments may be made with alkanolamines, ammonia or the carbonates of ammonia).

TABLE IV

	PERCENT BY WGT/VOLUME
Glyceryl Monothioglycolate	2.0 - 30.0%
Wetting Agent	0.5 - 2.0%
Hydrolyzed Silk Protein (Silk Amino Acids)	0.1 - 2.0%
Silicone-Based Compound	0.1 - 2.0%
Water	qs to 100%
pH adjusted to	6.0 - 8.5

(pH adjustments may be made with alkanolamines, ammonia or the carbonates of ammonia).

In order to prove the efficacy of the permanent waving composition of this invention, the permanent wave lotions detailed in Tables V and VI were prepared and the results were compared and analyzed. The composition in Table V represents a typical known ammonium thioglycolate permanent wave lotion, while the composition in Table VI defines a substantially similar lotion, except for the incorporation of the enhancing additives of this invention.

TABLE V

	% BY WGT/VOLUME
Ammonium Thioglylcolate	8.7%
Ammonia	1.2%
Wetting Agent	1.0%
Water	qs to 100%

TABLE VI

	% BY WGT/VOLUME
Ammonium Thioglylcolate	8.7%
Ammonia	1.2%
Wetting Agent	1.0%
Hydrolyzed Silk Protein (Silk Amino Acids)	1.0%
Silicone-Based Compound	1.0%
Water	qs to 100%

In conducting the comparative tests, both lotion compositions were prepared and tested using two grams of six inch strands of hair for each composition. As detailed herein, the curl permanency was tested using a "racking test", which we have developed and have employed for many years. The hair strands were shampooed and wound on 1/4 inch mandrels. Then the hair strands were processed with one of the two waving lotions for a set period of time and, finally, water rinsed and neutralized with a 2.3% hydrogen peroxide solution.

After water rinsing, the hair strands were combed and allowed to fall into a wave pattern without coaxing. The strands were then placed on a plexiglass board which is marked off in tenths of inches. The readings of each crest (ridge) were recorded, and the average crest to crest distance was determined as follows:

$$\frac{\text{Sum of the Lengths of Each Crest}}{\text{Number of Crests}} = \text{Average Crest-to-Crest Distance}$$

The hair strands were then placed on a racking board and stretched and held in a straightened

position for 24 hours at 100% humidity. Then, the strands were again placed on the plexiglass board and an average crest-to-crest measurement was determined. The percent relaxation was then determined as follows:

$$\frac{\text{Average Crest-to-Crest After Racking} - \text{Av. Crest-to-Crest Before Racking}}{\text{Average Crest-to-Crest Before Racking}} \times 100 = \%\ \text{Relaxation}$$

In Table VII, the results of the "racking test" on these two lotion compositions show a very significant difference in relaxation.

TABLE VII

AVERAGE CREST-TO-CREST CHANGE (MEASURED IN INCHES)

	BEFORE RACKING	AFTER RACKING	PERCENT RELAXATION
Composition according to Present Invention (Table VI)	0.8	0.85	6.25%
Prior Art Composition (Table V)	0.8	0.9	12.5%

In order to further evaluate these two lotion compositions, half-head tests were conducted on live models. Half-head tests are performed on the hair by licensed beauticians on volunteer models.

In these tests, all procedures on the hair were identical, except for the application of one permanent wave lotion to the left side of the head and the application of the other lotion to the right side of the head.

Each head of hair was shampooed, wrapped with the same number and diameter of rods on each side, processed for the same length of time, water rinsed and neutralized with the same amount and composition of neutralizer. The beauticians evaluated the models immediately after the perm was finished and again four weeks later when the models returned for check-ups.

Crest-to-Crest curl measurements, in inches, were made at the front, crown and nape areas of the head and subjective evaluations were made for wet combing, elasticity and scalp wave. The subjective evaluations for these three characteristics were graded Very Good, Good, Fairly Good, Fair, Poor and Very Poor. The average Crest-to-Crest measurements made initially and after four weeks were calculated as % relaxation by the following formula:

$$\frac{\text{Average Crest-to-Crest After 4 Weeks minus Av Crest-to-Crest Initially}}{\text{Average Crest-to-Crest Initially}} \times 100 = \%\ \text{Relaxation}$$

The results of these six half-head tests are shown in Table VIII.

TABLE VIII

AVERAGE EVALUATIONS FOR 6 HALF-HEAD TESTS

	% Relaxation After 4 Weeks	Wet Combing	Elasticity	Scalp Wave
Composition According to Present Invention (Table VI)	10.1%	Very Good	Very Good	Very Good
Prior Art (Table V)	13.7%	Fair	Fairly Good	Fairly Good

CLAIMS

1. A waving composition for use in the cold permanent waving of hair, said composition being characterised in that there are incorporated therein as additional additives (A) a strong hydrogen bonding amino acid compound and (B) a water soluble or emulsifiable silicone-based compound in amounts sufficient to provide enhanced curl retention.

2. A waving composition as claimed in Claim 1, wherein each of the additives (A) and (B) is present in an amount of from 0.001 to 10% by weight/volume.

3. A waving composition as claimed in Claim 2, wherein each of the additives (A) and (B) is present in an amount of from 0.1 to 2.0% by weight/volume.

4. A waving composition as claimed in Claim 1, 2 or 3, wherein additive (A) comprises hydrolyzed silk protein.

5. A waving composition as claimed in Claim 1, 2, 3 or 4, wherein additive (B) comprises a dimethicone copolyol or a quaternized silicone compound.

6. A waving composition as claimed in Claim 5, wherein additive (B) comprises a nonionic water soluble polymer of dimethylsiloxane with polyoxyethylene and/or polyoxypropylene side chains.

7. A waving composition as claimed in Claim 5, wherein additive (B) comprises a polysiloxane polydimethyl dialkylammonium acetate copolymer.

8. A waving composition as claimed in Claim 1, 2, 3 or 4, wherein additive (B) comprises dimethicone, amodimethicone, stearoxytrimethylsilane, stearoxy dimethicone, or polysiloxane polyalkyl betaine copolymer.

9. A waving composition in accordance with Claim 1 comprising:

A. from 2% to 10% by weight/volume of ammonium thioglycolate;

B. from 0.5 to 2% by weight/volume of a wetting agent;

C. from 0.1 to 2% by weight/volume of hydrolyzed silk protein;

D. from 0.1 to 2% by weight/volume of a water soluble or emulsifiable silicone-based compound; and

E. water forming the balance of the composition, with the final composition having its pH adjusted to a value in the range from 6 to 10.

10. A waving composition as claimed in Claim 9 and further comprising from 2 to 10% by weight/volume of ammoniun dithiodiglycolate.

11. A waving composition as claimed in Claim 9 or 10, wherein said pH is adjusted with an alkanolamine, ammonia, or a carbonate of ammonia.

12. A waving composition in accordance with Claim 1 comprising:

A. from 2 to 30% by weight/volume of glyceryl monothioglycolate;

B. from 0.5 to 2% by weight/volume of a wetting agent;

C. from 0.1 to 2% by weight/volume of hydrolyzed silk protein;

D. from 0.1 to 2% by weight/volume of a water soluble or emulsifiable silicone-based compound; and

E. water forming the balance, with the pH of the final composition being adjusted to a value in the range from 6 to 8.5.

13. A waving composition as claimed in Claim 12 and further comprising from 2 to 30% by weight/volume of diglyceryl dithiodiglycolate.

14. A waving composition as claimed in Claim 12 or 13, wherein said pH is adjusted with an alkanolamine, ammonia, or a carbonate of ammonia.

15. A permanent waving composition substantially as described with reference to the forego-

ing Table VI.

16. A method for the cold permanent waving of hair, wherein there is employed a waving composition as claimed in any preceding claim.

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