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HAIR WAVING COMPOSITIONS CONTAINING SECONDARY AMINO ALIPHATIC ALCOHOL DITHIOCARBAMATES

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The invention relates to a composition of matter and to a method for its preparation. More particularly, it pertains to a composition and a method for the treatment of hair which includes correlated improvements and discoveries whereby such treatment is markedly effective.

The shape or form of hair may be altered without injuring the structure of the hair by first winding the hair in the form of curls, as on mandrels, then treating with a solution or lotion which has a softening effect upon the hair and finally setting the new shape or form by various means, such as by the application of heat or by chemical means which may react to neutralize the action of the chemical first applied. Various agents have previously been used to bring about a change in the physical shape of hair and mention may be made of alkaline materials such as alkaline carbonates, phosphates, borax, ammonia, ammonium carbonate, alkali metal sulfites, ammonium sulfite, and sulfides, particularly ammonium sulfide. The utilization of the sulfites and the sulfides is attended with certain disadvantages such as a relatively high concentration being required with the sulfites, and the sulfides, while providing a satisfactory change in shape, are undesirable because of toxic effects and undesirable odor, e. g. the liberation of hydrogen sulfite. Further, the use of sulfides is attended by a retention thereof by the hair which leads to the liberation of an undesirable odor, particularly when the hair is wetted.

An object of the invention is the provision of a composition of matter which when applied to hair occasions a permanent change in its shape.

A further object of the invention is to provide a composition of matter which in the form of a lotion is particularly well adapted for the treatment of hair of various textures and types.

An additional object of the invention is the provision of a composition of matter which may be readily, economically and effectively prepared to a desired extent, and which may be utilized with facility for the permanent waving of hair.

A still further object of the invention is to provide a stable composition of matter for the waving of hair which is without deleterious effects to hair or to an individual, and which rapidly and successfully occasions a change in the shape of hair with such change being either that of imparting a wave or other alteration in form, or the removal of a wave, curl or other shape.

A more particular object of the invention is the provision of a method for preparing a hair waving compound by reacting a secondary amino aliphatic alcohol, carbon disulfide and a halogenated lower aliphatic monocarboxylic acid or salt thereof or glycerol monochlorohydrin.

An especial object of the invention is to provide a composition of matter having hair waving properties and which results from the reaction of a secondary amino aliphatic alcohol, carbon disulfide and monochloroacetic acid.

A specific object of the invention is the provision of a hair waving lotion containing as the essential ingredient

the reaction product of di-isopropanolamine or of diethanolamine, carbon disulfide and monochloroacetic acid.

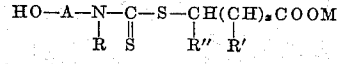
Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises a composition of matter possessing the characteristics, properties and relation of components and a method which comprises the several steps and the relation of one or more of such steps with respect to each of the others thereof, which will be exemplified hereinafter in the description, and the scope of the invention will be indicated in the claims.

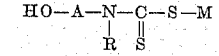
In the practice of the invention, a composition for altering the shape of hair may be prepared which contains as the essential ingredient a reaction product of a secondary amino aliphatic alcohol containing 2–10 carbon atoms, carbon disulfide and a member of the group consisting of a halogenated lower aliphatic monocarboxylic acid containing 2–8 carbon atoms, and a salt thereof. The secondary amino aliphatic alcohol more particularly, may be one or a compatible admixture of the following: diethanolamine, N-methyl ethanol amine, N-ethyl-ethanolamine, N-butyl ethanolamine, amino ethyl ethanolamine, di-isopropanolamine, and N,N'(dihydroxy ethyl)ethylene diamine. Further, the halogenated aliphatic acid may be monochloroacetic acid, monobromoacetic acid, alpha chloropropionic acid, alpha bromopropionic acid, alpha bromobutyric acid, beta chloropropionic acid, alpha bromocaproic acid, and alpha bromocaprylic acid.

The salt of the halogenated aliphatic acid may be the sodium, potassium, ammonium, calcium, magnesium and barium salts; salts derived from primary, secondary, tertiary alkanolamine.

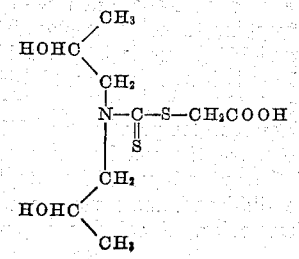
The compounds that are formed may be represented by the following structure:



wherein HO—A indicates an alkanol group derived from a secondary amino alcohol; R is alkyl and alkanol groups; R' and R'' indicate H and an alkyl group; M represents H, and mono and divalent cations such as sodium, potassium, calcium, magnesium, ammonium, an alkylammonium derived from an amine, and an alkanolammonium derived from an amino alcohol, and x equals 0–6. These compounds are made, e. g. by reacting a dithiocarbamate of the following structure:



wherein HO–A; R, and M indicate the same as above with a halogenated lower aliphatic monocarboxylic acid or salt thereof such as those above mentioned, and desirably at a temperature not greater than about 50° C. Further, the reaction medium may be aqueous, as water or substantially non-aqueous, as an ester or a ketone, e. g. ethyl acetate, isopropyl acetate, acetone, methyl ethyl ketone and the like. Specifically when diisopropanolamine, carbon disulfide and monochloroacetic acid enter into reaction, a compound is formed having the following formula:



In the event that the final stage of the reaction is effected with sodium monochloroacetate, then the hydrogen of the carboxylic group in the foregoing formula is replaced by sodium.

A waving lotion may be prepared from the compounds above described by combining the compound with an alkaline material as ammonium hydroxide, a wetting agent ,for example, the sodium salt of an alkylated aryl polyethersulfonic acid and an opacifier, for example an aqueous suspension of an acrylic copolymer or of a polystyrene containing from about 25% to about 30% solids, such as the products marketed as "Resin 69," an acrylic copolymer produced by Onyx Oil and Chemical Company, Jersey City, New Jersey, "Rhoplex WA5," a polyvinyl acetate emulsion with an anionic emulsifier produced by Rohm & Haas, Philadelphia, Pennsylvania, and "Resin XF," a polystyrene produced by Jersey State Chemical Company, Haldene, New Jersey, with the lotion having a pH value of about 9.5. Hair may be waved with the lotion by winding it on a curler and applying the lotion thereto and permitting it to remain for a period depending on the concentration and which may be for instance from about 30 to about 90 minutes. Thereafter, the hair is washed with water followed by neutralization with a suitable neutralizer, e. g. a potassium bromate, sodium perborate, ammonium persulfate and hydrogen peroxide solution in the proportion of about 1 oz. of the bromate to about 16 ozs. of water. After a period of about 10 minutes the hair may be released from the curler with the neutralizing solution being permitted to remain for a further period of about 10 minutes. Completion of the treatment is carried out by unwinding the hair, thoroughly washing with water, and drying. The waves obtained are highly satisfactory and the hair is characterized by having marked elasticity, spring, sheen and gloss.

As other wetting agents, utilization may be made of a partial fatty acid ester of a polyhydric alcohol, especially the higher fatty acids as lauric, myristic, steric, palmitic and oleic acids esterified with, for example, glycerol, the sugar alcohols as sorbitol, mannitol and dulcitol, and the inner anhydrides and ethers thereof; a salt of a sulfated higher alcohol as the sodium and potassium salts of lauryl sulfate and myristyl sulfate and an alkyl aryl polyglycol ethylene ether, e. g., an alkly phenyl polyethylene glycol ether in which the alkly may be heptyl, octyl and nonyl and specifically octyl phenyl polyethylene glycol ether, which may be prepared by reaction between octyl phenol and eleven ethylene oxide molecules. Mention may also be made of the following: diamyl ester of sulfosuccinic acid, diisobutyl sodium sulfosuccinate, isopropyl naphthalene sodium sulfonate, dioctyl ester of sodium sulfosuccinic acid, monobutylphenylphenol sodium monosulfonate, and decyl benzene sulfonate.

While ammonium hydroxide is the preferred alkaline reacting material, others may be used such as the hydroxides, carbonates and bicorbonates of sodium and potassium, an amine as methyl and ethyl amines, or an amino alcohol such as triethanolamine.

As an illustrative embodiment of a manner in which the invention may be practiced, the following examples are presented:

Example I

In a suitable reaction flask, fitted with stirrer, thermometer and dropping funnel were placed 2.5 liters isopropyl acetate and 760 grams carbon disulfide. This was cooled to 0° C. and then a mixture of 1490 grams triethanolamine and 1330 grams diisopropanolamine was added, maintaining the temperature at 0° C. After the addition was complete, the reaction mass was stirred for one hour, and the upper layer of isopropyl acetate was decanted. The dithiocarbamate residue was a viscous oil of pale yellow color. A solution prepared from 945 grams monochloroacetic acid dissolved in 600 grams water and neutralized by adding 667 cc. 28% ammonium hydroxide, was added to the dithiocarbamate with a temperature rise to 45° C., and stirred for three hours.

When the addition was complete, the reaction mass was chilled and filtered by suction to remove the formed crystalline triethanolamine hydrochloride. The filtrate as the essential ingredient in a waving lotion having a pH value of 9.6, gave an excellent wave. The waving lotion may be prepared with the following composition:

350 grams of the reaction product
100 cc. ammonium hydroxide, 28%
20 grams "Triton X200"—an alkylated aryl polyether sulfonate
30 grams "Resin XF"—a polystyrene, and
Water, q. s. to 1000 cc.

Example II

The process was the same as in Example I, except that 750 cc. of 28% ammonium hydroxide was submitted for the triethanolamine. The crystalline precipitate formed at the end of the reaction was ammonium chloride, and was removed by filtration. An excellent wave was obtained with a lotion containing the product so prepared having a pH of 9.4, and of the following composition:

471 grams of the reaction product
100 cc. ammonium hydroxide 28%
10 grams "Maypon 4CT"—triethanolamine salt of a protein condensation product
30 grams "Resin XF"—a polystyrene, and
Water, q. s. to make 1000 cc.

Example III

In a similar manner to the procedure of Example I, a compound was prepared from diethanolamine using diethanolamine as the base. 625 cc. isopropyl acetate and 190 grams carbon disulfide were cooled to 7° C. and then 525 grams diethanolamine were slowly added. When the diethanolamine had been added, the reaction mass was stirred for two hours, and the isopropyl acetate decanted. Then a solution prepared by dissolving 236 grams monochloroacetic acid in 250 cc. water and neutralized by adding 167 cc. ammonium hydroxide 28% was added to the dithiocarbamate so prepared in a way analogous to Example I.

A crystalline precipitate was not formed. The final product was clear, and when used in the usual waving lotion with a molar concentration of the dithiocarbamyl compound and at a pH of 9.5, as good wave was obtained with a processing time of about 40 minutes.

Example IV

In a method analogous to Example I, 750 cc. isopropyl acetate and 228 grams carbon disulfide were cooled and a mixture of 267 grams N-ethyl ethanolamine and 447 grams triethanolamine added. The triethanolamine salt of the N-ethyl ethanolamine dithiocarbamate was separated and reacted with a solution of three moles of monochloroacetic acid neutralized with ammonium hydroxide as in Example I. Triethanolamine hydrochloride crystals were filtered from the clear liquid portion. The usual waving lotion containing the reaction product and having a pH of 9.6, gave very satisfactory waves.

Example V

Procedure as in Example IV, except that an additional 267 grams of N-ethyl ethanolamine was used instead of the triethanolamine. An extra mole of N-ethyl ethanolamine was used as the base for the preparation of the amino alcohol salt of the amino alcohol dithiocarbamate. No crystal formation was observed, and the compound gave good waves.

Example VI

The triethanolamine salt of diisopropanolamine dithiocarbamate was prepared as described in Example I. This was reacted with a molar equivalent solution of α-bromo propionic acid which was neutralized with ammonia. When the reaction was complete, the crystals were filtered off and identified as triethanolamine hydrobromide. The clear solution contained the waving agent and it was utilized to prepare a waving lotion similar to that described in Example I. A good wave resulted.

Example VII

A procedure as in Example VI was followed in which the triethanolamine salt of the diisopropanolamine dithiocarbamate was reacted with a molar equivalent solution prepared by neutralizing α-bromo butyric acid with ammonium hydroxide. Crystals of triethanolamine hydrobromide were formed in the reaction mass and were removed by filtration. The usual waving lotion was prepared with the product, and satisfactory waves therewith were attained.

Example VIII

A procedure was followed as in Example VI, in which the triethanolamine salt of the diisopropanolamine dithiocarbamate was reacted with a solution prepared by the neutralization of β-chloro propionic acid with ammonia. The crystalline material in the final product was identified as triethanolamine hydrochloride and was removed by filtration. The solution was of a very light color, and in a regular waving lotion gave excellent waves.

Example IX

The usual procedure was followed with a diamino dialcohol being used as the reactant. 750 cc. isopropyl acetate and 228 grams carbon disulfide were reacted with 222 grams N,N'(dihydroxy ethyl)ethylenediamine and 447 grams triethanolamine. The ditriethanolamine salt of the dithiocarbamate of N,N'(dihydroxy ethyl)ethylenediamine was thus prepared, and it was reacted as in Example I with a solution of ammonium monochloroacetate.

The crystalline material obtained after filtration of the final product was found to contain triethanolamine hydrochloride, and the solution, i. e. the filtrate, was utilized in the formulation of a waving lotion.

Example X

210 grams of diethanolamine, 76 grams of CS_2, and 250 cc. of isopropyl acetate were reacted by adding the carbon disulfide to the mixture of the amino-alcohol and isopropyl acetate in an ice bath; the carbon disulfide being added over a two hour period. Isopropyl acetate was removed followed by the addition of a mole of sodium monochloroacetate dissolved in 250 cc. of water. A molar waving lotion was prepared from the reaction product in the manner above described and having a pH value of about 9.3. This lotion was used to occasion a wave in hair and gave a decidedly satisfactory wave.

Example XI

The reaction procedure utilized 133 grams diisopropanolamine, 75 cc. ammonium hydroxide 28%, 76 grams carbon disulfide, 100 cc. isopropyl acetate, 110 grams glycerol monochlorohydrin, and 100 cc. water. The isopropyl acetate was added to a mixture of the ammonium hydroxide and diisopropanolamine; the mixture cooled, and the carbon disulfide added over a period of one hour. The isopropyl acetate was decanted and then the aqueous solution of the glycerol monochlorohydrin was added. Stir for two hours at a temperature from 25° C. to 50° C. A waving lotion was prepared with a pH of 9.3, and of the following composition: 350 grams of the reaction product, 20 grams "Maypon 4CT," 30 grams "Resin XF," and water q. s. to make 1000 cc. The lotion had excellent waving properties.

Example XII

A dithiocarbamate was prepared by the use of 117 grams N-butyl ethanolamine, 75 grams ammonium hydroxide, 28%, 76 grams carbon disulfide, 125 cc. isopropyl acetate, 94 grams monochloroacetic acid, 70 grams ammonium hydroxide, 28%, and 100 cc. water. The N-butyl ethanolamine and ammonium hydroxide dissolved in the isopropyl acetate were treated with carbon disulfide over one hour period at a temperature of 5° C. The isopropyl acetate was decanted and the solution treated with the aqueous solution of monochloroacetic acid and ammonia. The 530 cc. of the product so prepared was made into a waving lotion by the addition of 105 cc. of ammonium hydroxide, 28%, 30 grams "Maypon 4CT," 45 grams "Resin XF," and q. s. to 1000 cc. with water, the lotion having a pH of 9.7.

Example XIII

125 cc. isopropyl acetate, 133 grams diisopropanolamine, 75 grams ammonium hydroxide, 28%, 76 grams CS_2, 108.5 grams alpha chloropropionic acid, 75 cc. ammonium hydroxide, 28%, and 50 cc. water were utilized. The diisopropanolamine and the ammonia were added to the isopropyl acetate and treated with carbon disulfide for a period of one hour. The isopropyl acetate was decanted, and the residue was treated with an aqueous solution containing the alpha chloropropionic acid and ammonia over a period of 2 hours. The solution was light colored and had an excellent odor. A regular waving lotion was prepared and excellent waves were obtained with it.

Example XIV

A reaction product was prepared employing 133 grams diisopropanolamine, 75 grams ammonium hydroxide, 28%, 76 grams carbon disulfide, 153 grams alpha bromopropionic acid, 75 cc. of ammonia, 28%, and 50 cc. water. The procedure followed was as set forth in Example XIII, and a waving lotion containing the reaction product in the usual formulation described herein, gave a good wave.

Example XV

A reaction mixture was made using 133 grams diisopropanolamine, 75 cc. amonimum hydroxide, 28%, 76 grams carbon disulfide, 100 cc. isopropyl acetate, 167 grams alpha bromobutyric acid, 100 cc. water, and 70 cc. ammonium hydroxide, 28%. The product was prepared by the procedure of Example XIII, and the reaction product utilized to prepare a waving lotion.

Example XVI

The potassium salt of diisopropanol dithiocarbamyl propionic acid was prepared utilizing the following; 133 grams diisopropropanolamine, 70 grams ammonium hydroxide, 28%, 100 cc. isopropyl acetate, 76 grams carbon disulfide, 108.5 grams alpha chloropropionic acid, 56 grams potassium hydroxide, and 100 cc. water, and proceeding as in Example XIII.

Example XVII

100 cc. isopropyl acetate and 38 grams carbon disulfide were cooled to 0° C. and a mixture of 67 grams diisopropanolamine and 75 grams triethanolamine were gradually added with stirring. It was stirred for 1½ hours after addition was complete. The isopropyl acetate was separated and a solution, prepared from 98 grams α-bromo caproic acid, 75 cc. distilled water and 33 cc. 28% ammonium hydroxide, was added to the dithiocarbamate, and stirred for one hour. The crystalline precipitate of triethanolamine hydrobromide was filtered off. The filtrate contained the diisopropanol dithiocarbamyl caproic acid, which gave an execellent wave when made into a lotion according to the usual formula.

Other dithiocarbamates may be prepared in similar manner by substituting equi molecular amounts of other

secondary amino alcohols for the diisopropanolamine. Further, water may be substituted for the inert solvent. In this case the reaction is somewhat slower and longer stirring will be necessary to react all the carbon disulfide, and the product will be aqueous solution of the salt of the dithiocarbamic acid.

Moreover, 108.5 grams of alpha or beta chloropropionic acid, or, if desired, 167 grams of alpha bromo butyric acid, or 195 grams of alpha bromocaproic acid, may be substituted for each 94.5 grams of monochloroacetic acid specified above. In the case of alpha bromo butyric acid and alpha bromo caproic acid, since their solubility in water is limited, complete solution will not be obtained until practically all the neutralizing base has been added. Furthermore, any of the above mentioned halogenated aliphatic acids may be neutralized with ammonium hydroxide or an equi molecular amount of another base, such as triethanolamine, diisopropanolamine, N-butyl ethanolamine and the like.

It will be realized that while the permanent waving of hair emphasized hereinabove, nevertheless, the invention may be utilized to reform the shape of hair as may be desired. Thus, the composition may be employed in a manner which is the reverse of waving, that is it may serve to remove curls, waves, kinks and for imparting creases and the like. Moreover, it is to be understood that the composition may be used not only for the treatment of hair as human hair, but for the treatment of other fibers which are composed wholly or in large measure of keratin.

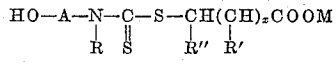
This application is a continuation-in-part of our copending application Serial No. 407,594, filed February 1, 1954, now abandoned.

Since certain modifications in the compositions and certain changes in the above method which embody the invention may be made in carrying out the above method and in the composition set forth without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

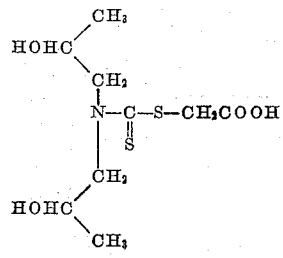
Having described our invention, what we claim as new and desire to secure by Letters Patent is:

1. As a composition of matter a compound having the following formula:

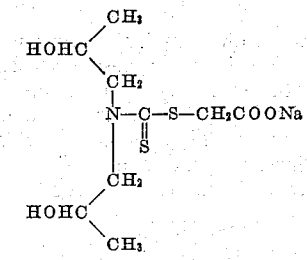


wherein HO—A represents an alkanol group derived from a secondary amino aliphatic alcohol having 2–10 carbon atoms, R is a member of the group consisting of alkyl groups having a carbon content C_1–C_4 and alkanol groups having a carbon content C_2–C_{10}, R′ and R″ are members of the group consisting of hydrogen and alkyl groups having a carbon content C_1–C_5, M is a member of the group consisting of sodium, potassium, calcium, magnesium, ammonium, alkyl ammonium groups derived from amines, and alkanol ammonium groups derived from amino alcohols, and x equals 0–6.

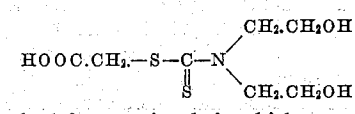
2. As a composition of matter a compound having the following formula:



3. As a composition of matter a compound having the following formula:

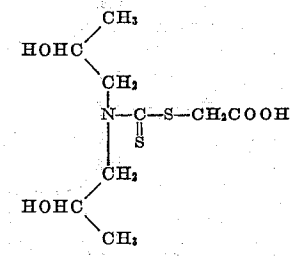


4. A composition for altering the shape of hair containing as the essential ingredient a compound having the formula:

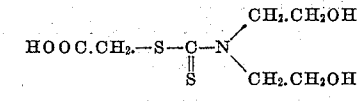


5. A method for treating hair which comprises applying thereto a lotion containing as the essential ingredient a compound having the formula defined in claim 1, said composition having a pH value of 9.0 to 9.7.

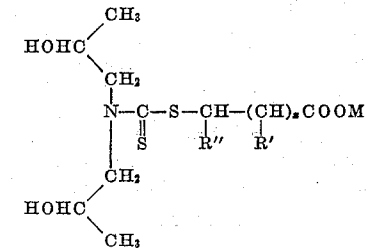
6. A method for treating hair which comprises applying thereto a lotion containing as the essential ingredient a compound having the formula:



7. A method for treating hair which comprises applying thereto a lotion containing as the essential ingredient a reaction product of diethanolamine, carbon disulfide and monochloroacetic acid in the mole ratio, respectively, of 2:1:1, said lotion having a pH value of about 9.5, and said reaction product having the formula:

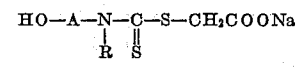


8. As a composition of matter a compound having the following formula:



wherein R′ and R″ are members of the group consisting of H and alkyl groups; said alkyl groups having a carbon content C_1–C_5; M is a member of the group consisting of H, sodium, potassium, calcium, magnesium, ammonium, alkylammonium groups derived from amines, and alkanolammonium groups derived from amino alcohols, and x equals 0–6.

9. As a composition of matter a compound having the following formula:



wherein HO—A represents an alkanol group derived from a secondary amino aliphatic alcohol containing 2–10

carbon atoms, and R is a member of the group consisting of alkyl and alkanol groups, said alkyl groups having a carbon content C_1–C_4 and said alkanol groups having a carbon content C_2–C_{10}.

10. A composition for altering the shape of hair containing as the essential ingredient a compound having the formula defined in claim 1, and which is the reaction product of an ethanolamine, carbon disulfide and a member of the group consisting of a halogenated lower aliphatic carboxylic acid containing 2–8 carbon atoms and salts thereof.

11. A composition for altering the shape of hair containing as the essential ingredient a compound having the formula defined in claim 1, and which is the reaction product of diethanolamine, carbon disulfide and a member of the group consisting of a halogenated lower aliphatic carboxylic acid containing 2–8 carbon atoms and salts thereof.

12. A composition for altering the shape of hair containing as the essential ingredient a compound having the formula defined in claim 1, and which is the reaction product of a secondary amino aliphatic alcohol containing 2–10 carbon atoms, carbon disulfide and sodium mono chloro acetate.

13. A composition for altering the shape of hair containing as the essential ingredient a compound having the formula defined in claim 1, and which is the reaction product of N,N'(dihydroxy ethyl) ethylene diamine, carbon disulfide and a member of the group consisting of a halogenated lower aliphatic carboxylic acid containing 2–8 carbon atoms and salts thereof.

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