

UNITED STATES PATENT OFFICE

2,600,624

HAIR-WAVING COMPOSITION

Menotti Del Zoppo, New York, N. Y., assignor of
one-half to Alice Parker, New York, N. Y.No Drawing. Application March 15, 1950,
Serial No. 149,899

7 Claims. (Cl. 167-87.1)

1

This invention relates to a method and composition for waving hair.

The invention is particularly useful in the so-called cold wave for human hair and will therefore be illustrated first by description in connection with such use.

The lotions in actual use for cold waving of hair today contain, in most instances if not universally, thioglycolic acid salts as the keratin softening agent along with such other ingredients as wetting agents, perfumes, and the like. While these solutions are generally satisfactory, there are certain disadvantages in them. Thioglycolic acid has a strong, objectionable odor. The thioglycolic acid is unstable in contact with air. Thioglycolic acid itself is a liquid and the lotions are necessarily shipped in liquid tight containers, such as bottles, with attendant expense in the original cost of the containers, filling the containers, capping them, packing them for shipment, and then paying freight on a solution which is ordinarily 85% to 90% water. Finally, the thioglycolic acid lotions cause overtreatment of the hair unless the treatment is discontinued at the proper time, a fact which is generally recognized, and is emphasized by one manufacturer who includes in his package a special dial for reading off the time for treatment of hair of different classes.

I have now discovered that these objections are overcome and that I may obtain a good, satisfactory waving effect by the use of any one of several polythio compounds of kind to be described herein. These compounds are either entirely odorless or are so nearly odorless that they may be perfumed to establish what is in effect the quality of odor of the perfume. They are solids. They may be shipped in special paper envelopes, instead of bottles or the like, and dissolved at or only shortly before the time of use. They are stable in contact with oxygen or air at ordinary temperatures. They seem to provide a buffer or like effect which practically eliminates the danger of overtreating the hair in normal use of the compositions.

Briefly stated, the invention comprises a hair waving composition including as the keratin softening agent a thiocarbonic acid ester of glycolic acid or like alpha-hydroxy fatty acid in conjunction with an amine in amount to establish the pH within the range 8 to 10. The invention comprises, also, the herein described method of waving hair by contacting it with the keratin softening agent of kind described and then removing the said agent.

2

In one embodiment, the invention comprises a waving composition including an alkali metal salt of the thiocarbonic acid derivative in conjunction with a surface active agent.

In a modification, the invention comprises a waving composition of the kind described and an enhancing agent to increase the effectiveness on human hair, the enhancing agent being a compound of mild reducing properties of which examples are ascorbic acid, sorbose, and glucose. For this purpose, the ascorbic acid is preferred.

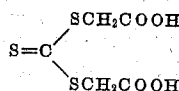
As the thiocarbonic acid ester used as the keratin softening agent, I employ an ester of an alpha-hydroxy fatty acid with another acid selected from the group consisting of di- or tri-thiocarbonic acid and dithiocarbamic acid. In the case of the dithiocarbonic acid, one of the acid hydrogens may be replaced by the radical of the alpha-hydroxy fatty acid and another by an alkyl group so as to make the product a mixed ester of the hydroxy acid and a lower alcohol such as one containing 1 to 4 carbon atoms to the molecule.

As the alpha-hydroxy fatty acid in the composition, I use to advantage glycolic acid although there may be used other like acids such as lactic or alpha-hydroxybutyric acid.

These thiocarbonic acid esters may be considered hypothetically as derived from carbonic acid by replacing the proper number of oxygen atoms by sulfur atoms, to give the di- or trithio-derivatives and then reacting the thiocarbonic acid with a hydroxyl attached to a CH or CH₂ group in the alpha-hydroxy fatty acid, to give an ester with the hydroxy acid. Actually this is not the way the esters are made but this consideration tends to simplify the understanding of the structure of the compounds. It will be seen that there will be left, in such esters, a free carboxyl group or groups which are available for forming salts with amines or other alkalies.

The examples of compounds illustrating the various classes of derivatives before neutralizing the carboxyl groups are the following:

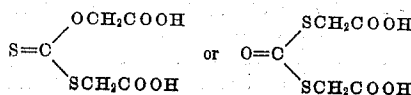
(1)



50

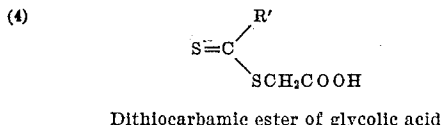
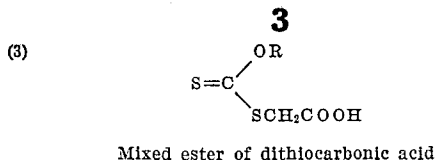
Glycolic acid ester of trithiocarbonic acid

(2)



55

Glycolic acid ester of dithiocarbonic acid



In the Formula 3 above, R stands for a lower alkyl group such as one containing 1 to 4 carbon atoms. In Formula 4, R' stands for an amine group, an alkyl substituted amine group, or a cyclic amine group of which examples are NH_2 , $\text{N}(\text{CH}_3)_2$, $\text{N}(\text{C}_2\text{H}_5)_2$, $\text{N}(\text{C}_3\text{H}_7)_2$, and $\text{NC}_4\text{H}_8\text{O}$ (morpholine radical).

In general the keratin softening agents are compounds of the class described that, in the form of simple amine or alkali metal salts are water soluble, stable in dry form and non-irritating and non-toxic under conditions of use. The agents must be stable in dry form. In the preferred embodiment of the invention, in which the softening agents are to be shipped in solid form the keratin softening agents must be themselves solids at ordinary temperatures.

As the alkali which is used to make the salt, by neutralizing the free carboxyl groups of compounds (esters) of the class shown above, there are used water soluble amines. Examples are methyl, ethyl, isopropyl and butylamines; alkylolamines such as ethanol, propanol, isopropanol, or butanol amines in the form of the mono-, di-, or tri-products of which monoisopropanolamine, diisopropanolamine and triisopropanolamines are examples; aminoethyl ethanolamine; tris-hydroxy methyl aminomethane; 2-amino 2-methyl 1-propanol; and cyclic amines such as morpholine, piperazine, and the like.

The alkali metal alkalies may be used to give the salts of the thio esters referred to above but the resulting salts are not as effective in waving hair as the amine salts. When alkali metal alkalies are used, a surface active agent is also incorporated to increase the rate of softening of keratin. Preferably an enhancing agent of the kind described, as, for instance, ascorbic acid is introduced to improve the waving properties.

For convenience in shipping, I may form a mixture of (1) the thio ester of the alpha-hydroxy carboxylic acid and (2) the salt of an amine, such as one of those described, with a mineral acid of which examples are hydrochloric, sulfuric, boric, or phosphoric. In such a mixture, the amine is liberated from its salt just before use by the addition of a caustic alkali preferably in approximately equivalent proportion. The amine so liberated is then free to react with the carboxyl groups of the thio ester, to form the amine salt waving compound.

Thus I may form, for shipment in paper envelopes, a mixture of the thio ester or keratin softening agent of kind described with monoisopropanolamine hydrochloride or other salt of the selected amine. Then, before the mixture of the keratin softening agent and the amine hydrochloride or the like is applied to the hair, the mixture is dissolved, along with lithium, sodium or potassium hydroxide or like alkali in proportion equivalent to the amine represented in the mixture. Alkali so added displaces the amine from the hydrochloride or like salt, to give the

free amine which then reacts at once, to form a salt with the thio ester. The result is the replacement of hydrogen of the carboxyl groups in the formulas given above by amine groups of which the monoisopropanolamine is particularly satisfactory.

It will be understood that the lithium or like alkali for the amine liberation may be shipped in a waterproof and alkali-proof container such as a sealed bag of plastic, as polyethylene.

It will be understood also that the thio esters which, in my invention are reacted with amines or other alkalies, are available on the market or are made by known methods. The amine salts themselves are considered to be new.

Examples of the surface active agents that may be used in my lotions are: the sodium salt of an alkyl aryl sulfonate, an example being one in which the alkyl group is dodecyl and the aryl is naphthyl, the sodium salt of keryl benzene sulfonate, sodium lauryl sulfate, ethylene oxide complex of a partial ester such as Tweens or Spans, and the sodium salt of sulfated octadecyl alcohol.

There may be incorporated into the waving lotion or solution conventional additives of which examples are perfuming, creaming, or coloring agents that are usual in hair treating compositions.

As to concentration, the salts of the thiocarbonic acid esters are dissolved to a concentration of 5 to 15 parts by weight, usually 8 to 11, for 100 of water.

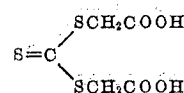
Compositions made as described are stable against oxidation in air, effective in waving hair with minimized danger of overtreatment, and of low or negligible odor.

The waving lotions are more active in softening keratin if the amine or other salt of the thiocarbonic and thiocarbamic acid esters selected for use is caused to stand for about one-half to 3 hours in solution in water before it is applied to the hair. This increase in effect is considered by me to be due in part at least to a change in degree of dispersion or change in solubility of the solids in water.

The invention will be further illustrated by detailed description in connection with the following specific examples of the practice of it.

Example 1

9 g. of trithiocarbonic acid ester of glycolic acid of the formula



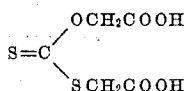
which is a yellow crystalline solid having a melting point of 173-174° C. was dissolved in 90 cc. of water containing 5.5 g. monoethanolamine. A clear yellow colored odorless solution is formed having a pH of 9.25.

The freshly prepared solution is applied on freshly shampooed hair, the hair is wound on usual waving rods and preferably on those described in U. S. Patent No. 2,426,343, issued to me on August 26, 1947. After about 20 minutes to 1 hour, depending on the quality of the hair, the hair is rinsed with cold water, then with a dilute solution of hydrogen peroxide, again with water, and then dried. The curl obtained is strong and the hair is soft and elastic.

5

Example 2

10.5 g. of the dithiocarbonic acid ester of glycolic acid of the formula

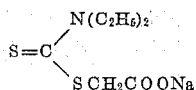


which is a white crystalline solid having a melting point of 136° C. was dissolved in 90 cc. of water containing enough hydroxyethyl ethylenediamine to bring the pH of the solution to 9.4. A small amount of an ionic surface active agent is added, such as sodium lauryl sulfate (Duponol C).

The solution was used on hair, as described for the other solution in Example 1. The wave produced by this solution, in 30 minutes after preparation of the solution, was as strong as one produced with a solution containing 5% thioglycolic acid with an excess of ammonia and other alkalies. The freshly prepared solution was yellowish in color, completely odorless, and the slight odor developed on longer standing was easily masked by the addition of a conventional perfume.

Example 3

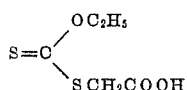
Sodium salt of N diethyl dithiocarbamic acid ester of glycolic acid which has the formula



is easily prepared from sodium N diethyl dithiocarbamate and sodium monochloracetate and is a stable odorless crystalline solid. 9.2 g. of it was dissolved in 90 g. water then the pH of the solution adjusted to 9.3 with mixed isopropanolamines. The permanent wave produced with this solution in the steps described in Example 1 is long lasting and the hair is soft, lustrous and resilient.

Example 4

Ethylxanthogene acetic acid of the formula



is obtained by reacting potassium ethylxanthogenate with sodium monochloracetate and is a crystalline odorless solid having a melting point of 53-54° C. 9 g. of it was dissolved in 90 g. water containing enough morpholine to bring the pH of the solution up to 9.2. The freshly prepared solution was odorless. The wave produced with the solution was equal to a wave produced using a 4.5% morpholine thioglycolate solution.

Example 5

The procedure of Example 1 is followed except that the thiocarbonic acid derivatives there described and representative of Formula 1 of the list given above is replaced by an equal weight of any of the other compounds of formulas given in the said list, namely, (2), (3), or (4) or by any other one of the thio esters referred to herein.

The solutions so made and neutralized by the alkali described in Example 1 are applied to hair and the steps given in Example 1 are followed. The result is a good wave.

Example 6

The procedure of any of the Examples 1-5 inclusive is followed except that the alkaline mate-

6

rial used to neutralize the thiocarbonic acid derivative is replaced by any one of the amines described herein.

Example 7

The thio acid derivative of kind used in Examples 1-5 inclusive is mixed with a mineral salt of any one of the amines described herein as, for instance, the chloride, sulfate, borate or phosphate. The salt is used in proportion to give amine component at least equivalent to the free carboxyl groups of the thio acid ester used. This mixture is then treated before use in waving hair with an amount of lithium, sodium, or potassium hydroxide in amount equivalent to the said thio acid. The alkali and the mixture are dissolved together in water. Or one of these materials may be dissolved in the water first. In any case the caustic alkali liberates sufficient amine to form the amine salt of the thio acid used and it is the amine salt that is the active keratin softening or waving ingredient.

Example 8

The procedure of any of the Examples 1-7 is followed except that the amine therein is replaced by one of the caustic alkalies such as an alkali metal hydroxide. The caustic alkali is used in proportion to establish the pH of the aqueous solution at 8 to 10. In this composition there is included any one of the surface active agents shown above, as, for instance, the sodium lauryl sulfate in the proportion 0.1 part for 100 parts of the solution.

Example 9

9 g. of the trithiocarbonic acid ester used in Example 1, 9 g. of monoisopropanolamine hydrochloride, and 3.4 g. of lithium hydroxide monohydrate were dissolved in 90 cc. of water at room temperature. The solution so obtained is odorless. It was applied to a freshly shampooed slightly moist hair in the form of strands and left in contact with the hair for various lengths of time ranging from 30 minutes to 2 hours. After removal of the waving lotion by washing the hair in a dilute solution of potassium bromate, the dry hair was compared. None of the treated strands were over processed but all were lustrous and resilient.

Example 10

10.5 g. of the thiocarbonic acid derivative of Example 2 was dissolved in 90 cc. of water at 40° C. together with 6.5 g. of anhydrous sodium carbonate and 0.75 g. ascorbic acid and 0.1 g. Tween. A clear odorless solution is formed which was applied on the hair for 1 hour.

The freshly prepared solution is then applied on freshly shampooed hair as described in Example 1.

Example 11

The procedure of Example 10 is followed except that the sodium carbonate thereof is replaced by any one of the amines disclosed herein, the amine being used in proportion 25% in excess of the chemically equivalent proportion of the sodium carbonate.

It will be understood also, that it is intended to cover all changes and modifications of the example of the invention herein chosen for the purpose of illustration which do not constitute departures from the spirit and scope of the invention.

What I claim is:

1. A hair waving composition comprising a

7

water soluble salt of a water soluble amine with an alpha-hydroxy fatty acid ester of an acid selected from the group consisting of di- and tri-thiocarbonic and dithiocarbamic acid and an excess of the water soluble amine in amount to establish a pH of at least 9.2, the said fatty acid containing 2 to 4 carbon atoms to the molecule.

2. A hair waving composition as described in claim 1 including water in the proportion of 100 parts by weight for 5 to 15 parts of the said salt, the said salt being the salt of a water soluble amine.

3. A hair waving composition comprising salt of a water soluble amine with a dithiocarbamic acid ester of an alpha-hydroxy fatty acid, the water soluble amine being used in excess of the amount required to form the salt and in proportion to establish the pH of the composition within the range 8 to 10.

4. A composition as described in claim 1, the alpha-hydroxy fatty acid being glycolic acid.

5. A hair waving composition comprising a water soluble salt of a water soluble aliphatic amine with the ester of trithiocarbonic acid with an alpha-hydroxy fatty acid containing 2 to 4 carbon atoms to the molecule and an excess of the water soluble aliphatic amine in proportion to establish the pH within the range 8 to 10.

6. A hair waving composition comprising a water soluble amine salt of a water soluble amine with a mixed ester of dithiocarbonic acid with (1) an alpha-hydroxy fatty acid and (2) a lower aliphatic alcohol containing 1 to 4 carbon atoms to the molecule and an excess of the water soluble amine in proportion to establish the pH within the range 8 to 10, the said fatty acid containing 2 to 4 carbon atoms to the molecule.

8

7. A hair waving composition comprising an amine salt of a water soluble amine with a thio-carbonic acid ester of an alpha-hydroxy fatty acid and an excess of the water soluble amine in proportion to establish the pH within the range 8 to 10.

MENOTTI DEL ZOPPO.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,939,692	Hardman	Dec. 19, 1933
1,973,130	Turley	Sept. 11, 1934
2,169,147	Jaeger	Aug. 8, 1939
2,201,929	Speakman	May 21, 1940
2,238,672	Arthur	Apr. 15, 1941
2,389,755	Baker	Nov. 27, 1945
2,405,166	Reed	Aug. 6, 1946
2,418,664	Ramsey	Apr. 8, 1947
2,442,461	Karrer	June 1, 1948

FOREIGN PATENTS

Number	Country	Date
117,071	Australia	June 3, 1943

OTHER REFERENCES

- Holmberg, J. Prakt. Chemie, volume 71. (2nd Series) (1905), pages 269, 274 and 284, 285.
- Holmberg, J. Prakt. Chemie, volume 79. (2nd Series) (1909), pages 257, 258, 263, 267, 268 and 269.
- Bulletin 460, May 1942, Conn. Agr. Exp. Station, 34th Report on Drug Products, pages 448 to 450.