United States Patent Office

2,976,216

Patented Mar. 21, 1961

2,976,216

PERMANENT WAVING AGENT

Louis E. De Mytt, Chicago, Ill., assignor to The Gillette Company, Boston, Mass., a corporation of Massachusetts

No Drawing. Filed Nov. 4, 1959, Ser. No. 850,760

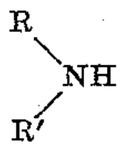
7 Claims. (Cl. 167—87.1)

This invention relates to the cold permanent waving of hair and pertains more specifically to a stable, dry, solid composition which, while itself inactive toward hair, is capable of reacting, upon dissolution in an aqueous solution of a nitrogen base, to produce a novel hair waving agent capable of reducing the disulfide bonds in hair keratin.

Ammonium thioglycolate has been conventionally employed on a wide scale with satisfactory results as an agent for the cold permanent waving of hair, by which is meant waving of hair without the external application of heat so that the maximum temperature to which the hair is subjected during the waving process is about 35° C. However, it has been necessary to supply this material in the form of a lotion or aqueous solution because it is not stable in dry solid form. Supplying the material in lotion form results in increased expense of shipping and packaging, and it is therefore desirable to provide a waving agent which is stable over reasonably long periods of time in storage in dry solid form.

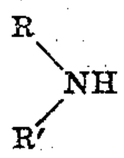
It has now been discovered that thioparaconic acid and certain salts thereof, while not themselves capable of reducing the disulfide bonds in hair keratin even when dissolved in water, are readily converted into the salts of half-amides of thioitamalic acid when dissolved in an aqueous solution of a nitrogen base and that the resulting aqueous solution of the half-amide is an effective reducing agent for hair keratin.

Among the salts of thioparaconic acid which may be employed in the present invention are those of the alkali metals such as sodium, potassium or lithium, of alkaline earth metals such as calcium or magnesium, and of amines such as those having the structure

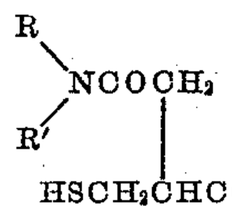


in which R and R′ may be hydrogen, lower alkyl groups, or hydroxy-substituted lower alkyl groups. By "lower alkyl group" is meant one containing 1 to 4 carbon atoms. Among the amine salts which may be employed are those of methylamine, dimethylamine, ethylamine, n-propylamine, di-n-propylamine, t-butylamine, mono- or di-ethanolamine, mono- or di-isopropanolamine, 2-amino-2-methylpropanediol-1,3, etc.

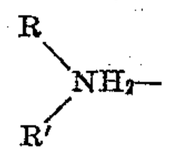
The aforementioned salts of thioparaconic acid are all readily soluble in water, while thioparaconic acid itself is soluble in aqueous alkaline media; when sufficient alkaline material is present, as pointed out hereinafter, dissolution is accompanied by hydrolysis and ring cleavage to form a salt of thioitamalic acid. The latter salts are found to be relatively ineffective hair waving agents. Surprisingly enough, however, when certain nitrogen bases are mixed with such a salt of thioitamalic acid in an aqueous medium, there is formed a half-amide of the salt which is found to be an effective hair waving agent. Among the nitrogen bases which may be employed for this purpose are those having the structure



in which R and R′ are hydrogen, lower alkyl groups, or hydroxy-substituted lower alkyl groups, or combinations thereof, including ammonia as well as the amines described above. The half-amides so produced have the composition

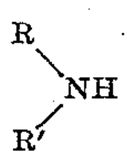


in which R and R′ represent hydrogen, lower alkyl groups, or hydroxy-substituted lower alkyl groups and M represents an alkali metal, an alkaline earth metal, or a radical having the structure



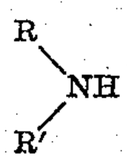
in which R and R′ are defined as above. The aqueous solutions of half-amides of salts of thioitamalic acid are stable lotions at room temperature which may be used in the same manner as conventional ammonium thioglycolate lotions for the cold permanent waving of hair.

When thioparaconic acid itself is employed as the precursor of the active waving agent, the thioparaconic acid may be mixed into water simultaneously with an alkaline material having a cation defined as M above, or either ingredient may be added first, if desired. The nitrogen base employed to form the half-amide is added subsequently. At least one mole of amine having the structure



(where R and R′ are defined as above) is required for each mole of acid in order to form the half-amide. The same nitrogen base may be used for forming the salt as for forming the half-amide, if desired, in which case it may all be added simultaneously, or a different alkaline material may be used for salt formation. Mixtures of two or more different alkaline materials and two or more different amines may also be employed. Dry solid mixtures of thioparaconic acid and non-volatile alkaline materials and amines in the desired proportions selected from the classes above may be supplied to the user who simply dissolves the mixture in water to provide a hair waving lotion. The non-volatile solid amine 2-amino-2-methylpropanediol-1,3 is preferred for this purpose.

When a salt of thioparaconic acid is employed as the dry solid precursor of the waving agent, the alkaline material with which it is reacted in an aqueous medium to form the desired half-amide of thioitamalic acid is a nitrogen base such as an amine having the structure

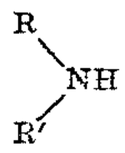


in which R and R′ are defined as above, including ammonia as well as the other amines. In this case, also, the composition may be supplied to the consumer in the form of a dry solid mixture of the thioparaconate salt with a non-volatile solid amine such as 2-amino-2-methylpropanediol-1,3, or the separate ingredients may be added to water in any desired order.

The concentration of the salts of the half-amides of thioitamalic acid as produced in the aqueous medium

may vary widely. However, for the purposes of use as a hair waving lotion, it is found that best results are obtained with solutions containing from 0.4 to 1.0 mole of the product per liter of solution.

The relative proportions of thioparaconic acid and of alkaline material may vary over a considerable range, preferably with the alkaline material being present in excess, over the quantity theoretically required. It will be appreciated that two equivalent proportions of alkaline material are theoretically required for the reaction with one equivalent proportion of thioparaconic acid. One equivalent of the alkaline material reacts to form the salt portion of the product, while the second equivalent produces the amide portion of the molecule. Accordingly, at least one equivalent of a nitrogen base such as an amine having the structure



in which R and R′ are defined as above is required to react with each equivalent proportion of thioparaconic acid, the remaining equivalent of alkaline material being either such an amine or an inorganic alkaline material such as an alkali or alkaline earth metal hydroxide, carbonate, bicarbonate, etc.

When a salt of thioparaconic acid is employed as the precursor of the active waving agent, at least one equivalent of a nitrogen base as described above is required to form the desired half-amide of thioitamalic acid; an excess of alkaline material over the amount theoretically required is preferred, and this excess may be either a nitrogen base such as an amine or an inorganic alkaline material, just as in the case when thioparaconic acid is used as the precursor.

In both cases, i.e., when either thioparaconic acid or a salt thereof is used as the precursor, the amount of excess or free alkaline material over and above that required to react with the acid or slat may be as much as 0.8 equivalent proportion. One equivalent proportion of such an alkaline material is the weight of the material (measured in the same units as those used for measuring the molecular proportions of thioparaconic acid or salt in the composition) required to neutralize one molecular proportion (in the same units) of a strong monovalent acid such as hydrochloric acid.

The aqueous solutions of the salts of the half-amides of thioitamalic acid prepared in accordance with the present invention may be employed in any of the conventional processes for permanent waving of hair. For example, the solution may be employed to saturate a tress of hair which thereupon is wound upon a conventional curling rod, resaturated with the solution if desired, then permitted to stand for a period of time from ten minutes to an hour or more, at the end of which time the hair tress is rinsed and then either permitted to become oxidized by aerial oxidation, which involves exposure to the atmosphere for two to six hours or more, or neutralized by pouring through the tress an aqueous solution of a conventional neutralizer such as sodium bromate, sodium perborate, or the like. After neutralization, the hair is removed from the curling rod and is found to have acquired a permanent wave.

The following specific examples are intended to illustrate more clearly the nature of the invention without being a limitation on the scope thereof.

Example 1

Thioparaconic acid (M.P. 108°–109° C.) in the form of a white, amorphous solid material was found to be a stable material, giving no evidence of decomposition even after storage over a period of several months. The sodium salt of thioparaconic acid was prepared by suspending 73 parts by weight (0.5 mole) of the latter in 200 parts by weight of water. A 20% aqueous solution of sodium hydroxide was then added slowly to the suspension with stirring and cooling until the mixture had been neutralized to a pH of 7. The water was thereupon removed by evaporation at reduced pressure, leaving the white, solid, amorphous sodium thioparaconate which was also stable.

Other salts of thioparaconic acid including other alkali metal salts, alkaline earth metal salts such as calcium and magnesium salts, as well as salts of amines such as 2-amino-2-methylpropanediol-1,3, were prepared by the same procedure and were likewise found to be stable in their dry solid form. The ammonium salt of thioparaconic acid was prepared by passing ammonia gas in excess into a suspension of thioparaconic acid in alcohol.

Example 2

There was dissolved in the minimum quantity of water required for solution 16.8 parts by weight (0.1 mole) of ammonium thioparaconate. To this solution there was added slowly and with stirring 15 parts by weight (0.21 mole) of aqua ammonia. The reaction mixture became warm, indicating the formation of the half-amide of the ammonium salt of thioitamalic acid.

The resultant solution was diluted to a concentration of 0.6 mole of the half-amide per liter and was found to remain stable at room temperature over an extended period of time.

The foregoing dilute solution of the half-amide was employed as a waving agent by applying the solution to a hair tress in the usual manner, winding the saturated tress upon a curler, then resaturating the wound tress and permitting it to stand at room temperature for sixty minutes. The hair tress was then thoroughly rinsed with water and allowed to dry for a period of six hours at room temperature while still in wound form, during which period aerial oxidation of the reduced hair occurred and the hair became hardened or set in its new curled configuration. Ppon removal from the hair curler, the hair was found to have a highly satisfactory permanent wave.

Example 3

There was suspended in 60 parts by weight of water 7.3 parts by weight (0.015 mole) of thioparaconic acid. There was then added slowly and with stirring sufficient aqua ammonia to neutralize the aqueous medium, leading to complete dissolution of the suspended acid. An excess of aqua ammonia was then added to provide an alkaline solution (pH 9.2) of the ammonium salt of the half-amide of thioitamalic acid. This solution was found to be stable upon storage at room temperature over extended periods of time.

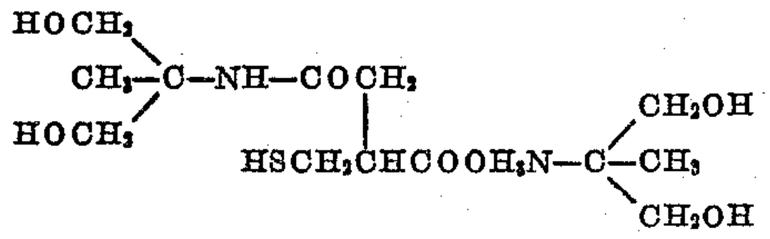
When diluted with water to provide a solution containing 0.6 mole per liter of the half-amide, the solution was employed for the permanent waving of hair as described in the preceding example with substantially equivalent results. Satisfactory results were also obtained when a solution of a conventional neutralizer, sodium perborate, was poured through the tress to neutralize it instead of permitting the tress to be neutralized by aerial oxidation.

Example 4

There was suspended in 50 parts by weight of water 7.3 parts by weight (0.015 mole) of thioparaconic acid. To this suspension was added sufficient 2-amino-2-methylpropanediol-1,3 to produce a neutral solution (pH7). To this solution of the amine salt of thioparaconic acid concentrated aqua ammonia was added until the pH of the resultant solution remained constant at 9.2 to 9.3. This solution of the amine salt of the half-amide of thioitamalic acid was found to be quite stable, both at room temperature and at moderately elevated temperatures and, when diluted to a concentration of 0.6 mole of the half-amide per liter, was found to be an effective hair waving lotion when employed as described in Example 3 above.

Similar results were obtained when an excess of 2-amino-2-methylpropanediol-1,3 was employed in place

of aqua ammonia. In this case the resultant amide has the structure



Example 5

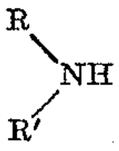
There was prepared a dry, solid, particulate mixture containing 7.3 parts by weight (0.1 mole) of thioparaconic acid and 26.8 parts (0.26 mole) of 2-amino-2-methylpropanediol-1,3. The mixture was found to be stable upon storage at room temperature over extended periods of time. When dissolved in 166 parts by weight of water, a waving lotion was obtained which could be employed as described in Example 2 above to produce satisfactory permanent waves.

This application is a continuation-in-part of my copending application Serial No. 641,019 filed February 19, 1957, and now abandoned.

Although specific embodiments of the invention have been described herein, it is not intended to limit the invention solely thereto, but to include all of the obvious variations and modifications within the spirit and scope of the appended claims.

What is claimed is:

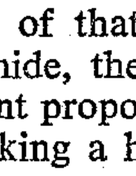
1. A dry solid composition soluble in an aqueous medium to form a hair waving lotion comprising (1) one molecular proportion of a member of the class consisting of thioparaconic acid, alkali metal salts of thioparaconic acid, alkaline earth metal salts of thioparaconic acid, ammonium salt of thioparaconic acid, mono-(lower alkyl)-amine salts of thioparaconic acid, di-(lower alkyl)-amine salts of thioparaconic acid, mono-(hydroxy-substituted lower alkyl)-amine salts of thioparaconic acid, and di-(hydroxy-substituted lower alkyl)-amine salts of thioparaconic acid, and (2) a non-volatile alkaline material including at least one molecular proportion of a non-volatile amine having the structure



wherein R and R′ are selected from the class consisting of hydrogen, lower alkyl groups, and hydroxy-substituted lower alkyl groups, the total quantity of said alkaline material being in excess of the amount required to react with the first said member to form an amide salt, the amount of said excess being up to 0.8 equivalent proportion.

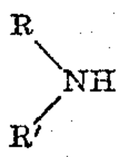
2. A dry solid composition soluble in an aqueous medium to form a hair waving lotion comprising (1) one molecular proportion of a member of the class consisting of thioparaconic acid, alkali metal salts of thioparaconic acid, alkaline earth metal salts of thioparaconic acid, ammonium salt of thioparaconic acid, mono-(lower alkyl)-amine salts of thioparaconic acid, di-(lower alkyl)-amine salts of thioparaconic acid, mono-(hydroxy-substituted lower alkyl)-amine salts of thioparaconic acid, and di-(hydroxy-substituted lower alkyl)-amine salts of thioparaconic acid, and (2) a non-volatile alkaline material including at least one molecular proportion of 2-amino-2-methylpropanediol-1,3, the total quantity of said alkaline material being in excess of the amount required to react with the first said member to form an amide salt, the amount of said excess being up to 0.8 equivalent proportion.

3. The method of making a hair waving lotion which comprises reacting, in an aqueous medium, (1) a member of the class consisting of thioparaconic acid, alkali metal salts of thioparaconic acid, alkaline earth metal salts of thioparaconic acid, ammonium salt of thioparaconic acid, mono-(lower alkyl)-amine salts of thioparaconic acid, di-(lower alkyl)-amine salts of thioparaconic acid, mono-(hydroxy-substituted lower alkyl)-amine salts of thioparaconic acid, and di-(hydroxy-substituted lower alkyl)-amine salts of thioparaconic acid, with (2) a member of the class consisting of amines having the structure



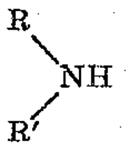
in which R and R′ are members of the class consisting of hydrogen, lower alkyl groups, and hydroxy-substituted lower alkyl groups, the last said member being present in excess of the amount required to react with the first said member to form an amide salt, the amount of said excess being up to 0.8 equivalent proportion.

4. The method of making a hair waving lotion which comprises reacting, in an aqueous medium, an alkali metal salt of thioparaconic acid with a member of the class consisting of amines having the structure



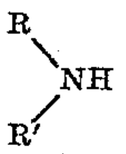
in which R and R′ are members of the class consisting of hydrogen, lower alkyl groups, and hydroxy-substituted lower alkyl groups, the last said member being employed in an amount in excess of that required to react with said salt to form an amide, the amount of said excess being up to 0.8 equivalent proportion.

5. The method of making a hair waving lotion which comprises reacting thioparaconic acid in an aqueous medium with more than two molecular proportions of an amine having the structure



in which R and R′ are selected from the class consisting of hydrogen, lower alkyl groups, and hydroxy-substituted lower alkyl groups, the amount of the excess amine being up to 0.8 equivalent proportion.

6. The method of making a hair waving lotion which comprises reacting, in an aqueous medium, (1) a 2-amino-2-methylpropanediol-1,3 salt of thioparaconic acid and (2) a member of the class consisting of amines having the structure



in which R and R′ are members of the class consisting of hydrogen, lower alkyl groups, and hydroxy-substituted lower alkyl groups, the last said member being employed in an amount in excess of that required to react with said salt to form an amide, the amount of said excess being up to 0.8 equivalent proportion.

7. The method of making a hair waving lotion which comprises reacting, in an aqueous medium, (1) a 2-amino-2-methylpropanediol-1,3 salt of thioparaconic acid and (2) 2-amino-2-methylpropanediol-1,3 in an amount in excess of that required to react with said salt to form an amide, the amount of said excess being up to 0.8 equivalent proportion.

References Cited in the file of this patent

UNITED STATES PATENTS

2,405,166	Reed et al.	Aug. 6, 1946
2,458,425	Rocchini et al.	Jan. 4, 1949
2,577,710	McDonough	Dec. 4, 1951

OTHER REFERENCES

Burger: Chem. Abst. 35:2112–3 (1941).
Morse: Chem. Abst. 44:4423e (1950).