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HAIR WAVING COMPOSITIONS

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This invention relates to an improved composition for the cold permanent waving of hair. More specifically, it concerns the addition of certain bifunctional amides and nitriles to wave lotions, comprising previously known keratin-reducing agents, for the improvement of wave characteristics and for the protection of physical properties of the hair.

The cold permanent waving of hair is accomplished by contacting it with some chemical composition, often a salt of a mercapto-alkanoic acid, which will soften and plasticize the hair at room temperature. According to the present understanding in the art, such compositions break, or reduce, part of the disulfide bonds which are cross-links holding polypeptide chains of the keratin together. It is presently thought that the reaction of keratin, kSSk, with mercaptan, RSH, can be represented in a schematic way as follows.

$$kSSk + RSH \rightleftharpoons RSSR + 2kSH$$

A disulfide of the reactant mercaptan, RSSR, and reduced keratin, kSH, are the products of the reaction. Ammonium and monoethanolammonium thioglycolate are examples of frequently employed reducing agents. While the hair tresses are mechanically held in a new configuration, the disulfide linkages are restored, at least in part, by oxidation to fix the tresses in the new configuration. The oxidizing agent may be applied as a solution, for example, of sodium perborate, potassium bromate, or hydrogen peroxide; or the oxidizing agent may simply be the oxygen of the air. In this latter case, the wave is known as a "no neutralizer" wave; because the action of the reducing agent has not been neutralized by an applied oxidizing agent.

It has long been a problem in the cold permanent waving of hair to achieve curls of the desired tightness and of adequate permanency without running the risk of undesirably tightly waving the hair and of damaging the hair. Damage may result in a harsh feel and a decrease in tensile strength of the hair fibers. Choosing the correct reaction conditions of time, pH, concentration of the active ingredient, etc., to achieve sufficient, but not excessive reaction, is aggravated by the variation of hair from person to person with a resulting variation of rate of reaction of reducing agent and hair keratin. These problems are more fully discussed and a solution is presented in the prior art; particularly notable is U.S. Patent 2,719,815. This patent discloses that dithiodiglycolates, when used in combination with thioglycolates, in a limited range of proportions, have the characteristics of limiting damage to the hair without, at the same time, preventing the satisfactory waving of the hair.

Another problem in the cold waving of hair is that, while the freshly prepared curls may have the desired tightness, the curls tend to relax or fall out. This problem is often particularly important when, in the interest of simplicity and saving of manipulative time, chemical oxidation of the reduced hair is replaced by simple exposure to the air for insufficient time. The same problem can exist when an oxidizing solution is employed; penetration of the solution into the wound curl, penetration into the hair fiber, and reaction of the oxidizing agent with the reduced keratin are, in total, time consuming steps.

It can be postulated that lack of permanency of the curls arises from insufficient reduction and breaking of the disulfide cross-links between polypeptide chains or from insufficient reestablishment of such cross-links after the hair has been wound in the desired configuration, or from a combination of both. Going too far in the disulfide bond breaking step, in the interest of a long lasting wave, leads to hair damage; achieving the maximum degree of disulfide bond restoration is difficult and often will be slighted as a matter of convenience.

It is an object of this invention to provide a hair waving composition which will give improved, longer lasting waves.

A further object is to provide a waving composition which will decrease damage to the physical properties of the hair.

These and other objects are accomplished by adding alpha, omega bifunctional amides or nitriles to mercapto-alkanoate waving compositions at from 10% to 100% of the weight of mercapto-alkanoic acid. The additives have the general formulas:

$$H_2NC(=O)-Z-C(=O)NH_2 \text{ and } N\equiv C-Y-C\equiv N$$

where Z and Y are saturated aliphatic radicals which will be more fully defined below.

While this invention is, of course, not dependent on an explanation of the chemistry involved, it may be helpful to provide a hypothesis concerning the mechanism by which the desirable results are obtained. Like the disulfide cross-links of keratin, these additives can be thought of as acting to hold the polypeptide chains together; unlike the disulfide cross-links they presumably are not an integral part of the keratin. The amide and nitrile functional groups probably attach themselves to appropriate functional groups of polypeptide chains by means of hydrogen bonds.

Compounds which are suitable additives for the practice of this invention are alpha, omega diamides and dinitriles in which the terminal amide or nitrile groups are linked by saturated, branched or straight chain, aliphatic radicals. Specifically, the additives are

$$H_2NC(=O)-Z-C(=O)NH_2$$

where Z is $(CH_2)_n$, n being a whole number from 1 to 4

$$-CH_2CH(CH_3)-,\ -CH_2CH(CH_3)CH_2-$$

$$-CH(CH_3)CH_2CH_2-, \text{ and } N\equiv C-Y-C\equiv N$$

where Y is

$$-C_2H_4-,\ -CH_2CH(CH_3)-$$

$$-CH_2CH(CH_3)-CH_2-,\ -CH(CH_3)CH_2CH_2-$$

Longer and shorter chains than these are ineffective for the purpose of this invention. It may be postulated that the chain length requirements are set by the spacings between the polypeptide chains of the keratin fibers; the bifunctional compound serving to link adjacent chains together must necessarily be of the proper length. The decrease in solubility and in diffusion rate with increase in molecular weight also contribute to establishing an upper limit of chain length. Adipamide, for example, is rather insoluble in water; but it proved to be sufficiently soluble in alkaline waving lotions for the purposes of this invention. Preferred additives are malonamide, succinamide, glutaramide, adipamide, and succinotrile. Mixtures of the additives can be employed as can the addi-

tives which bear an amide group on one end of the molecule and a nitrile group on the other end.

The quantities of additive to be employed will generally be from 10 to 100% of the mercapto-alkanoic acid concentration. For example, in a waving lotion containing 5% thioglycolic acid, from about 0.5% to 5% additive would preferably be employed. However, no less than 0.5% additive is employed in an aqueous lotion; and the concentration of the additive in use, as diluted by the water in the wet hair, will generally be greater than about 0.3%. For additives which are sufficiently soluble—adipamide is not—it is especially preferable to employ the additive at from about 30% to about 100% of the mercapto-alkanoic acid concentration. Too little additive will not produce an appreciable effect, and too much additive is uneconomical and produces little greater effect than the specified amount.

In the pH range of from about pH 7 to about pH 10, usually employed in waving, the keratin-reducing mercapto-alkanoic acid will be at least partly present as a salt or mercapto-alkanoate. However, in the interest of simplicity in terminology, concentrations will be given in terms of the acid. These and all other concentrations will be expressed in weight percent.

Low molecular weight water-soluble mercaptans containing another functional group, such as carboxyl, hydroxyl, or amide, in addition to the mercaptan group are suitable keratin-reducing agents for the waving lotions of this invention. The mercapto-alkanoic acids described in U.S. Patent 2,736,323 and containing 2 to 6 carbons are preferred keratin-reducing substances because of their effectiveness and because they are not skin sensitizers. Among these, thioglycolic acid is especially preferred in the practice of this invention, and mercapto-propionic acid is almost equally suitable. It is desirable to have the pH of the waving lotion above 7 to obtain rapid and effective action and to have the pH below 10 to avoid damaging the hair. A particularly desirable range is from pH 8.5 to pH 9.5. Any suitable alkali may be used to neutralize the mercapto-alkanoic acid and to adjust the pH; but it is preferred to use a weak base as a substantial portion of the alkali, thereby providing desirable buffering capacity. Suitable weak bases have dissociation contents of less than 10^{-3} and preferably less than 10^{-5}; they include ammonia, monoethanolamine, diethanolamine, tris(hydroxymethyl)aminomethane and 2-amino-2-methyl-1,3-propanediol. Triethanolamine and glycerylamine are further examples of bases which may be used. Ammonia and monoethanolamine are especially preferred weak bases. When the pH of the lotion is adjusted to the preferred range with a weak base, there will usually be present free base in excess of that required to form the salt of the mercapto-alkanoic acid. Mixtures of weak bases can be employed, and it is often advantageous to do so. Soluble carbonates and bicarbonates, such as amonium salts, can be added for their pH stabilizing effect. Use of a salt of a mercapto-alkanoic acid in preparing a waving composition is intended to be equivalent to preparing the salt in situ from mercapto-alkanoic acid and the appropriate base. Examples of strong bases which may be used in minor proportions in conjunction with a major proportion of weak bases in this invention are the alkali metal hydroxides, such as sodium hydroxide, lithium hydroxide, potassium hydroxide. The usual occasion when a portion of strong base will preferably be used is when the waving composition is in the form of a powder or an impregnated pliable sheet as will be exemplified hereinafter. The mercapto-alkanoic acid will preferably be added in the form of a salt of a strong base in these cases; for example potassium thioglycolate can be employed. Preferably no more strong base than the equivalent of the mercapto-alkanoic acid will be used. Minor quantities of strong base can also be used when the waving composition is in the form of an aqueous solution.

The keratin-reducing-agent is incorporated into an aqueous lotion at a level equivalent to from 1% to about 10% thioglycolic acid based on the total composition. The preferred compositions, in the form of aqueous lotions, contain keratin-reducing agent at a level of from about 3% to about 6% thioglycolic acid. The keratin-reducing agent may be packaged in dry form, in which case the directions for use will provide for a solution of the proper mercapto-alkanoic acid concentration to contact the hair.

Various minor ingredients can be added to make the product pleasant to use or to leave the hair in particularly desirable condition. A perfume and a wetting agent will usually be incorporated in the compositions of this invention. A propellant gas in liquefied or dissolved form can be incorporated in the aqueous compositions of this invention so that they can be dispensed from a pressurized container.

Specific examples of certain aspects of the invention are set forth in the following. In each example the hair was shampooed immeditaely before use.

Example I

Loss of tensile strength of hair fibers, through the reactions of hair waving, is a property which can be measured objectively. Hair switches of comparable character were immersed in loose, uncurled condition for one hour in the waving lotion. The lotion was a solution of 5% thioglycolic acid containing bifunctional agent at the level indicated below, and adjusted to pH 9.3 with ammonia. The hair switches were removed from the reducing solution, rinsed and then fixed by a 15 minute immersion in a solution of 9.0 grams of sodium perborate monohydrate and 6.7 grams of citric acid per pint of water.

Additive:	Average breaking strength in relative units
Malonamide, 5.0%	235
Adipamide, 0.5%	400
None (a blank)	135

The breaking strength was about 170% to 300% higher when the additives were used than when they were not.

These results were obtained using a Scott IP2 Serigraph which records the stretching of fibers caused by application of a uniformly increasing load. The instrument is equipped with two clamps between which the strand of 12 hair fibers is mounted. The strand is surrounded by a water-saturated wicking arrangement which keeps the hair wet during stretching One of the clamps is fixed to a bar which is tilted away from a horizontal position at a uniform rate when the machine is in operation, and the other clamp is attached to a weighted carriage adapted to travel along the bar and away from the first mentioned clamp when the bar is inclined. As the inclination of the bar increases, the stretch load applied by the carriage increases at a uniform rate and the strand of fibers is elongated. The relation between load and elongation is continuously recorded on a chart by a pen fixed to the moving carriage. While presumably each hair fiber does not break at exactly the same instant, this is practically so; and the load which caused breaking of the strand can be read from the recorder chart. The result for each composition is an average of 6 to 15 tests.

Example II

The quality and permanency of waves obtained in the practice of this invention were measured by the switch wave technique. This is a substantial duplication, in the laboratory, using switches, of the process used by women at home. A "no neutralizer" procedure was employed in this example.

The curls are formed in the following manner. The switches containing 2 grams of human hair and 6" long are shampooed, rinsed, and blotted with a damp towel. They are held straight and saturated with waving lotion. An end paper is slid down to cover the ends of the hair;

the switch is wound smoothly on a 4 mm. diameter curler; and the wound curl is secured with a rubber band. Timing is started. After 15 minutes the curls are resaturated with additional lotion. At 25 minutes they are rinsed four times under running warm water. The switches are then wrapped in a towel and are left for six hours, in this case of a "no neutralizer" wave, after which they are unwound, combed, and graded.

The waved switches are graded by comparing them with a photograph of a standard series of nine curled switches. This series is shown in the drawing of U.S. Patent 2,869,559. These switches were waved to varying degrees of tightness in approximately a linear relationship by adjusting either the time of waving, strength of waving lotion, or both. The switches used in establishing the photoscale were similar to those described as being used in the tests of this example. The grading scale runs from 0 to 8 photoscale units. A grade of 7 is optimum, lower grades being applied to switches too loosely waved. A grade of 8 is applied to a switch which is overwaved. It is always necessary to run several replicates and to average the results. Increasing photoscale grades are paralleled by decreasing crest-to-crest distances in the curled switches. The average crest-to-crest distance is measured in some instances, but it does not characterize the wave as fully as the photoscale grade does.

In order to judge the permanency of the curls, they are held straight in an atmosphere of greater than 90% relative humidity for 24 hours and are again graded after being released. A further grade is taken after one week of being held straight at the same humidity.

The waving lotion consisted of 2.5% additive (except in the blank), 5% thioglycolic acid, and ammonia to neutralize the thioglycolic acid and adjust the pH to 9.3. The following results were obtained.

Additive, 2.5%	Average Switch Grade, Photoscale Units		
	Initial	24 hours	1 week
None (a blank)	6.6	2.9	2.7
Glutaramide	7.0	4.5	3.3
Malonamide	7.0	4.5	3.4
Succinonitrile	7.0	4.1	3.3

The results show that glutaramide, malonamide, and succinonitrile improved the initial switch grade, and especially, improved the lasting qualities of the curls.

Succinamide and adipamide give similar results when they are employed as additives. Monoethanolamine can be used to replace part or all of the ammonia in neutralizing the thioglycolic acid and adjusting the pH. Good results are also obtained when thioglycolic acid is replaced by mercapto-propionic acid. One-quarter of the thioglycolic acid can be neutralized with sodium hydroxide (instead of ammonia), the remaining neutralization and pH adjustment being carried out with ammonia, without adversely affecting the action of the additive.

Example III

The effects of additives on the initial wave grade and on lasting quality of waves produced by a 5% thioglycolic acid lotion, neutralized and adjusted to pH 9.3 by ammonia, were measured. The switch wave procedure described in Example II was followed except that the switches were removed from the towel 55 minutes from the start of the timing and were saturated four times by application of "neutralizer" solution having a composition of 9.0 grams of sodium perborate monohydrate and 6.7 grams of a citric acid per pint of water. The curls were then rinsed in warm water, combed, and graded.

A

Additive	Initial Switch Grade		
	Initial	24 Hours	1 Week
None (a blank)	6.2	3.4	3.0
Glutaramide, 0.5%	7.0	3.3	—
Glutaramide, 2.5%	7.3	4.3	3.5
Glutaramide, 5.0%	7.2	4.5	—
Glutaramide, 7.5%	7.2	4.0	—
Malonamide, 0.5%	7.3	3.5	—
Malonamide, 2.5%	6.9	4.2	3.6
Succinonitrile, 2.5%	6.7	3.8	3.3

A dash indicates that no data were taken.

Glutaramide, malonamide, and succinonitrile added to the ammonium thioglycolate lotion at a level of 2.5% gave higher photoscale grade initially, after 24 hours, and after 1 week. The initial grade was raised by as little as 0.5% glutaramide or malonamide.

B

Additive	Average Switch Grades		Average crest-to-crest in inches	
	0 hrs.	24 hrs.	0 hrs.	24 hrs.
Malonamide, 2.5%	7.3	5.7	0.725	0.860
None (a blank)	5.7	3.3	0.840	1.09

Operator B, in a different laboratory, using the formulation of Operator A except that 0.1% of a wetting agent (t-octylphenol condensed with 9–10 moles of ethylene oxide) was included, also found that malonamide improved the photoscale grades initially and after 24 hours holding in an extended configuration. Operator B measured the crest-to-crest distances on the switches and found that the average crest-to-crest distance was shorter (a tighter wave) when malonamide was used.

The compounds $H_2NC(O)CH_2CH_2CH(CH_3)C(O)NH_2$ or $NCCH_2CH(CH_3)CN$ can be substituted for the additives of this example to give qualitatively similar results.

Example IV

The following composition was used in the conventional way to reduce hair on the heads of eight women.

	Percent
Thioglycolic acid	5.0
Malonamide	2.5
t-Octylphenol condensed with 9–10 moles ethylene oxide	0.1
Ammonia to bring pH to 9.3.	
Water	Balance

After expiration of appropriate reduction time, the reduced hair was rinsed and neutralized with a pint of solution of 9.0 grams of sodium perborate monohydrate and 6.7 grams of citric acid.

Good, long-lasting, waves were obtained, and the hair was left soft and in excellent condition.

The utility of the additives of this invention is not limited to hair waving compositions in the form of aqueous solutions. The additives may with profit be used as a constituent of mixtures for coating and impregnating sheets which are used as a means of applying waving ingredients to hair tresses according to the teachings of U.S. Patent 2,869,559. Also, the additives of this invention may be employed in hair waving compositions in the form of a powder which is to be dis-

solved, to prepare an aqueous lotion, before its application to the hair. In both cases, the composition is activated by contact with water. The equivalent thioglycolic acid content of the aqueous solution on the hair must be sufficient to wave hair; such concentration is greater than about 0.6% and preferably is from about 1.8% to about 3.6%. These limits correspond, respectively, to 1%, 3%, and 6% thioglycolic acid in a lotion, taking into account the dilution occurring on the wet hair.

Example V

A composition suitable for coating and impregnating thin pliable sheets in accordance with U.S. Patent 2,869,559, or for use by itself in the form of a powder from which a lotion is prepared, is as follows:

	Percent
Patassium thioglycolate	40
Tris(hydroxymethyl)aminomethane	40
Malonamide	20

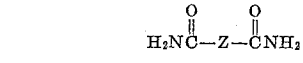
When properly employed in conditions of use such that the solution in contact with the hair contains potassium thioglycolate equivalent to about 5% thioglycolic acid, a good wave of superior lasting quality is obtained; and the hair is left in excellent condition.

All or part of the tris(hydroxymethyl)aminomethane can be replaced by 2-amino-2-methyl-1,3-propanediol with comparable results.

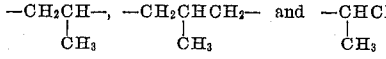
The term "consisting essentially of" as used in the definition of the ingredients present in the composition claimed is intended to exclude the presence of other materials in such amounts as to interfere substantially with the properties and characteristics possessed by the composition set forth but to permit the presence of other materials in such amounts as not substantially to affect said properties and characteristics adversely.

What is claimed is:

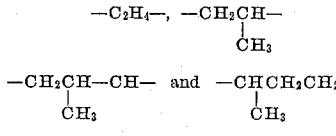
1. A composition of matter suitable for use, when in aqueous solution, in cold waving of hair comprising: 10 parts of a mercapto-alkanoic acid keratin-reducing agent; from about 1 to about 10 parts of an alpha, omega bifunctional compound selected from the group consisting of: (1)



where Z is selected from the group consisting of $(CH_2)_n$, n being a whole number from 1 to 4,



and (2) N≡C—Y—C≡N where Y is selected from the group consisting of



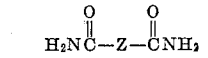
and in an amount sufficient to promote curl tightness and reduce hair damage; and an alkaline material, at least a substantial part of which has a dissociation constant of less than 10^{-3}, imparting a pH above 7 and below 10 to the composition in use, the concentration of the mercapto-alkanoic acid in use being sufficient to wave hair and greater than about 0.6%.

2. The composition of claim 1 in which the mercapto-alkanoic acid is selected from the group consisting of thioglycolic acid and mercapto-propionic acid.

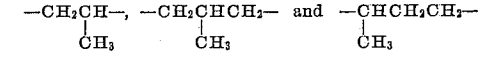
3. The composition of claim 1 in which at least a substantial part of the alkaline material is selected from

the group consisting of ammonia, monoethanolamine, diethanolamine, 2-amino-2-methyl-1,3-propanediol, tris-(hydroxymethyl)aminoethane and mixtures thereof.

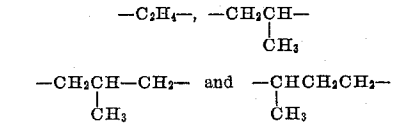
4. A hair waving lotion comprising: from 1% to 10% of a keratin-reducing agent selected from the group consisting of thioglycolic acid and mercapto-propionic acid; from 0.5% to 10% of alpha, omega bifunctional compound selected from the group consisting of: (1)



where Z is selected from the group consisting of $(CH_2)_n$, n being a whole number from 1 to 4,

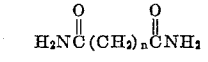


and (2) N≡C—Y—C≡N where Y is selected from the group consisting of



and in an amount sufficient to promote curl tightness and reduce hair damage; and an alkaline material imparting a pH of from 8.5 to 9.5 to the lotion, at least a substantial part of the alkaline material being selected from the group consisting of ammonia, monoethanolamine, diethanolamine, 2-amino-2-methyl-1, 3-propanediol, tris(hydroxymethyl)aminomethane, and mixtures thereof; and water.

5. A hair waving composition consisting essentially of: from about 3% to about 6% thioglycolic acid; from about 0.5% to 5% of an alpha, omega bifunctional compound



n being a whole number from 1 to 4, and in an amount sufficient to promote curl tightness and reduce hair damage; and an alkaline material imparting a pH of from 8.5 to 9.5 to the lotion at least a substantial part of the alkaline material being selected from the group consisting of ammonia, monoethanolamine, diethanolamine, 2-amino-2-methyl-1,3-propanediol, tris(hydroxymethyl)aminomethane and mixtures thereof; and water,

6. The composition of claim 5 wherein the bifunctional compound is malonamide.

7. The composition of claim 5 wherein the bifunctional compound is succinamide.

8. The composition of claim 5 wherein the bifunctional compound is glutaramide.

9. The composition of claim 5 wherein the bifunctional compound is adipamide.

10. The composition of claim 5 wherein the substantial part of the alkaline material is ammonia.

11. The composition of claim 5 wherein the substantial part of the alkaline material is monoethanolamine.

12. A hair waving composition consisting esssentially of: from about 3% to about 6% thioglycolic acid; from about 0.5% to 5% of succinonitrile; and an alkaline material imparting a pH of from 8.5 to 9.5 to the lotion at least a substantial part of the alkaline material being selected from the group consisting of ammonia, monoethanolamine, diethanolamine, 2-amino-2-methyl-1,3-propanediol, tris(hydroxymethyl)aminomethane and mixtures thereof; and water.

13. The composition of claim 12 wherein the substantial part of the alkaline material is ammonia.

14. The composition of claim 12 wherein the substantial part of the alkaline material is monoethanolamine.

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