

UNITED STATES PATENT OFFICE

2,615,828

COMPOSITIONS FOR TREATING KERATIN-CONTAINING MATERIALS

John W. Haefele, Cincinnati, Ohio, assignor to
The Procter and Gamble Company, Ivorydale,
Ohio, a corporation of Ohio

No Drawing. Application February 15, 1951,
Serial No. 211,183

16 Claims. (Cl. 167—87.1)

1

This invention relates to the art of treating hair and other keratin-containing substances such as wool. The invention has particular relevance to the art of altering the physical form and shape of hair and to the provision of new softening agents for use in the treatment of keratin-containing materials.

This application is a continuation-in-part of my applications, Serial Numbers 93,191 and 93,192, filed May 13, 1949, and Serial Numbers 142,725 and 142,726, filed February 6, 1950.

The use of mercaptans as softening agents in hair waving procedures is well known. These materials have met with considerable success, especially in the development of a kit to be used in administering cold permanent waves at home without the aid of a professional operator. In the use of such kits, an alkaline solution or lotion of a mercaptan such as thioglycolic acid is applied to the hair before or after the hair has been formed or wound into the desired configuration. This solution or lotion is allowed to remain in contact with the hair until desired softening has been effected. Then while the softened hair is held in the desired configuration, the mercaptan lotion is rinsed out, following which the hair is treated with an oxidizing agent to effect permanent setting or fixing in the configuration established.

The mercaptan which has been used with greatest commercial success is thioglycolic acid, but, as is known in the art, other mercaptans may be used, such as for example ethyl mercaptan; benzyl mercaptan; mercapto ethyl sulfonic acid; beta amino ethyl mercaptan; beta mercapto ethyl methyl amine; beta mercapto ethyl dimethyl amine; beta mercapto ethyl alcohol; mercapto carbinol; mercapto carbonyl; mercapto dimethyl ketone; mercapto ethyl acetate; beta mercapto diethyl ether; 3-amino-2-hydroxy propyl mercaptan; glyceryl monomercaptan (thioglycerol); trithiohexitols; mono- and poly-thio polyoxyethylene glycols (such as tetraglycol dimercaptan); mercapto ethyl hydroxy ethyl amine; monothio polyhydroxy acids; monothiomucic acid; mono- and dimercapto succinic acid; thio-citric acid; mercapto acetaldehyde; alpha mercapto methyl-furane, -thiophene, -pyrrole, -pyrimidine, and -thiofurfuralcohol; mercapto alkyl pseudothioureases; mercapto ethyl urethane; mercapto ethyl acetamide; mercapto ethyl guanidine; and mercapto alkyl betaines and taurines. Substituted mercaptans such as thioglycolic acid and thioglycerol, for example, are especially suitable for such use.

As used herein, throughout both the specifica-

2

tion and the claims, the term "mercaptan" refers to a compound containing the sulfur analogue of an alcoholic hydroxy group, i. e. the thiol group ($-SH$), attached to an aliphatic carbon atom. In other words, thiophenols are specifically excluded from the scope of the word "mercaptan" which can be considered here as being limited to alkyl, alkenyl, and substituted alkyl and alkenyl thiols.

Even the most successful and most popular of these mercaptan hair softening agents such as thioglycerol and thioglycolic acid suffer the disadvantages that they will render the hair harsh and lower tensile strength if allowed to remain in contact therewith for an extended period. Thus in using the readily available commercial solutions of thioglycolic acid which contain the equivalent of about 6% of the pure acid by weight, a maximum contact time of 3 hours is usually recommended for coarse hair, and shorter times such as $\frac{1}{2}$ to 2 hours are recommended for hair of fine texture. The undesirable effect of longer periods of contact may be evident by visual inspection, feel, laxity of the waved hair, or by comparison of the tensile strengths of the hair before and after treatment.

It is an object of the present invention to provide a composition for use in hair or wool softening which is rapid and efficient but surprisingly gentle in its action.

Another object is to provide a composition which efficiently softens hair or wool or other keratin-containing substances but which can be held in contact therewith for extended periods of time without objectionable damage.

Another object is to provide an improved composition for use in permanent hair waving.

A further object is to provide an improved composition for imparting improved properties to wool.

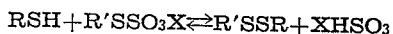
A still further object is to provide a process for reducing the tendency of mercaptan solutions to damage hair, wool, or other keratin-containing substances and particularly hair of fine texture, when such solutions are used for effecting desired changes in structure of such keratin-containing substances.

Other objects and advantageous features of the invention will be apparent from a consideration of the detailed description which follows.

I have discovered that the above objects are attained by incorporating in the solution of mercaptan of the general formula, RSH , one or more water-soluble salts of organic thiosulfuric acids of the general formula $R'SSO_3H$ wherein each of the symbols, R and R' , represents a

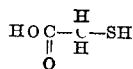
3

monovalent organic radical which is free of the concomitant presence of a carboxyl group and an amino group, and in which the free valence is on an aliphatic carbon atom. These thiosulfates react with the mercaptans to form a certain quantity of disulfides and bisulfites until an equilibrium is reached for the reaction

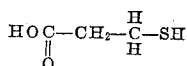


where X represents a monovalent salt-forming radical. Under normal conditions, the equilibrium is such that appreciable amounts of all four types of compounds are present at equilibrium. The radicals represented by R and R' in this disclosure are not limited in character or size except as above noted and except by the requirement that the compounds in which they are contained are sufficiently soluble and are compatible with each other at least insofar as they remain soluble under the conditions of use. Thus the organic radicals represented by R or by R' are not necessarily all alike and each radical, whether represented by R or R', can be of any type which is free of the concomitant presence of amino and carboxyl groups, such as alkyl, amino alkyl, carboxy alkyl, amido alkyl, alkyl sulfonate, hydroxy alkyl, amino hydroxy alkyl, carboxy hydroxy alkyl, alkoxy alkyl, hydroxy alkoxy alkyl, or cycloaliphatic, for example, and the number of carbon atoms is limited only by requirements of solubility and compatibility in the mixed solution. With most classes of compounds solubility will limit the use of appreciable amounts of those members in which R or R' contain 10 carbon atoms or more. As pointed out in detail below, the manner in which the ultimate solution of mercaptan and organic thiosulfate is formed is not critical.

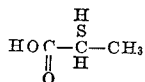
The carboxylic acid substituted alkyl mercaptans and their simple derivatives are of special importance in preparing agents for treating hair. I have discovered that the soluble carboxylic acid substituted alkyl mercaptans and the corresponding thiosulfates containing only the elements C, H, O, and S and the soluble amides of said mercaptans and thiosulfates are particularly efficient for permanently waving hair while maintaining the safety of protective action against hair damage which is characteristic of all the keratin-treating agents of this invention. Included in this class of compounds are the following.



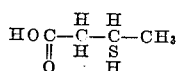
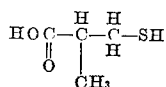
Thioglycolic acid



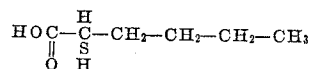
Thiohydraacrylic acid



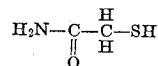
Thiolactic acid

 β -Mercapto butyric acid β -Mercapto isobutyric acid

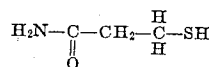
4

 α -Mercapto hexanoic acid

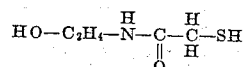
and other soluble homologues and corresponding thiosulfates.



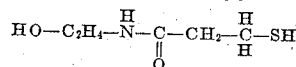
Mercapto acetamide

 β -Mercapto propionamide

and other soluble homologues and corresponding thiosulfates.



Monoethanol amide of thioglycolic acid



Monoethanol amide of thiohydraacrylic acid

and other soluble homologues and corresponding thiosulfates.

In their preferred form, the compositions of the present invention are aqueous solutions. When these solutions are employed in the treatment of living human hair as in permanent hair waving, the alkalinity of the solutions is preferably controlled from a pH of about 9 to a pH of about 9.5. Thus the reaction of the mercaptan with the keratin proceeds at a good rate and yet the alkalinity is not sufficiently high to present a problem. However, in the use of the compositions of my invention in the treatment of wool, leather, etc., the use of lower and higher alkalinities can be tolerated, such as pH values from about 7.0 up to about 10.5. Although the reaction of mercaptan agents with keratin tends to be more vigorous at the higher alkalinities, the protective characteristics of the compositions of my invention greatly reduce the undesirable damage to the keratin which would otherwise occur. The preferred condition of pH for operation in individual cases depends not only upon the type of material being treated but also somewhat upon such other conditions as the temperature of operation and the strength of the treating solution.

The aqueous solutions of the present invention can be made up in several different ways. Thus the undiluted constituents can be marketed as a mixture with directions as to amount of water to be used in preparing the ultimate solutions of the desired concentration for a given purpose. I have discovered one particularly convenient, economical, and especially suitable method of preparing these solutions. This method is specifically disclosed and claimed herein.

If these ultimate solutions are prepared by the direct procedure of dissolving mercaptan (RSH) and thiosulfate (R'SSO₃H) together with any alkaline material which it is necessary to add in order to control pH, an equilibrium reaction will occur in the resulting solution with the conversion of a certain amount of the mercaptan (RSX) and thiosulfate (R'SSO₃X) to disulfide (RSSR') and sulfite (X₂SO₃) (where X represents a monovalent salt-forming radical introduced in the alkalizing agent or in the original mercaptan or thiosulfate molecules. Ammonia

5

is very often used as the alkalinizing agent in hair waving, and in this case X would be the NH_4^+ ion.) Because of the equilibrium reaction which exists between these four types of compounds, the aqueous solutions of the present invention can be prepared equally well by dissolving together the appropriate organic disulfide (RSSR') and a water-soluble sulfite reducing agent such as normal sulfites, bisulfites and hydrosulfites in place of the direct solution of mercaptan (RSX) and thiosulfate ($\text{R'SSO}_3\text{X}$). As used herein, the term water-soluble sulfite and similar expressions are taken to mean all of the above three classes and combinations thereof, namely water-soluble normal sulfites, water-soluble bisulfites, water-soluble hydrosulfites, and mixtures of these. Equivalent solutions can be prepared in both ways. For example, an equimolar mixture of dithiodiglycerol and a soluble normal sulfite salt will react in aqueous alkaline solution to form a keratin-treating solution equivalent to that formed by mixing the corresponding water-soluble glyceryl monomercaptide and glyceryl thiosulfate also in equimolar proportions. At the same total concentrations, both solutions have the same advantageous properties.

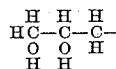
In general, the type of disulfide employed when it is desired to form organic thiosulfate and mercaptan in situ is a disulfide which is soluble in water at pH 7 to about 10.5 and which has the formula RSSR' where R and R' are each organic radicals which can be the same, similar or entirely different thereby forming either symmetrical or unsymmetrical disulfides or mixtures thereof. The essential features of this constituent of my composition are the presence of the reducible disulfide ($-\text{S}-\text{S}-$) linkage and solubility in water at pH 7 to about 10.5 to the extent of being able to form at least a 0.05 molal solution ($\sim$ to about a $\frac{1}{2}$ -2% by weight). Among the disulfides which fall within the scope of my invention and which can be employed to replace those recited in the various examples given at the end of this description, preferably on an equimolar basis, are for example: dithiodiglycerol; dithiodiethanol; dithiodipropanol; disulfide of 2-mercapto-1-propanol; dithiodierythritol; dithiodiarabitol; dithiodisorbitol; disulfide of 2-mercapto sorbitol; α,α' -dimethyldithiodiglycerol; disulfide of 3-mercapto-1,2-butanediol; disulfide of 1-mercapto-2,4-hydroxypentane; dithioditetraethylene glycol; hydroxyethyl glyceryl disulfide; diethylene glycol sorbityl disulfide; dibutylene glycol sorbityl disulfide; the disulfides of thioglycolates, thiosalicylates, thiohydracrylates, beta mercapto butyrates, beta mercapto isobutyrate, alpha mercapto caproates, thiolactates and other salts of thio acids; disulfide of mercapto ethanol; disulfide of mercapto ethyl amine; disulfides of thioglycolic amides; and disulfide of sulfothioglycerol. Other suitable disulfides which are soluble in water at pH 7 to about 10.5 will be readily apparent to those versed in the art.

The corresponding mercaptans and organic thiosulfates of the above disulfides can likewise be substituted, preferably on an equimolar basis, for the mercaptans and organic thiosulfates called for in the complete examples to be described later herein.

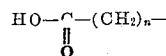
Three individual disulfides and their corresponding mercaptan and thiosulfate derivatives are of particular interest in waving hair. These are dithiodiglycerol, dithiodiglycolic acid com-

6

pounds and the dithiodihydracrylic acid compounds. Solutions containing only thioglycerol and derivatives thereof may be described as those in which the organic radicals, R and R', are both thioglycerol residues having the chemical structure,



Solutions containing only thioglycolic and/or thiohydracrylic acids and derivatives thereof may be described as those in which the organic radicals, R and R', are both residues of primary mercapto carboxylic acids containing 2 to 3 carbon atoms, the general chemical structure of said residues being



where n is a whole integer from 1 to 2.

The second essential constituent of those compositions involving the formation of mercaptan and organic thiosulfate in situ from the disulfide is the reducing agent. Water-soluble sulfites such as sodium hydrosulfite, sodium bisulfite and sodium sulfite are especially useful. Corresponding salts of other alkali metals such as potassium (potassium hydrosulfite, potassium bisulfite, etc.) as well as corresponding ammonium and substituted ammonium (amine) salts (ammonium and monoethanol amine sulfite, or hydrosulfite e. g.) can be employed without departing from the spirit of the invention. Water-soluble hydrosulfites containing formaldehyde of crystallization and sometimes referred to in the art as sulfoxylates can also be employed, but insofar as the present invention is concerned such compounds are to be considered as coming within the scope of the term "hydrosulfite" as used herein.

Compatible mixtures of these various sulfites, bisulfites, and hydrosulfites can also be advantageously employed since mixtures of these reducing agents alone have been found to possess the desired potential necessary for the reduction of the disulfide in aqueous solution.

When compositions of the present invention are formed by reducing an organic disulfide as disclosed more specifically herein above, the proportion of reducing agent to the disulfide is not sharply critical, but sufficient reducing agent must be present to provide for the potential formation of an adequate amount of mercaptan and organic thiosulfate. Although I prefer to employ about one to two moles of reducing agent per mole of disulfide, products formed by the use of proportions of up to 10 moles of reducing agent per mole of disulfide are suitable. The proportion of reducing agent may also be as low as $\frac{1}{8}$ mole per mole of disulfide provided the actual concentration of reducing agent is at least equivalent to 0.05 molal. However it is usually impractical to employ less than $\frac{1}{2}$ mole of sulfite per mole of disulfide.

As is known in this art, the alkalinity of softening compositions in aqueous solutions is instrumental in achieving the desired changes in the keratin-containing substance. The lower the pH the longer the time required. Accordingly, pH values below 7 are not recommended for use in the present invention. In the use of these compositions in waving hair, I prefer to employ alkalinities no higher than 9.5. It has been observed that an alkalinity within the range of pH 7 to pH 10.5 can be used safely for the period of

time required to effect the desired waving with the present compositions. However, in order that irritation to the skin may be held to a minimum, a pH range of 9.0 to 9.5 is especially suitable for waving human hair.

Some reducing agents, such as sodium sulfite, impart to the disulfide solution sufficient or more than sufficient alkalinity for effectively softening hair. Adjustment to desired alkalinity with an acid substance such as, for example, acetic acid, citric acid, tartaric acid, hydrochloric acid, sulfuric acid, and sulfurous acid may be desirable in cases where alkalinities are above pH 10.5. However, other reducing agents such as sodium or potassium bisulfite are not sufficiently alkaline and when these are employed additional alkalizing materials must be added. Different reducing agents of different degrees of alkalinity can be used in admixture to give desired alkalinity control, e. g. a mixture of sodium sulfite and sodium bisulfite, but other alkalizing materials which will render the solution of the mixture of organic disulfide and reducing agent alkaline to an extent not exceeding 10.5 are of course suitable. Ammonia is preferred because of its ready availability, relatively low cost, and relatively low irritating effect.

Water-soluble amines, which are compatible with the other materials of the composition such as the mercaptan, the disulfide and the reducing agent, and reaction products of same, can be employed. Examples of such amines are methylamine, ethylamine, monoethanolamine, diethanolamine, and morpholine. Water-soluble quaternary ammonium bases such as tetraethyl ammonium hydroxide or tetraethanol ammonium hydroxide can also be used. Alkali metal hydroxides such as sodium hydroxide or potassium hydroxide are suitable for use but care must be exercised to avoid excesses which will raise the alkalinity of the solution to a point above pH 10.5. In this connection also water-soluble carbonates such as sodium carbonate, potassium carbonate, the corresponding bicarbonates as well as water-soluble phosphates can be used if proper control of alkalinity is exercised. In order that the maximum alkalinity of 10.5 is not exceeded, water-soluble buffers such as ammonium acetate, diammonium phosphate, ammonium carbonate and borax can be employed if desired.

Because the equilibrium mixture of my invention containing disulfide, sulfite, and organic thiosulfate in addition to mercaptan has high protective characteristics, the strength of the solution used in contact with hair or wool as measured in terms of potential mercaptan concentration is not seriously critical. Satisfactory treatment of keratin-containing substances can be carried out with the use of solutions with a potential mercaptan concentration equivalent to less than 0.1 molal ($\approx$ about $\frac{1}{2}$ to 2% by weight), but it should be borne in mind that the action of the composition is slower with such low concentrations. Also the action of compositions of this invention are slowed somewhat by large amounts of the organic thiosulfate.

Of course, for heat waving a low potential mercaptan concentration of no more than 0.2 molal is almost always sufficient.

My preferred solutions for cold waving, however, contain a potential mercaptan concentration of about 0.3-0.8 molal ($\approx$ about 1-15% mercaptan by weight depending upon the molecular weight of the substances used). With such solutions, the time required for effecting suitable soft-

tening with hair operations on the human head may be as short as 20 minutes at 80° F. However, depending upon the temperature and alkalinity of the solution, and the potential concentration of organic thiosulfate, longer periods of time may be required with such solutions, such as 60 to 120 minutes, or even 180 minutes when the potential concentration of organic thiosulfate becomes as high as 100 molar per cent of the potential mercaptan concentration. If desired, this time can be shortened somewhat, if higher potential concentrations of mercaptan, such as 1.5 molal, are used when the potential thiosulfate is very high. With the compositions of this invention, outstanding protection is provided against objectionable damages even if the exposure is continued for times far in excess of that necessary for achieving the desired softening effect, even for as long as 16 to 24 hours at 80° F. for example.

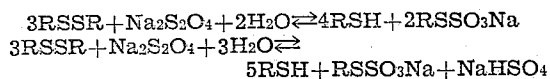
As is indicated in certain of the examples below, the softening operation may be followed by a fixing operation which comprises first rinsing the solution from the softened hair, then treating the hair with a fixing or oxidizing agent. Thus chlorine water, peroxides, tartaric acid, sodium chlorite, potassium bromate and others known in the art may be provided and used.

It has been found that the organic thiosulfate itself which is present in the softening compositions of this invention has special advantages as a fixative. When the potential concentration of this material in my softening solutions is quite high, i. e. generally 100 molar per cent or more of the potential mercaptan concentration, the re-establishment of some of the broken disulfide linkages of the reduced hair keratin is effected by the softening solution itself. Use of organic thiosulfate in this manner to oxidize or fix reduced keratin of hair appears to result in the chemical introduction of the organic group of the thiosulfate into the keratin molecule, and when the organic radical of the thiosulfate is relatively high in molecular weight (C_{12} for example), then such chemical introduction seems to impart an improved luster or sheen to the hair.

In this specification I have referred repeatedly to the waving of hair. However, it is to be understood that the invention is not limited to this field of application. It is possible to change the shape or configuration of the hair as is desired, and the invention can be employed with equal success in operations involving the reverse of waving such as "dekinking." Furthermore, as is shown in Examples 4, 10, 17 and 27, my invention can be applied to the treatment of other fibrous keratin-containing substances such as wool. Wool is particularly susceptible to damage by chemical substances which attack keratin, but I have found that surprisingly less damage is suffered in the use of the compositions of the present invention than in the use of softening agents heretofore proposed. Also, I am not limited to changes in configuration in the practice of my invention. My solutions can be employed generally for preliminary treatment of keratin-containing materials in processes wherein the linkages are rebuilt not only with oxidizing agents but also with such materials as formaldehyde, glyoxal, and alkyl dibromides for example, for the purpose of modifying the fiber structure with or without changing the configuration. An illustration of this effect is given in Examples 10 and 15 where treatment of wool with solutions

containing organic thiosulfate in potential concentrations of 100 molar per cent and more of the potential mercaptan concentration is shown to result in marked improvement in shrink resistance. Apparently this improvement is due to the introduction of the organic group of the thiosulfate into the keratin molecule because an appreciable gain in weight of the wool was noted. This chemical introduction can be used to advantage to modify other physical properties of keratin-containing materials, such as wettability, appearance, etc., depending upon the character of the organic group introduced.

It should be borne in mind that, with keratin-treating solutions of the type disclosed herein, the mercapto group is still functionally the group of primary importance insofar as reaction with the keratin is concerned. Accordingly, the most significant method of expressing solution strengths is in terms of molal concentrations of mercaptan or really of mercapto groups (since one molecule may contain more than one mercapto group) or alternately in terms of mercaptan or mercapto group equivalents since each disulfide group is potentially capable of being reduced to a mercaptan group and a thiosulfate group by the sulfite reducing agent if the equilibrium is disturbed in that direction, as it is, for example, by consumption of mercaptan during the reaction with keratin. Molal concentrations of materials will therefore be given in most cases in this description, and the total potential or equivalent molal concentration of mercapto groups will be used as a measure of the relative keratin-modifying capacity of the various solutions, regardless of how these groups are introduced into a given solution, i. e. whether added as straight mercaptans, straight disulfides, or a mixture of the two types of compound. It should be pointed out in this regard that whereas the sulfites or bisulfites reduce each mole of disulfide to one mole of mercaptan and one mole of thiosulfate, the hydrosulfites react to form mostly mercaptan and each mole of disulfide in this case is potentially equivalent to even more than one mole of mercaptan. According to my theory, one or more reactions such as the following probably take place in this case:



where R represents organic radicals which may be either all alike or of more than one kind.

Whatever the actual mol ratio of thiosulfate to mercaptan in ultimate solutions prepared by mixing disulfides and hydrosulfites, such solutions have been found to be considerably less damaging to hair and other keratin-containing substances on prolonged exposure than a comparable solution containing only the equivalent concentration of mercaptan with no thiosulfate when employed under comparable conditions.

If the compositions of this invention are prepared by mixing disulfides and normal sulfite or bisulfite reducing agents and no extra mercaptans or thiosulfates are added, the mol ratio of thiosulfate to mercaptan in the treating solution will be 1 : 1. And if solutions are made up using disulfides and hydrosulfites with no added mercaptans or thiosulfates, the mol ratio of potential thiosulfate to potential mercaptan will always be less than 1 : 1. However, if the solutions are pre-

pared from mercaptans and thiosulfates directly or by adding extra amounts of either of these materials as described to the mixture of disulfide and sulfites, the initial mol ratio of potential thiosulfate to potential mercaptan can be varied indefinitely at will. For any set concentration of mercaptan or total mercapto group equivalents, the maximum possible value for the molal ratio of thiosulfate to mercaptan in that case will of course be determined by the extent of the solubility of the thiosulfate in question.

In the compositions of my invention it is preferable that the potential or equivalent molal concentration of thiosulfate be at least one fifth that of the equivalent or potential molal concentration of the mercaptan. This is about the molal ratio which is believed to result from reducing disulfide with hydrosulfite, as suggested by the reactions shown above. However, measurable reduction in the damage done to hair or wool by mercaptans is evidenced by use of equivalent molal concentrations of thiosulfates as low as $\frac{1}{10}$ to $\frac{1}{20}$ of the equivalent concentration of mercaptan. The potential protection against hair or wool damage will of course increase with increase in the proportion of thiosulfate present. However, for a given equivalent concentration of mercaptan, the length of time required to effect the desired softening of keratin-containing substances also increases with increase in the proportion of equivalent thiosulfate present. This will be illustrated later by examples. Suffice it to say for the present that addition of 35 to 50 molar per cent of potential organic thiosulfate based on the potential mercaptan provides outstanding protection against damage to hair exposed as long as 16 hours at 80° F. to the action of waving lotions of average mercaptan concentration. I prefer that the total potential or equivalent concentration of mercapto group in the aqueous compositions of my invention be from about 0.10 molal to about 0.6 molal but in special cases concentrations as low as 0.05 may be useful and concentrations as high as 1.5 to 2.0 molal may be used if desired and if solubilities permit.

To the compositions of the present invention can be added opacifying agents, perfumes, and other ingredients to impart desired qualities thereto. In the permanent waving of hair, the solution or lotion thus formed is used in substantially the same way as that previously described for presently available home waving kits. However, appreciably longer contact times can be tolerated without the danger of undesirable hair damage.

Protection of both hair and wool against perceptible damage over extended periods of even more than 24 hours' exposure to mercaptan is effected by compositions in which the equivalent organic thiosulfate is over 100 molar per cent of the total equivalent mercaptan concentration. At 200 molar per cent thiosulfate, protection is extended to as long as 60 hours. Of course, even higher molar percentages of organic thiosulfate, such as 300 to 600 per cent, can be employed to achieve very high protection as may be desired, for example, in waving very delicate hair such as that which has been subjected to a chemical bleach. Also, it is sometimes desirable to provide for increased protection if the solution is to be employed in effecting a permanent wave at high temperature, sometimes referred to in the art as "heat permanent waving." It is therefore clear that my present invention includes compositions

which are extremely safe for use in contact with human hair as well as other keratin-containing substances, thereby adding materially to the convenience of that user who may have preference for a long but safe exposure time over the shorter and more critical exposure times which are now necessary with present waving lotions, etc.

The invention will be more fully understood from the following specific examples taken in conjunction with the accompanying detailed description of variants, but it is to be understood that the invention is not limited thereto but rather to the scope of the appended claims. In the examples given below "parts" means parts by weight and, except where indicated to the contrary, treatment with the compositions was conducted at 100° F. It is to be noted also in connection with some of the examples that the effectiveness of the solutions is indicated by diameter measurements of curls of hair produced on curlers 6.5 mm. in diameter under certain permanent waving conditions, the smaller diameter indicating greater effectiveness of the keratin-softening solution. Moreover, when freshly formed curls such as those produced in the examples are suspended by one end and shaken up and down, the elasticity or spring of the formed spiral may be observed. The degree of laxity of the spiral coil is indicative of the degree of hair damage effected by the softening solution. Numerical indication of the degree of hair damage is obtained by measuring the length of the spiral coil when suspended by one end; the greater the length, the greater the damage, assuming the hair has been exposed at least long enough to produce a curl.

Example 1.—A solution of glyceryl thiosulfate was prepared by heating together in aqueous solution equimolar quantities of glycerin alpha monochlorhydrin and hydrated sodium thiosulfate of the formula $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. The resulting solution contained about 32.3% glyceryl thiosulfate and 8.8% sodium chloride by weight. This solution was used in making up a composition as follows:

- 6.0 parts thioglycerol (0.055 mole)
- 12.4 parts of the above solution (i. e. 4 parts or 0.019 mole sodium glyceryl thiosulfate and 1.1 parts sodium chloride)
- 81.6 parts water and ammonium hydroxide (28% NH_3 by weight) to bring to a pH of 9.3.

The above composition represents a solution, the potential concentration of mercaptan in which is about 0.63 molal, and the potential concentration of thiosulfate in which is about 0.22 molal or 35 molar per cent of the mercaptan concentration. Some solution of this composition was used to saturate two strands of 12 human hairs each, each strand being 100 mm. in length from knot to end and being wound on a curler having a diameter of 6.5 mm. One strand was exposed to the solution for 10 minutes at 100° F. and the other strand was exposed for 16 hours at 80° F. In each case, at the end of exposure, the solution was rinsed from the strand of hair which was then treated with a 1% solution of sodium chlorite to set or fix the curl before it was unwound.

As a basis for comparison the same procedure was carried out on two comparable strands of hair with the use of a 6% solution of thioglycerol at pH 9.3, no organic thiosulfate being present.

The following observations were made in con-

nection with the curls formed in the comparison of this example.

Solution	Diameter of curl in mm. after exposure for—		Coil length of Curl in mm. after exposure for—	
	10 min. at 100° F.	16 hours at 80° F.	10 min. at 100° F.	16 hours at 80° F.
10 Mixture of thioglycerol and glyceryl thiosulfate of this example.....	7.5	16.0	28	129
Thioglycerol alone.....	6.9	2 6.9	32	2 67

¹ Qualitatively the hair of this curl was not perceptibly damaged.

² Qualitatively the hair of this curl was harsh and broke or tore readily when only a slight tension was applied. The greater coil length noted here is also indicative of this greater damage.

Example 2.—A solution of glyceryl thiosulfate was prepared as in Example 1 by heating together in aqueous solution equimolar quantities of glycerin alpha monochlorhydrin and hydrated sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. The resulting solution contained about 33.2% glyceryl thiosulfate and 8.8% sodium chloride. This solution was used in making up a composition as follows.

- 6.1 parts thioglycerol (0.056 mole)
- 50.5 parts of the above solution of glyceryl thiosulfate (i. e. 16.3 parts or 0.077 mole sodium glyceryl thiosulfate and 4.4 parts sodium chloride)
- 43.4 parts water and ammonium hydroxide (28% NH_3) to bring to a pH of 9.3.

The above composition is potentially about 0.77 molal in mercaptan and about 1.06 molal in thiosulfate, the potential thiosulfate therefore being about 138 molar per cent of the potential mercaptan. This solution was used to saturate 3 strands of 12 human hairs each, each strand being 100 mm. in length from knot to end and being wound on a curler having a diameter of 6.5 mm. One strand was exposed to the solution for 30 minutes at 100° F., another strand was exposed for 16 hours at 80° F., and the third strand was exposed for 80 hours at 80° F. In each case, at the end of the exposure the solution was rinsed from the wound strand of hair which was then treated with a 1% solution of sodium chlorite to set or fix the curl.

Each strand of treated hair was removed from its curler and permitted to assume a circular curl without assistance from external forces. The following observations were made on these curls.

Time	Temperature	Diameter of Curl in mm. after Exposure	Length of Coil in mm. after Exposure
30 min.....	100° F.	8.4	37
16 hrs.....	80	7.2	38
80 hrs.....	80	7.0	42

These data show reasonable tightness of the curl and little damage to the hair in the 30 minute period of exposure at 100° F. They also show an improvement in tightness of curl with but very little increase in damage by exposure times of 16 and 80 hours respectively at 80° F. Visual examination of the curls produced by this example indicated no perceptible damage.

As a basis of comparison, it is to be noted that the 6% solution of thioglycerol at pH 9.3 and containing no organic thiosulfate produced a curl of about 6.9 mm. diameter and 67 mm. coil length

after exposure for 16 hours at 80° F. as was shown in Example 1. Qualitatively the curl of hair so formed was harsh and broke or tore readily when only slight tension was applied.

In place of the 50.5 parts of the glyceryl thiosulfate solution in the above example there can be substituted, with substantially the same results, 60 parts of a 30% solution of the hydrobromide of amino ethyl thiosulfate (≈ 0.69 mole). Such a solution can be prepared by reacting bromoethylamine hydrobromide with sodium thiosulfate.

Example 3.—5 parts or 0.064 mole of mercapto ethanol were diluted with 30 parts of water. To this solution were added 23.5 parts or 0.08 mole of sulfoglyceryl thiosulfate in the form of an aqueous solution of about 30% strength. The sulfoglyceryl thiosulfate was prepared by the reaction of sulfoglyceryl chloride with sodium thiosulfate in aqueous solution. The mixture of mercap-
 20 tan and organic thiosulfate was adjusted to an alkalinity of about pH 9.3 and a total weight of 100 parts. This solution was then about 0.90 molar in potential mercaptan and about 1.12 molar in potential thiosulfate, giving a thiosulfate concentration of about 125 molar per cent of the equivalent mercaptan.

This solution was employed to curl strands of human hair as described in preceding examples. A 40 minute exposure at 100° F. resulted in a curl having a diameter of about $9\frac{1}{4}$ mm. A 16
 30 hour exposure at 100° F. resulted in a curl having a diameter of about $8\frac{1}{4}$ mm. and a coil length of 37 mm. The hair appeared undamaged and was soft and normal in feel.

Example 4.—The solution of Example 3 was employed to curl a 12-fiber strand of South American carpet wool, wound on a 6.5 mm. curler, by exposure for 2 hours at 100° F. The curled wool had a diameter of about $7\frac{1}{4}$ mm. and a coil length of 42 mm. The treatment did not appear to damage the wool. It is to be noted that, in the case of wool, greater coil lengths are consistently noted than in the case of hair, due no doubt to the difference in fiber structure rather than to excessive degradation.

In the several examples which follow, alternative procedures for preparing softening solutions of my invention are described. Basically this procedure involves the conversion of the mercap-
 50 tan to the corresponding disulfide by oxidation and the addition of a sulfite or bisulfite to form an equimolar mixture of mercaptan and organic thiosulfate or the addition of a hydro- sulfite to form a greater than equimolar mixture of mercaptan to thiosulfate. Additional quantities of organic thiosulfate or mercaptan may then be added to adjust the molar ratio of potential thiosulfate to potential mercaptan to the desired value or part of the original mercaptan can be retained unoxidized throughout. These are convenient and simple procedures which hold to a minimum the amount of organic thiosulfate that otherwise must be prepared by more intricate and expensive organic reactions.

Example 5.—50 parts by weight of a 10% solution of thiosorbitol at a pH of 9.3 by alkalization with ammonia was oxidized at room temperature with a 30% solution of hydrogen peroxide until the combination of one drop of the mixture on a spot plate with one drop of sodium nitroprusside just failed to produce the typical red mercaptan reaction. The resulting solution containing about 0.013 mol of dithiodisorbitol is mixed with 4 parts or 0.032 mol sodium sulfite and the mixture is ad-
 70

justed to 70 parts total at a pH of 9.3 with added water and acetic acid. This solution, potentially about 0.22 molal in both mercaptan and organic thiosulfate can be employed to wave hair as in previous examples without visual damage thereto.

A mixture of disulfides including a mixed disulfide and resulting from the oxidation of a mixture of mercapto ethanol and thioglycerol can be used in place of the dithiodisorbitol in this example with substantially the same improved result. Also the disulfides resulting from the oxidation of a mixture of the monomercaptans of diethylene glycol and of sorbitol can be employed. In all cases, the mixture of mercaptan and organic thiosulfate resulting from the reaction of the disulfide and reducing agent is surprisingly less damaging to the hair than when the mercaptan is used alone.

Example 6.—7 parts or 0.076 mole of thio- glycolic acid were diluted with 50 parts of water and 5 parts of ammonia water (28% NH_3). To the solution was added a 10% solution of hydrogen peroxide until the combination of one drop of the mixture on a spot plate with one drop of sodium nitroprusside just failed to produce the typical red mercaptan reaction. The mercaptan, ammonium thioglycolate, had then been oxidized to the disulfide, dithiodiglycolate. Heat liberated during this reaction was removed by cooling the reaction vessel with water.

To the resulting solution were added 4 parts or 0.038 mol sodium bisulfite and sufficient water and ammonia water (28% NH_3) to bring the alkalinity to a pH of 9.3 and the total weight of the mixture to 100 parts. The bisulfite reacted with the disulfide (dithiodiglycolate) to form an equimolar mixture of mercaptan (thioglycolate) and organic thiosulfate (carboxy methyl thio- sulfate). Potentially this solution was about 0.44
 40 molal in both mercaptan and thiosulfate.

The above composition was used as in previous examples to saturate two strands of 12 human hairs each wound as in previous examples. One strand was exposed to the solution for 10 minutes at the standard temperature of 100° F. and the resulting curl was 12 mm. in diameter. The second curl was $9\frac{1}{2}$ mm. in diameter and 35 mm. in coil length after exposure for 60 minutes at 100° F. There was no visible damage to the hair in either case.

For comparative purposes, two comparable strands of hair were wound and treated under the same conditions with a commercial hair waving lotion containing about 6% thioglycolic acid as the active ingredient. After rinsing and fixing, the curl formed by 10 minutes' exposure to this solution had a diameter of 7.2 mm. and a coil length of 48 mm. The 60 minute exposure in this case produced a curl of 8.5 mm. diameter and a coil length of 86 mm. Severe damage to the hair was observed in the hair treated by 60 minutes' exposure as indicated by its shriveled appearance, its low strength, and its high tendency to elongate on exposure to humid air.

Example 7.—6 parts or 0.057 mole of thiohy- dracrylic acid were dissolved in 60 parts of water and 5 parts of ammonia water containing 28% NH_3 were added. To the solution thus formed was added a 10% solution of hydrogen peroxide until a combination of one drop of the mixture on a spot plate with one drop of sodium nitroprusside just failed to produce the typical red mercaptan reaction. The solution was cooled during this oxidation step in which the
 75

ammonium thiohydrylate was converted to the corresponding disulfide.

To the resulting solution were added 5.7 parts of a 61% solution of ammonium bisulfite (≈ 0.035 mole) and an amount of water and ammonia water to bring the alkalinity to a pH of 9.3 and the weight to a total of 100 parts. As in examples 5 and 6, the reaction between the sulfite (bisulfite) and disulfide produces mercaptan and organic thiosulfate in equimolar proportion, the total potential concentration of each being equivalent to about 0.32 molal solutions.

The above composition was used to curl strands of human hair according to the technique previously described. One strand exposed for 40 minutes was curled to a diameter of 15 mm. while 16 hours' exposure resulted in a curl diameter of 10 mm. and a coil length of 31 mm. In neither case was the hair perceptibly damaged.

As an auxiliary example mixed disulfides can be employed in place of the disulfides of Examples 5 and 6. Thus the oxidation of a mixture of thioglycolic and thiohydrylate with hydrogen peroxide produces a disulfide mixture which can be reacted with sulfite or bisulfite to yield an equimolar mixture of mercaptan which can be successfully used to give the same improved result as the solutions of these examples.

Example 8.—6.8 parts or 0.057 mole of beta mercapto butyric acid were dissolved in 60 parts of water to which were added 7 parts of ammonia water (28% NH_3). The solution was cooled and oxidized as in Examples 6 and 7, with just sufficient 10% hydrogen peroxide to convert the mercapto acid to the corresponding disulfide.

To the resulting solution were added 6 parts or 0.038 mole of potassium sulfite and sufficient water and acetic acid to bring the pH to 9.8 and the total weight to 100 parts. The resulting composition had an equivalent concentration of both mercaptan and organic thiosulfate of about 0.34 molal.

This composition was used to effect curling of two strands of human hair in accordance with the procedures previously described. The curl formed after 40 minutes' exposure had a diameter of 15 mm. and the curl formed after 16 hours' exposure had a diameter of 13 mm. and a coil length of 43 mm. The hair was soft and unchanged in feel and appearance.

6.8 parts of beta mercapto isobutyric acid were substituted for the beta mercapto butyric acid and 8.9 parts of monoethanol amine sulfite were substituted for the potassium sulfite in the above example. Then using added monoethanolamine as the alkalizing agent in place of ammonia, the following results were obtained at pH 9.3. A 40 minute exposure resulted in a curl having a diameter of 26 mm., and a 16 hour exposure resulted in a curl having a diameter of 14 mm. and a coil length of 43 mm. In neither case was the hair perceptibly damaged. In this case the potential concentration of each of the mercaptan and organic thiosulfate was about 0.36 molal.

Example 9.—6 parts or 0.057 mole of thiolactic acid were diluted with 60 parts of water and 5 parts of ammonia water containing 28% NH_3 . The solution was oxidized as in previous examples with 10% solution of hydrogen peroxide to convert the mercapto acid to the corresponding disulfide.

To the above solution were added 6 parts or 0.058 mole of sodium bisulfite and sufficient water and ammonia water to adjust the alkalinity

to a pH of 9.3 and the weight to a total of 100 parts. The disulfide produced on oxidation of the thiolactic acid was thus reduced to yield mercaptan and the corresponding organic thiosulfate in equimolar amounts, the total potential concentration of each being about 0.33 molal.

This solution was also used as in previous examples to prepare curls from human hair. A 40 minute exposure of the hair to the solution above prepared resulted in a curl having a diameter of 15½ mm. 16 hours' exposure at 80° F. resulted in a curl having a diameter of slightly less than 13 mm. and a coil length of 38 mm. The hair was soft and normal in feel and appearance.

8.4 parts or 0.057 mole of alpha mercapto hexanoic acid diluted with 50 parts of water containing sufficient ammonia to render the solution slightly alkaline were substituted for the thiolactic acid, water, and ammonia water, and 7 parts (or 0.051 mole) of 85% ammonium sulfite for the sodium bisulfite in the above example. Test curls prepared from human hair using this solution yielded the following data: Exposure for 40 minutes resulted in a curl having a diameter of 12.5 mm. and a coil length of 48 mm. Exposure for 16 hours at 80° F. resulted in a diameter of 8.3 mm. and a coil length of 48 mm. In neither case was the hair substantially damaged by this solution which was potentially about 0.34 molal in both mercaptan and organic thiosulfate.

8.7 parts or 0.056 mole of thiosalicylic acid can be substituted for the alpha mercapto hexanoic acid in this example to yield a composition having substantially the same properties.

Even higher molecular weight materials than mercapto hexanoic acid and thiosalicylic acid can be used if they are sufficiently soluble in such hair treating solutions. For example, mercapto carboxylic acids containing 10 carbon atoms are sufficiently soluble in the form of their alkali metal and ammonium salts.

Example 10.—11.4 parts of 74% thioglycolic acid ($\approx$ about 0.092 mole) were dissolved in 150 parts of water to which had been added 5.3 parts of ammonia water containing 28% NH_3 . To the solution was added a 10% solution of hydrogen peroxide as previously described to convert the mercaptan to the corresponding disulfide.

The disulfide thus formed was reduced by the addition of 5.9 parts of 84% ammonia sulfite (≈ 0.043 mole), mercaptan and an equimolar amount of organic thiosulfate being formed. Water and ammonia were then added to bring the pH to about 9.3 and the total weight to 200 parts. The total potential concentration of both mercaptan and organic thiosulfate was equivalent therefore to about a 0.24 molal solution.

A piece of wool flannel was soaked in this solution for 40 minutes at 100° F., then thoroughly rinsed. It was found that the treated cloth was more resistant to shrinkage during laundering than was a sample of the same cloth without the treatment with the above solution.

A strand of 12 fibers of South American carpet wool was wound on a mandrel and exposed to the solution of this invention for 2 hours, then rinsed and fixed as in the case of human hair. A permanent curl was imparted to the wool and no perceptible damage was observed.

Example 11.—A solution was made from 5 parts (0.054 mole) of thioglycolic acid and 50 parts of water. To this solution was added a slight excess of ammonia over that required for

neutralization and just sufficient hydrogen peroxide to oxidize the resulting thioglycolate to the corresponding disulfide. To this solution, now containing 0.027 mole of ammonium dithioglycolate, were added 2.7 parts (0.027 mole) of ammonium bisulfite and 2.5 parts (0.012 mole) of sodium glyceryl thiosulfate. Water and ammonium hydroxide solution containing 28% NH_3 were added to bring the total weight to 100 parts and the pH to 9.3. The resulting solution possessed a total mercaptan forming potential equivalent to about 0.31 molal and a total organic thiosulfate forming capacity equivalent to about 0.44 molal or 142 molar per cent of the potential mercaptan concentration.

This solution was used in making test curls according to the procedure which has been described before. The following observations were made in connection with the curls so formed.

Time	Temperature	Diameter of curl in mm. after exposure	Coil length in mm. after exposure
1 hr.-----	° F. 100	10.8	40
16 hr.-----	80	9.8	35

These curls produced with this solution were soft and, as indicated by the coil lengths and visual observations, no damage was evident even after exposure for 16 hours at 80° F.

Example 12.—The solution of Example 11 was used to soften a strand of 12 human hairs wound on a curler of 6.5 mm. diameter by exposure for 10 minutes to the solution at a temperature substantially above body temperature. The solution was at 194° F. at the time of initial contact, but at the end of the 10 minute exposure period the temperature had dropped to about 130° F. The hair thus softened was rinsed and treated with 1% sodium chlorite as usual. The curl formed had a coil length of 41 mm. and an average diameter of 7.7 mm. From these data and from visual observation it was evident that the solution did not cause undesirable damage to the hair in the heat waving process employed.

Example 13.—6 parts (0.057 mole) of thiohydraacrylic acid were mixed with 50 parts water and 5 parts concentrated ammonium hydroxide containing 28% NH_3 . A 10% solution of hydrogen peroxide was added to this mixture until, as indicated by the nitroprusside test, the oxidation of the mercaptan to the corresponding disulfide was just complete.

To the resulting solution were added 4.2 parts of a 61% solution of ammonium bisulfite (≈ 0.026 mole) and 34.8 parts of a 33.6% solution of disodium carboxy methyl thiosulfate (≈ 0.054 mole). Sufficient ammonia and water to bring the alkalinity to a pH of 9.3 and the total weight to 100 parts were then added.

Any disulfide molecule which reacts with the sulfite thus added forms a molecule of mercaptan and a molecule of organic thiosulfate. Were the reaction to continue until all of the sulfite was used up, the solution would be about 0.34 molal in mercaptan and 1.04 molal in thiosulfate or about 300 molar percent of the potential mercaptan concentration.

This solution was used to saturate strands of hair wound on curlers as in previous examples, a 16 hour exposure at 100° F. resulting in a curl diameter of about $13\frac{1}{4}$ mm. and a coil length of 46 mm. The curled hair was soft and unchanged in feel and appearance.

Example 14.—5 parts or 0.054 mole of thioglycolic acid were dissolved in 50 parts of water containing 5 parts of 28% concentrated ammonia water. To the mixture was added a 10% solution of hydrogen peroxide to convert the mercaptan to the corresponding disulfide, the temperature of the mixture being held below 20° C. during the oxidation. To the resulting mixture were added 4.2 parts of a 61% solution of ammonium bisulfite (≈ 0.026 mole) and 17.4 parts of a 33.6% solution of disodium carboxy methyl thiosulfate (≈ 0.027 mole) (prepared by the reaction of sodium chloracetate and sodium thiosulfate and therefore containing sodium chloride equivalent to the organic thiosulfate). Water and concentrated ammonia were then added to bring the pH to about 9.3 and the total weight to 100 parts.

The potential concentration of mercaptan in the resulting solution was about 0.35 molal, and the total potential concentration of thiosulfate was about 0.70 molal or about 200 molar per cent of the potential mercaptan concentration.

The above solution was used to curl strands of human hair using a 6.5 mm. curler as described in previous examples. A 40 minute exposure at 100° F. resulted in a curl diameter of 17 mm. Exposure for 16 hours at 100° F. resulted in a curl diameter of 11.4 mm. and a coil length of 34 mm. The hair was soft and normal in feel and appearance and not perceptibly damaged.

7.7 parts of mercapto ethyl sulfonic acid can be substituted for the 5 parts of thioglycolic acid in this example to yield a composition having substantially the same properties.

Example 15.—11.4 parts of 71% thioglycolic acid (≈ 0.088 mole) were diluted with 120 parts of water and the solution was made slightly alkaline by the addition of ammonia. The mercaptan was oxidized to the corresponding disulfide with a 10% solution of hydrogen peroxide. To the resulting solution were added 3.6 parts of solid 84% ammonium sulfite (≈ 0.026 mole) and 33.2 parts of a 25% solution of disodium carboxy methyl thiosulfate (≈ 0.038 mole). To the mixture were added water and concentrated ammonia to increase the alkalinity to a pH of about 9.3 and the total weight to 200 parts.

The potential mercaptan concentration in the above solution is about 0.25 molar while the total potential thiosulfate concentration is about 0.47 molal or 188 molar per cent of the potential mercaptan concentration.

A 6-inch square of wool flannel soaked in this solution for 40 minutes at 120° F. and thoroughly rinsed shrank in washing only 14.6% of its area, as compared with an area shrinkage of 41.9% for a portion of the original, untreated wool flannel washed at the same time under the same conditions.

Example 16.—5.1 parts or 0.055 mole of thioglycolic acid were dissolved in 70.0 parts water and the solution was made alkaline by the addition of 12 parts of ammonium hydroxide containing 28% NH_3 . To this solution was added 0.8 part of a 30% solution of hydrogen peroxide, 1.3 parts of thioglycolic acid (≈ 0.014 mole) being oxidized thereby to about 1.3 parts of dithioglycolic acid (as the ammonium salt) (≈ 0.007 mole). Caution was taken to keep the solution cool during oxidation. To the resulting solution were added 5.2 parts of an ammonium bisulfite solution prepared by dissolving 74 parts of SO_2 in 100 parts of concentrated ammonia water containing 28% NH_3 (≈ 0.035 mole ammonium bisul-

five). The mixture was then adjusted to a total weight of 100 parts and to a pH of 9.3 by the addition of water and ammonium hydroxide.

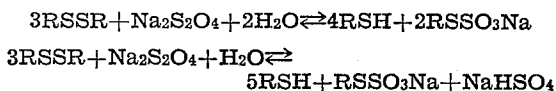
The potential mercaptan concentration of the above solution is about 0.55 molal while the potential organic thiosulfate concentration is about 0.08 molal or about 15 molar per cent of the potential mercaptan concentration.

Test curls of human hair prepared with this solution using a 6.5 mm. curler substantially in accordance with the procedures already described had the following characteristics.

Diameter of curl in mm. after exposure—		Coil length of curl in mm. after exposure—	
10 min. at 100° F.	16 hrs. at 100° F.	10 min. at 100° F.	16 hrs. at 100° F.
7.1	6.8	34	57

As a basis of comparison, similar test curls were made with commercial waving lotion containing ammonium thioglycolate equivalent to about 5% thioglycolic acid and no organic thiosulfate. A curl of human hair produced by 30 minutes contact at 100° F. with this commercial lotion resulted in a coil length of 57 mm. and a strand of hair treated for 16 hours at 100° F. was almost completely destroyed as the damage was so great that the treated hair did not fall into curls for diameter measurement in the usual manner, but gave a coil length of 92 mm. Thus it is seen that the presence of only 15 molar per cent of potential organic thiosulfate based on the potential mercaptan concentration in the above experimental solution greatly reduced hair damage, since such a solution produced a coil length of only 57 mm. instead of 92 mm., after 16 hours exposure at 100° F. Of course, even greater protection against hair damage at 100° F. will result with solutions such as the above if proportions are adjusted to give more potential thiosulfate-forming capacity in the mixture. The monoethanol amide of thioglycolic acid can be used to replace a part of the 0.055 mole of thioglycolic acid in the test solution of this example by substantially the same result.

Example 17.—75 parts of an 8% solution of thioglycerol (≈ 0.055 mole) were first rendered alkaline with ammonia, then carefully oxidized by the addition of a 15% solution of hydrogen peroxide until the mixture just failed to give a positive mercaptan reaction with nitroprusside. The resultant solution, now containing the disulfide, dithiodiglycerol, at a pH of about 9.0, was used to dissolve 6 parts or 0.034 mole of sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$). Several hours after this mixture was prepared, enough ammonia and water were added thereto to increase the weight to 100 parts and the pH to 9.3. The mixture after standing contained thioglycerol and glyceryl thiosulfate in a molar ratio greater than 1:1 as a result of the reaction of disulfide with hydrosulfite which reaction is believed to take place according to one or more of the following mechanisms:



As a result of this reaction, the potential concentration of mercaptan is about 0.43 to 0.54

molal and the potential concentration of organic thiosulfate is about 0.11 to 0.21 molal or between 20 and 50 molar per cent of the potential mercaptan concentration in the above solution.

This solution was used to saturate a strand of 12 human hairs wound in the usual way on a curler of 6.5 mm. diameter. Exposure to this solution for 10 minutes at 100° F., subsequent fixing of the curl, etc. produced a tight curl having a diameter of 7 to 8 mm. The hair was soft and unchanged in feel and appearance.

This solution was also used in waving the hair of a living human being as follows: The hair of the subject was first shampooed, then blocked and divided into strands. Each strand was thoroughly wet with the solution. The wetted strands of hair were then wound on curlers and each curl was then saturated with an additional portion of the solution. The head was then covered with a turban to reduce evaporation to a minimum. After about 25 minutes, the turban was removed and the hair, while held in the desired configuration, was rinsed with water and then treated with a sodium chlorite solution to fix the curl. The hair was then unwound from the curlers, treated again with sodium chlorite solution, set and dried. An excellent permanent wave resulted, the hair being soft and unchanged in feel and appearance.

The solution used in this example was also successfully used to curl South American carpet wool. Strands were curled in 6 hours with considerably less damage than that noted when a mercaptan alone was used under comparable conditions.

In all of the uses of this example, potassium hydrosulfite can be substituted for the sodium hydrosulfite with substantially the same results.

Example 18.—50 parts by weight of a 10% solution of thiosorbitol (≈ 0.025 mole) at a pH of 9.3 by alkalization with ammonia were oxidized at room temperature with a 30% solution of hydrogen peroxide until the nitroprusside test became negative, indicating conversion of the thiosorbitol to dithiodisorbitol. Six parts of ammonia water containing 28% NH_3 and 4 parts or 0.023 mole of sodium hydrosulfite were mixed with the dithiodisorbitol solution and the resulting mixture allowed to stand overnight. The following day the solution was adjusted to a total of 70 parts and to a pH of 9.3 by the addition of water and ammonia. The potential mercaptan concentration of such a solution would be about 0.28 to 0.36 and the potential concentration of organic thiosulfate would be about 0.07 to 0.14 or between 20 and 50 molar per cent of the potential mercaptan concentration according to the probable reaction mechanisms which have been postulated.

When this solution was used to permanently wave strands of human hair in the manner previously described, an exposure time of 30 minutes at 100° F. produced curls of 8.5–9 mm. diameter without perceptible damage to the hair.

Example 19.—A mixture of 3.9 parts or 0.050 mole of mercapto ethanol and 5.4 parts or 0.050 mole of thioglycerol was dissolved in 50 parts of water and made alkaline with $\frac{1}{2}$ part of 28% ammonia water. A 15% solution of hydrogen peroxide was added until the nitroprusside test for mercaptan became negative. Three disulfides were formed in the oxidation, dithiodiglycerol, dithiodiethanol, and hydroxy ethyl glyceryl disulfide. To this solution were added 9.2 parts or 0.053 mole of sodium hydrosulfite, 12.2 parts of 28% ammonia water, and water to a total of

167 parts. The final pH of the solution was 9.3 after standing for several hours.

The potential mercaptan concentration of this solution was about 0.46 to 0.57 molal and the potential organic thiosulfate totaled about 0.11 to 0.23 molal or between 20 and 50 molar per cent of the potential mercaptan concentration.

Tight curls of about 9 mm. diameter were obtained when this solution was used in short exposures at 100° F., in accordance with the procedure already outlined. In overnight exposures to the solution at 80° F., the hair remained soft and was normal in feel and appearance. Coil lengths of 43-47 mm. were observed in contrast to coil lengths of 65-95 obtained under the same conditions of prolonged exposure with the use of a commercial mercaptan waving solution containing ammonium thioglycolate as the mercaptan.

Disulfide mixtures containing dimethyl disulfide, methyl sorbitol disulfide and dithio sorbitol may be prepared by the oxidation of a mixture of methyl mercaptan and thiosorbitol substantially as described in the above example, then reduced with hydrosulfite and similarly used for permanent waving with improved results.

The examples above (5 through 19) include the preparation of the organic disulfide, the method given being one of the most practical and economical possible. In any of the above examples, air, oxygen, iodine and other oxidizing agents known in the art may be used in place of the hydrogen peroxide shown. The organic disulfides can also be prepared from sources other than that shown without impairment of their usefulness in the practice of the invention. In the examples which follow, the disulfides may be obtained from any convenient source.

Example 20.—The following hair softening solution was prepared:

5.0 parts or 0.023 mole dithiodiglycerol
2.9 parts or 0.023 mole sodium sulfite
92.1 parts of water and acetic acid to give pH of 9.6

This solution, potentially about 0.25 molal in both mercaptan and thiosulfate, was used to curl a strand of 12 human hairs (length=100 mm. from knot to end) wound on a curler having a diameter of 6.5 mm. as in preceding examples. After 22 minutes the solution was rinsed from the hair and a 1% solution of sodium chlorite used to set or fix the curl. After removal of the strand from the curler, it was observed that the resulting curl had a diameter of about 9 mm. and that the hair was not perceptibly damaged.

A solution of about this same concentration was made up using ammonium bisulfite in place of sodium sulfite with added ammonia to produce a final pH of 9.3. A test curl exposed to this solution for 10 minutes had a curl diameter of 9.5 mm. and the hair was not perceptibly damaged.

Potassium sulfite can be used as the reducing agent in these solutions with substantially the same result. Moreover the time of exposure of the hair to the softening solution can be extended for 10-15 hours with surprisingly less damage than with similar solutions containing only the mercaptan without the thiosulfate.

Dithio diethanol can be substituted for the dithiodiglycerol in these solutions with substantially the same result also.

Example 21.—The following ingredients were mixed and formed into a solution:

10.7 parts dithiodiglycerol ($\approx$ 0.050 mole)
6.3 parts sodium sulfite ($\approx$ 0.050 mole)
2.9 parts sodium chloride
125.1 parts water

145.0 parts total (pH=about 10.45)

This solution, potentially about 0.40 molal in both mercaptan and thiosulfate, was used to wave a strand of 12 human hairs as in other examples. The spiral coil length after 16 hours contact with this solution at 80° F. was 31 mm. The shortness and springiness of the curl so formed plus visual observation indicated that no perceptible damage had resulted to the hair from this treatment.

Example 22.—A 63% solution of the sulfite of monoethanolamine, $(\text{CH}_2\text{OH}\cdot\text{CH}_2\text{NH}_2)_2\text{SO}_3$, was prepared by dissolving 15.8 parts of sulfur dioxide in a mixture of 30.2 parts ethanolamine and 33.9 parts water.

The following ingredients were then mixed and formed into a uniform solution:

6.4 parts dithiodiglycerol ($\approx$ 0.030 mole)
11.1 parts 63% solution of monoethanolamine sulfite ($\approx$ 0.034 mole)
1.1 parts monoethanolamine
81.4 parts water

100.0 parts total (pH=about 9.3)

This solution, potentially about 0.35 molal in both mercaptan and thiosulfate, was used in making test curls in the usual manner, using a curler of 6.5 mm. diameter. Exposure to this solution for 10 minutes at 100° F. resulted in a test curl diameter of about 9.5 mm. and the hair was not perceptibly damaged by such treatment.

Example 23.—A solution was made using the following ingredients:

5.0 parts dithiodiethanol ($\approx$ 0.032 mole)
6.0 parts sodium hydrosulfite ($\approx$ 0.345 mole)
8.6 parts ammonium hydroxide containing 28% NH_3
80.4 parts water

100.0 parts total (pH=about 9.5 after standing for several hours).

This solution is estimated to have a potential mercaptan concentration of 0.49 to 0.62 molal and a potential concentration of organic thiosulfate of 0.12 to 0.25 molal, or about 20 to 50 molar per cent of the potential mercaptan concentration.

Tests curls of human hair were formed using the above solution in the usual manner. The following measurements were made on these test curls.

	Coil length in mm. after treatment
For 10 min. at 100° F.	30
For 16 hours at 80° F.	31
For 16 hours at 100° F.	39

From these data it will be observed that the spiral coil waved by even prolonged exposure to the solution of the present invention was surprisingly short and springy, indicating very little hair damage under these conditions. These results confirmed visual observations on the waved strands.

Example 24.—The following solution was pre-

pared and used to wave a strand of 12 human hairs as in past examples:

3.0 parts dithiodipropanol (≈ 0.0165 mole)
6.0 parts sodium hydrosulfite (≈ 0.0345 mole)
8.6 parts ammonium hydroxide containing 28% NH_3
82.4 parts water

100.0 parts total (pH $\approx$ about 9.5 after standing for several hours).

A tight curl was obtained on exposure to the above solution for 10 minutes at 100° F. without perceptible damage to the hair. The potential mercaptan concentration of this solution is estimated at 0.25 to 0.31 molal and the potential concentration of organic thiosulfate at 0.06 to 0.12 molal.

Example 25.—The following solution was prepared.

5.0 parts dithiodiglycerol (≈ 0.023 mole)
1.0 part thioglycerol (≈ 0.009 mole)
5.0 parts sodium hydrosulfite (≈ 0.028 mole)
7.1 parts ammonia water (28% NH_3)
81.9 parts water

100.0 parts total (pH $\approx$ about 9.4)

The potential mercaptan concentration of the above solution is estimated at 0.44 to 0.53 molal and the potential concentration of the organic thiosulfate at 0.09 to 0.17 molal or about 17 to 40 molar per cent of the potential mercaptan concentration.

After the above solution was allowed to stand for several hours, it was used in preparing test curls in accordance with the standard procedure. The following results were obtained.

Solution	Diameter of curl in mm. after exposure—		Coil length of curl in mm. after exposure—	
	10 min. at 100° F.	16 hrs. at 100° F.	10 min. at 100° F.	16 hrs. at 100° F.
Solution of this example...	7.0	6.5	33	42

Here again even prolonged exposure is seen to result in only slightly greater damage, as evidenced by somewhat greater coil length. In both cases the hair appeared to be substantially unchanged in quality and strength.

In a series of cold permanent waves conducted on living human hair substantially in accordance with the procedure of Example 18 but employing the composition of my invention prepared according to the procedure described above in this example, excellent results were obtained without perceptible damage to the hair in exposure times varying from 10 to 70 minutes depending upon the texture of the hair being waved.

Example 26.—6 parts or 0.028 mole of dithiodiglycerol were dissolved in 40 parts of water containing 10 parts of concentrated ammonium hydroxide (28% NH_3). To the solution were added 4 parts or 0.023 mole of solid sodium hydrosulfite. The mixture was allowed to stand overnight during which time the hydrosulfite reacted with the dithiodiglycerol yielding an equilibrium mixture containing some of the corresponding mercaptan and organic thiosulfate. To this mixture were added 41.8 parts of an aqueous solution containing 31.4% sodium glyceryl thiosulfate

≈ 0.0625 mole

To the resulting mixture were added sufficient water and ammonia to bring the pH to 9.3 and the total weight to 100 parts. Based upon the hypothesized reactions between hydrosulfite and disulfide previously given, the resulting solution is estimated to contain a potential mercaptan concentration of about 0.51 to 0.64 molal and a potential concentration of organic thiosulfate of 0.99 to 1.11 molal or about 150 to 220 molar per cent of the potential mercaptan concentration.

This solution was used to form test curls according to the standard procedure already outlined. The curl resulting from 40 minutes' exposure at 100° F. had a diameter of about 11.8 mm. The curl exposed for about 16 hours had a diameter of about 8 mm. and a coil length of 37 mm. These data indicate that exposure for the extended period of 16 hours at 100° F. resulted in a tight curl but did not result in objectionable hair damage, as indicated by the short coil length. Visual examination of the curled hair likewise failed to reveal perceptible damage. Contrast this with the action of 6% thioglycerol solution containing no thiosulfate. Under comparable conditions a test curl formed by 16 hours' exposure to this solution at 100° F. had a coil length of 65 mm.

Example 27.—The solution of Example 26 was employed to curl a 12-fiber strand of South American carpet wool by two hours' exposure at 100° F. The curled wool had a curl diameter of 8¼ mm. and a coil length of 55 mm. As previously pointed out, the coil lengths in the case of wool are consistently appreciably greater than in the case of human hair, even when no perceptible damage is done. The wool in this case appeared unharmed by the above treatment.

Example 28.—In accordance with my invention the following solution was prepared:

4.5 parts thioglycerol (≈ 0.042 mole)
1.5 parts dithiodiglycerol (≈ 0.007 mole)
5.2 parts ammonium bisulfite solution containing 66% NH_4HSO_3 (≈ 0.034 mole)
88.8 parts water and ammonia water (28% NH_3) to pH 9.3

The potential mercaptan concentration of this solution is about 0.55 molal and the potential concentration of organic thiosulfate is about 0.08 molal or about 15 molar per cent of the potential mercaptan concentration.

Test curls prepared with the aid of this solution in accordance with the standard procedure were soft, appeared undamaged, and had the following characteristics in contrast to those test curls produced by 6% thioglycerol alone.

Solution	Diameter of curl in mm. after exposure for—		Coil length of curl in mm. after exposure for—	
	10 min. at 100° F.	16 hrs. at 80° F.	10 min. at 100° F.	16 hrs. at 80° F.
Solution of this example.	6.8	6.8	27	33
6% thioglycerol (alone)...	6.9	6.9	32	67

In a series of cold permanent waves conducted on living human hair substantially in accordance with the procedure of Example 17 but employing the composition of my invention as prepared in this example, excellent results were obtained

without perceptible damage to the hair in exposure times varying from 13 to 25 minutes depending upon the texture of the hair being waved.

Example 29.—The following solution was prepared:

- 2.0 parts dithiodiglycerol (0.009 mole)
- 4.2 parts 95% thioglycerol (0.037 mole)
- 11.1 parts of a 63% solution of monoethanolamine sulfite prepared by dissolving 15.8 parts of SO_2 in a mixture of 30.2 parts of monoethanolamine and 33.9 parts water (≈ 0.034 mole $(\text{CH}_2\text{OH} \cdot \text{CH}_2\text{NH}_2)_2\text{SO}_3$)
- 1.3 parts monoethanolamine
- 81.4 parts water

100.0 parts total (ph $\approx$ about 9.3)

The potential mercaptan concentration of this solution is about 0.54 molal and the potential concentration of organic thiosulfate is equivalent to about 0.11 molal or about 20 molar per cent of the potential mercaptan concentration.

A test curl exposed 10 minutes at 100° F. had a diameter of 7.5 mm. The hair was soft and unchanged in feel and appearance.

Instead of those reducing agents and disulfides and/or the equivalent mercaptans and/or thiosulfates used in the above examples, other similar compounds can be substituted as is apparent from the description which preceded these examples.

Having thus described my invention, what I claim and desire to secure by Letters Patent is:

1. A new composition comprising an aqueous solution at pH 7 to 10.5 of the equilibrium reaction mixture of (a) water-soluble mercaptan of the general formula RSH and (b) water-soluble salt of thiosulfuric acid of the general formula $\text{R}'\text{SSO}_3\text{H}$ wherein each of the symbols, R and R', represents a monovalent organic radical which is free of the concomitant presence of a carboxyl group and an amino group, and in which the free valence is on an aliphatic carbon atom, the total potential concentration of mercaptan in said solution being between 0.05 and 2.0 molal.

2. A new composition comprising an aqueous solution at pH 7 to pH 10.5 of the equilibrium reaction mixture of (a) organic disulfide of the general formula RSSR' wherein each of the symbols, R and R', represents a monovalent organic radical which is free of the concomitant presence of a carboxyl group and an amino group, and in which the free valence is on an aliphatic carbon atom, and (b) water-soluble sulfite salt, the concentrations of (a) and (b) being such that the molal concentration of mercaptan potentially producible in such a solution by their complete reaction is between 0.05 and 2.0.

3. A composition for the treatment of keratin-containing fibers, comprising in aqueous ammoniacal solution at pH 9.0 to 9.5 a mixture of compounds occurring on reaction of the disulfide of thioglycolic acid, in the form of the ammonium salt, with ammonium sulfite, the concentration of the solution expressed as disulfide equivalent, being not substantially less than one per cent by weight, and the molar ratio of sulfite to disulfide being not substantially less than $\frac{1}{2}$ mole and not substantially more than 10 moles sulfite per mole disulfide.

4. A composition for treating keratin-containing substances comprising an aqueous solution at pH 7 to pH 10.5 of (a) sulfite salt, (b) organic disulfide of the general formula RSSR' , and (c)

an added amount of water-soluble material chosen from the group consisting of mercaptan of the general formula $\text{R}'\text{SH}$, salt of thiosulfuric acid of the general formula $\text{R}''\text{SSO}_3\text{H}$, and mixtures thereof wherein each of the symbols—R, R', R'' and R'''—represents a monovalent organic radical which is free of the concomitant presence of a carboxyl group and an amino group, and in which the free valence is on an aliphatic carbon atom, the total potential mercaptan concentration being between 0.05 and 2.0 molal.

5. A composition as in claim 4 wherein the radicals represented by R, R', R'', and R''' are, in part at least, organic radicals containing at least one alcoholic hydroxyl group.

6. A composition as in claim 4 wherein the radicals represented by R, R', R'', and R''' are, in part at least, organic radicals containing at least one sulfonate group.

7. A composition as in claim 4 wherein the radicals represented by R, R', R'', and R''' are, in part at least, organic radicals containing at least one carboxyl group.

8. A composition as in claim 4 wherein the radicals represented by R, R', R'', and R''' are, in part at least, organic radicals containing at least one amide group.

9. A composition as in claim 4 wherein the radicals represented by R, R', R'', and R''' are, in part at least, organic radicals containing at least one ether group and at least one alcoholic hydroxyl group.

10. A composition for permanently changing the configuration of keratin-containing substances consisting essentially of an aqueous ammoniacal solution at pH 9.0 to pH 9.5 of ammonium thioglycolate and in addition thereto the compounds occurring on reaction of water-soluble dithiodiglycolate with water-soluble sulfite to substantial equilibrium.

11. A composition for permanently changing the configuration of keratin-containing substances comprising in aqueous ammoniacal solution at pH 9.0 to pH 9.5 ammonium thioglycolate and water-soluble salt of carboxymethyl thiosulfuric acids, the molar ratio of the thiosulfuric acid salt to thioglycolate being greater than 1:1.

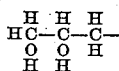
12. A composition for permanently waving hair without substantial damage thereto comprising in aqueous solution at pH 9.0 to 9.5 substituted alkyl mercaptan and organic thiosulfate each chosen from the group consisting of (a) soluble carboxylic acid derivatives containing only the elements C, H, O, and S, (b) soluble amides of said derivatives, and (c) mixtures thereof, the total potential concentration of the mercaptan being between about 0.10 molal and about 1.5 molal and the molar ratio of thiosulfate to mercaptan being at least 1/10.

13. A composition for permanently waving hair without substantial damage thereto comprising in aqueous solution at pH 9.0 to 9.5 mercaptan of the general formula RSH and salt of thiosulfuric acid of the general formula $\text{R}'\text{SSO}_3\text{H}$ wherein R and R' each represents an organic radical which is free of the concomitant presence of both a carboxyl group and an amino group, and in which the free valence is on an aliphatic carbon atom, the total potential concentration of mercaptan being between $\frac{1}{2}$ and 15% by weight and the molar ratio of thiosulfate to mercaptan being at least 1/20.

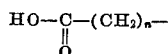
14. A composition as in claim 13 in which R

27

and R' are both thioglycerol residues having the chemical structure,



15. A composition as in claim 13 in which R and R' are both residues of primary mercapto carboxylic acids containing two to three carbon atoms, the general chemical structure of said residues being



where n is a whole integer from 1 to 2.

16. A composition for treating keratin comprising in aqueous solution at pH 7 to pH 10.5, a mixture of compounds occurring on reaction of (a) water-soluble organic disulfide of the general formula RSSR' wherein each of the symbols, R and R', represents a monovalent organic radical which is free of the concomitant presence of a carboxyl group and an amino group, and in which the free valence is on an aliphatic carbon atom, and (b) a water-soluble reducing agent chosen from the group consisting of water-soluble normal sulfites, bisulfites, hydrosulfites, and mixtures thereof, the concentrations of (a) and (b) being such that the concentration of mercaptan potentially producible in such a solution by their complete reaction is between about 0.10 and about 1.5 molal.

JOHN W. HAEFELE.

REFERENCES CITED

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

28

UNITED STATES PATENTS

Number	Name	Date
2,180,262	Sturm	Nov. 14, 1939
2,238,672	Arthur	Apr. 15, 1941
2,389,755	Baker	Nov. 27, 1945
2,418,664	Ramsey	Apr. 8, 1947
2,479,382	Mace	Aug. 16, 1949

FOREIGN PATENTS

Number	Country	Date
117,071	Australia	June 3, 1943
453,700	Great Britain	Sept. 10, 1936

OTHER REFERENCES

- 15 Michaelis—"A Study of Keratin," Journal of the American Leather Chemists Association, November 1935, volume XXX, number 11, pages 557 to 568, especially page 562.
- 20 Schoberl and Krume—"Unterschiede in der Reaktionsfähigkeit von Sulfhydryl- und Disulfidgruppen in organischen Verbindungen," Berichte, volume 71B (1938), pages 2361 to 2371.
- 25 Footner et al.—"Reactions of Organic Thio-sulphates," Chemical Soc. Journal, volume 127, July to December 1925, pages 2887 to 2891.
- Mirsky and Anson—"Sulfhydryl and Disulfide Groups of Proteins," Journal Genl. Physiol., 1934 to 1935, volume 18, pages 307 to 323, especially pages 317 and 318.