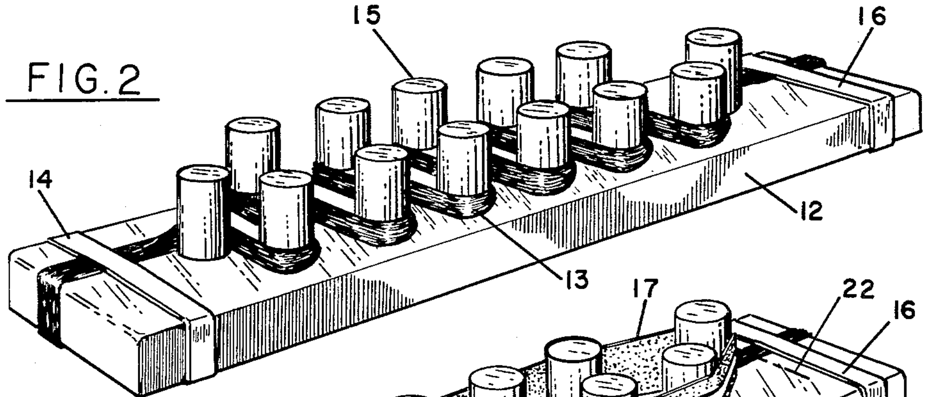
May 27, 1958 L. R. B. HERVEY 2,836,185

PROCESS OF PERMANENTLY SETTING HAIR WITH A HAIR-SWELLING SOLUTION OF A BISULFITE AND A NITROGEN-CONTAINING COMPONENT

Filed May 27, 1954 3 Sheets-Sheet 1

FIG. 1

FIG. 2



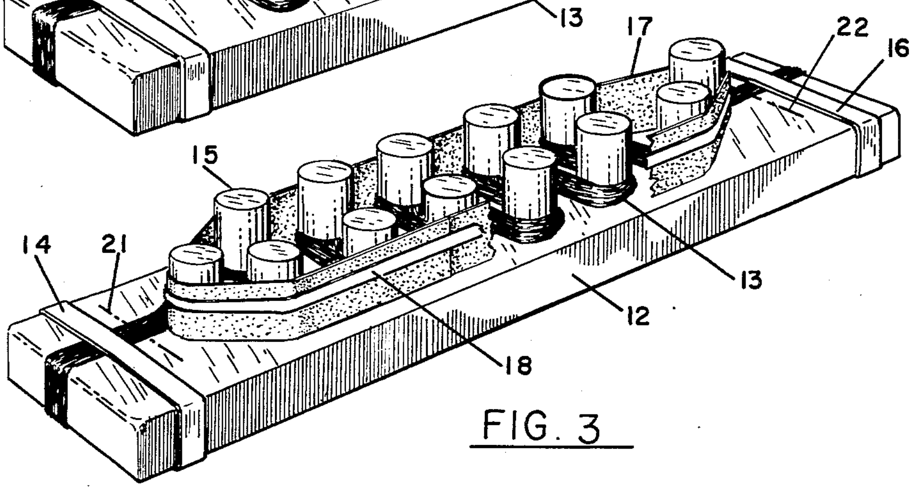


FIG. 3

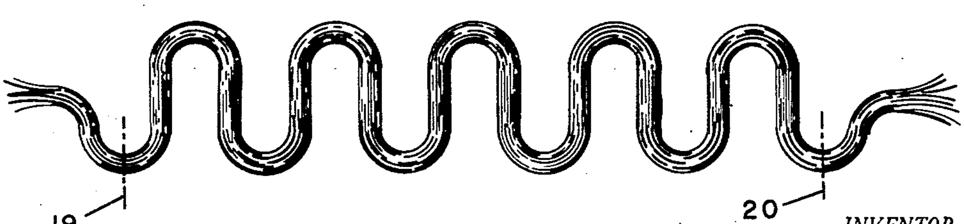


FIG. 4

INVENTOR.
LAURENCE R.B. HERVEY
BY
ATTORNEY

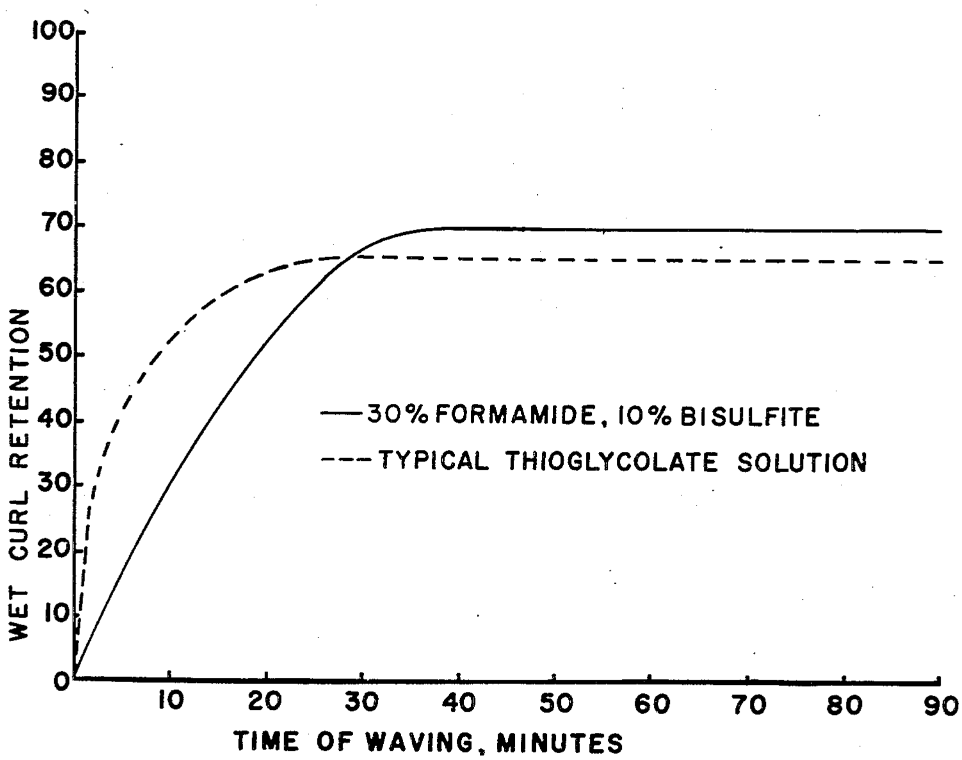


FIG. 5

INVENTOR.
LAURENCE R.B. HERVEY
BY Alfred [signature]
ATTORNEY

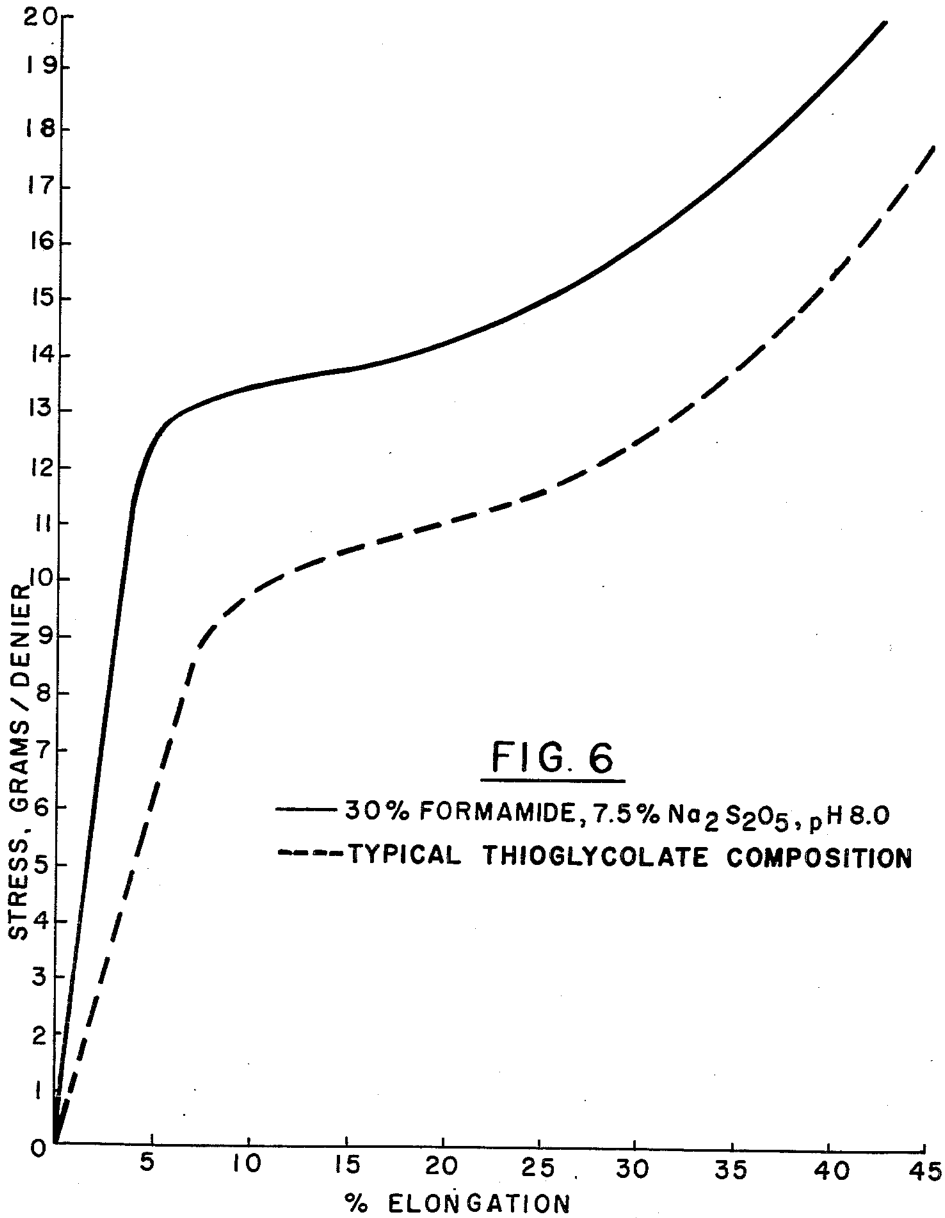


FIG. 6

INVENTOR.
LAURENCE R.B. HERVEY
BY

ATTORNEY

United States Patent Office

2,836,185

Patented May 27, 1958

2,836,185

PROCESS OF PERMANENTLY SETTING HAIR WITH A HAIR-SWELLING SOLUTION OF A BISULFITE AND A NITROGEN-CONTAINING COMPONENT

Laurence R. B. Hervey, West Concord, Mass., assignor to Arthur D. Little, Inc., Cambridge, Mass., a corporation of Massachusetts

Application May 27, 1954, Serial No. 432,765

4 Claims. (Cl. 132—7)

This invention relates to the treatment of hair, and more particularly to the treatment of hair to cause it to conform to a predetermined configuration, which configuration will return upon drying after repeated wetting with water. The application is a continuation-in-part of Serial No. 171,570, filed June 30, 1950, now abandoned, in the name of Laurence R. B. Hervey.

So-called "cold waving" of hair has been practiced for several years with considerable consumer acceptance. The basis of all of the successful cold waving formulations to date is the incorporation of a thioglycolate therein. Considerable speculation and research work has been directed to the determination of the action of this compound, but it is believed that the precise mechanism has not been finally determined. The process employed for waving hair consists, generally, in applying the treating agent to the hair, wrapping the hair in curlers, allowing the treatment to continue for the desired length of time (usually less than one hour), removing the treating agent by destroying it, as by oxidation, or by washing it out with water, and drying the hair.

Many careful studies have shown that thioglycolic acid and ammonium thioglycolate tend to damage hair and skin by prolonged or repeated treatment. This damage is more pronounced on hair which has been bleached or dyed. The odor of thiols in general is objectionable, and thioglycolic acid and ammonium thioglycolate are no exception. The disagreeable odors of the thioglycolates has made it undesirable and impractical to make a hair preparation which could be applied to wave, straighten, or train hair without curlers and which could be applied and left on the hair over a period of time. The lack of odor of the preparation in this invention, on the other hand, permits it to be so applied and retained on the hair over a period of time. Thus, in summary, the cold wave preparations available until now have the disadvantage of the possibility of hair damage, disagreeable odor, and incapability of being used as a hair treatment to be left on the hair for a period of time.

Soluble sulfites, including sodium bisulfite, have been employed as hair treating agents, but their action is so slow at room temperature as to preclude their use as the cold waving agent.

Other agents and combinations of agents have been employed for waving hair at room temperature, but they are either too severe in their action, or have other disadvantages such as unpleasant odor. It is known that ammonium sulfide and thioglycerol wave hair well, but they are toxic.

It is to be understood that the term "hair treating", as hereinafter used, includes curling or waving, straightening, training and any other treatments which give the hair desired configurations.

It is an object of this invention to prepare a hair treating composition which can be effectively employed at room temperatures.

Another object is to prepare a hair treating composition which is substantially odorless.

Still another object is to prepare a hair treating composition which damages hair less than those now in use.

A further object is to prepare a hair treating composition which exhibits less "wash-out", i. e., retains the curl over a larger number of washings.

Another object is to prepare a solution which readily swells hair at room temperature thereby rendering the hair amenable to permanently setting it in a predetermined configuration. These, and other objects, will become apparent hereinafter.

Hair is composed of keratin, and keratin is largely made up of relatively long chain polyamides cross linked by disulfide linkages. In the waving of straight hair, or the straightening of curled hair, it is necessary first to break the disulfide linkages and then to swell the thus modified fiber. I have found that a soluble bisulfite such as an alkali metal bisulfite, is particularly useful for this purpose. Sodium bisulfite and sodium metabisulfite, $Na_2S_2O_5$ (which hydrolyzes in the presence of water to yield $NaHSO_3$) have been found to be particularly effective.

As in any setting operation, the swelled and chemically reduced fiber is placed in the predetermined position desired, and the reducing agent is neutralized with an oxidizing agent, such as potassium bromate; the resulting product and the swelling agent are removed by washing with water. The fiber so set, permanently assumes the altered shape and remains thus fixed indefinitely.

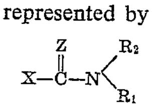
In accordance with this invention, I provide a composition comprising a mixture of a water-soluble sulfite, as the agent for breaking the disulfide linkages, and as the swelling agent a water-soluble nitrogen-containing compound of the amide or imide class of the proper concentrations and the proper pH and a method of applying the composition to the hair. This serves as an excellent hair treating formulation in that it permits training hair or setting it to a desired configuration without the use of solutions having undesirable odors or harmful effects on the hair.

The sulfite introduced into the mixture may be most conveniently a bisulfite, such as sodium bisulfite, sodium metabisulfite (which hydrolyzes in the presence of water to yield sodium bisulfite), potassium bisulfite, ammonium bisulfite, or an amine bisulfite, such as normal propyl amine bisulfite.

The amide or imide must be water-soluble to the extent that at least about 15 percent of the weight thereof required in the composition of this invention is soluble in the water content of the composition.

Among the amides and imides which are suitable nitrogen-containing components are the mono-, di- and tri-ammonia substituted analogs of formic acid, their esters, and their alkyl and alkanol substituted derivatives. These analogs are those derived by displacing one or more of the three substituents on the carbon atom of formic acid with ammonia. The ester group may be attached through the hydroxyl group of the formic acid molecule. The alkyl and alkanol substituents are desirably substituted in place of the hydrogen atom of formic acid, although they may be substituted on the ammonia substituents. The alkyl and alkanol substituents should not exceed four carbon atoms when taken together. In the case of guanidine, which is the tri-ammonia analog of formic acid, it is preferable that there be no further substituents on the compound.

Some of the particularly effective nitrogen-containing components for the purpose of the present invention may be defined as those represented by the formula



wherein X is a member of the group consisting of hydrogen, alkyl and alkanol radicals containing not more than three carbon atoms, the radical

$$-(CH_2)_n-\overset{O}{\overset{\|}{C}}-NH_2$$

wherein n is the integer one or two, $-NR_3R_4$, and $-OR$, wherein R is an alkyl radical containing not more than three carbon atoms. The groups R_1, R_2, R_3 and R_4 are members of the class consisting of hydrogen, alkyl and alkanol radicals which when taken together shall contain not more than four carbon atoms. Z is either oxygen or =NH, but preferably oxygen. Examples of such effective nitrogen-containing compounds are acetamide, ethanol formamide, diethanol formamide, monoisopropanol formamide, ethyl formamide, formamide, dimethyl formamide, N-mono-ethyl acetamide, n-propionamide, n-butyramide, urethane, guanidine, ethanol urea, methyl urea, urea, and the amides and imides of dibasic acids containing not more than five carbon atoms, such as succinimide and malonamide.

The preferred nitrogen-containing components include formamide, $HCONH_2$: urea, H_2NCONH_2; urethane, $C_2H_5OCONH_2$; and acetamide, CH_3CONH_2, and will hereinafter be referred to as the amide component.

The pH of the mixture is important, and the effective pH range is between 6 and 9, while the preferred range is between 6 and 7. If the pH exceeds about 7.5 or 8, the wet curl retention drops materially, and if it is above 9, the action of alkali becomes harmful.

The concentration of both sulfite and amide is also important. The most effective range for sulfite, based on the SO_2 content by weight, is from 2.0 percent to 10 percent of the total composition, while the preferred range is from 3.0 percent to 6.0 percent. The most effective range of the amide is from 15 percent to 40 percent, and the preferred range from 20 percent to 35 percent, although about 30 percent has been found to be the optimum concentration.

The concentrations of the sulfite and amides are, however, directly dependent upon each other, thus making it inadvisable to choose concentrations from each of the ranges stated without giving consideration to the over-all concentration of the solution. Thus, if high concentrations of amide are used along with the higher limits of sulfite, an exceptionally effective hair setting or treating solution is formed, but the amide might salt out and crystallize on the hair. Thus, the combined solubility of these components at room temperature (or slightly below) becomes an important factor in the determination of concentrations, for it is undesirable that there be any solids present at normal room temperatures in a hair treating solution. Generally, as the amide concentration is increased, the sulfite concentration must be decreased. Using urea and sodium metabisulfite ($Na_2S_2O_5$) as an example, it has been found that the concentrations listed below are the most effective at 25° C. and at a pH of 6.8.

Percent by weight of Urea	Percent by weight $Na_2S_2O_5$	SO_2 Equivalent weight [1]
20	15	10.1
30	6 to 12.5	4 to 8.4
40	3 to 9	2 to 6.1

[1] 67.3 percent of $Na_2S_2O_5$ weight.

Amide concentrations above 40 percent by weight have been found to have a deleterious effect on the hair, causing excessive swelling of the keratin of the hair. In fact, above about 40 percent amide concentrations, the damage to hair is so severe that hair waving compositions should be limited to concentrations below that figure.

The amide may be premixed with the sulfite and dispensed as a ready-made solution; concentrated solutions may be made up separately of the amide and sulfite and then mixed and diluted when used; or the two components may be packaged separately as solids and then put into solution previous to use. However, in the case of formamide, it is preferable to mix fresh solutions of formamide and sulfite just before application.

The temperature at which these solutions are used is limited usually to a range between room temperature, or slightly lower, and body temperature. This means a temperature range of about 20° to 30° C. Temperatures above body temperatures may conceivably be used up to a comfortable maximum, perhaps as high as 37–40° C. As the temperature increases, the effectiveness of the solution increases. At the higher concentrations, the rate of increase in effectiveness is even more marked at higher temperatures. The time of exposure of the hair to the solution depends upon the temperature used, the effectiveness of the particular solution and the degree of permanence of the final hair configuration desired. Normal exposures are of the order of 30 to 90 minutes.

It is desirable to stop the action of the treating solution by the use of a "neutralizer." Such a neutralizer should be capable of removing the sulfite ion and must not, of course, be harmful to the hair or skin. Examples of neutralizers include water or a mild oxidizing agent, such as a dilute solution of perborate, or alkaline bromate.

Experimental work has shown that the degree of curl retained permanently depends upon the amount of swelling imparted to the hair while wrapped on curlers and the degree to which the shrinkage of the hair is subjected by the oxidizing agent and subsequent removal of the compounds by washing. Unless the hair is swelled at least 18% adequate permanent set cannot be obtained by the process of this invention. Swelling action far in excess of 18% may be readily secured. Hair varies in thickness and in chemical composition so that hair from different sources will swell to varying extents with a given treatment under identical conditions. The concentration of soluble bisulfite required to break the disulfied linkages and the concentration of the swelling agent required to impart a desired degree of swelling of hair also depends upon the quantity employed. In general, the swelling action increases with increasing concentration and as the pH of the mixture approaches 7.0. Under usual conditions encountered in hair waving sufficient swelling is obtained with 5% sodium bisulfite and 1% sodium bisulfite may be employed in some instances. The concentration of swelling agent must be sufficient to cause at least 18% swelling within one hour under the usual conditions, as stated above, but swelling in the order of 30% to 80% within one hour at room temperature is preferable for the usual treatment. Swelling of hair in excess of 80%, and particularly in excess of about 110%, requires care in its management since the hair becomes so greatly weakened that it may break if handled improperly.

The measure of the effectiveness of a hair waving solution is the degree to which the curl is retained after treatment. Thus, the minimum concentrations of amide and bisulfite are dictated by an acceptable degree of curl retention. Such minimum concentrations are about 15 percent amide by weight and about 3.4 percent SO_2 equivalent by weight. Below these concentrations, curl retention is very low.

Because curl retention is the important factor in making a desirable cold wave solution, I have devised means for accurately measuring this property. The means are shown in Figures 1–4.

Figure 1 is a bundle of about 50 parallel strands of straight hair to be tested. Figure 2 is a prespective view of a device for curling hair; Figure 3 is the same view wherein the device is surrounded by a wetted web; Figure 4 is a view of a typical flat curled swatch of hair, and Figure 5 is a graph showing the relative effectiveness (in terms of wet curl retention achieved against time of treatment) of an ordinary thioglycolate mixture, and a typical amide-sulfite mixture. Figure 6 illustrates the marked decrease in hair damage achieved by the sulfite amide solution as compared with a typical thioglycolate solution.

A bundle of about 50 parallel strands of individual hairs, Figure 1 is processed at a time. The bundle is combed so that the strands are parallel.

Referring now to Figure 2, one end of the bundle **13** is bent over the end of waving-form **12** and attached as by an elastic band **14**. The bundle is then bent around pegs **15**, as shown, bent over the other end of waving form **12**, and secured as with elastic band **16**. After the hairs have been arranged on waving form **12**, a narrow strip of blotting paper **17**, as shown in Figure 3, is wound around the pegs and held in place by an elastic band **18**.

The blotting paper **17**, is saturated with waving lotion, thus wetting the bands of hair and keeping them wet over the desired treating period. The whole form with the hair is then left at a fixed temperature for the time desired. After exposure to the waving solution for a specific length of time, the wave formed is immersed in water or in a neutralizer which may be a mild oxidizing compound, the straight ends of hair are cut at positions **21** and **22** on wave form **12**, Figure 2, and the entire bundle of hair springs is floated on water.

A value for what is termed "wet curl retention" is determined immediately after the hair is placed in the water and again after a specified length of time (generally thirty minutes). The bundle of hair is measured to obtain the length of the bundle of springs, usually the distance between the centers of the first and last, or next to the last, crests; for example, between the peak of crests **19** and **20**, Figure 4. This distance is compared with distance between the centers of the corresponding pegs of the waving form and the result is called the "wet curl retention." This is calculated by the formula:

$$100 \times \frac{(L-l)-(L'-l)}{(L-l)}$$

where

L=drawn-out length of a strand of hair used to span the distance from the center of the two pegs selected on the waving form.

L'=length of hair springs after curling measured from the center of the two crests corresponding to the centers of the two pegs selected on the waving form; and

l=distance between the centers of the two pegs chosen on the waving form.

Wet curl retention is taken as the true measure of the effectiveness of the waving solution, inasmuch as many substances, including water, will impart a curl which will be retained as long as the hair remains dry. Figure 5 illustrates the effectiveness to be expected from typical thioglycolic solutions and the amide-sulfite solutions. It is seen that the amide-sulfite solutions have an over-all effectiveness equal to or better than the thioglycolic solutions at or after 30 minutes waving time. Since thirty minutes is a normal waving period, it may be said that the amide sulfite solution is equivalent in treating effectiveness to the thioglycolate solution. In addition, actual panel testing has shown that hair waved with the amide-sulfite solutions achieved a desirable wave which will last longer.

Figure 6 illustrates the achievement of less damage to the hair by use of a typical composition of this invention. In Figure 6 percent elongation is plotted against stress which was applied to a hair strand after subjection to the hair treating solution for 30 minutes and subsequent neutralization. For example, at approximately the inflection point, about 7.5 percent elongation, around 13.6 grams/denier are required for hair waved with the formamide-sulfite composition while only 9.3 grams/denier are required for hair waved with a typical thioglycolate solution. The added stress required is a measure of hair strength and this a measure of decreased hair damage. Thus, the formamide-sulfite composition of this invention shows a decrease in hair damage of about 47 percent over the commonly used thioglycolate composition.

This decreased hair damage shown by the sulfite-amide composition is unexpected since it is known that with such compositions containing in excess of 40 percent amide, the protein in hair can be dissolved and destroyed. Thus, by the dilution of the composition to the ranges used in these hair treating compositions the possibility of hair damage is reduced to below the now acceptable limits of the compositions currently in use. The reasons for this practical elimination of hair damage brought about through dilution are not known, but are clearly illustrated in Figure 6.

The following examples are illustrative of the type of cold waving solutions which have been found to achieve the objects of this invention. This invention is not, however, limited by these examples.

Example I

A solution of 20 percent urea and 7.5 percent sodium bisulfite by weight was made up in water and strands of hair subjected for one hour to this solution by means of the waving form device described. Temperature was maintained at 25° C. Maximum wet curl retention, obtained at pH 6.5 (adjusted with NaOH), was 61 percent compared with 65 percent for a typical thioglycolate solution. In each case, the hair was allowed to remain in water at 25° C. for one half hour.

Example II

A cold wave solution, containing 20 percent by weight of urea, was made up with weight percents of sodium sulfite varying from 3 to 15 percent (2.0–10.1 percent SO_2). The solutions were maintained at a pH of 6.5 (adjusted with NaOH) and hair strands were subjected to them for one hour at 25° C. Neutralizing was accomplished by permitting the strands to remain in water at 25° C. for 30 minutes. Maximum wet curl retention was achieved with a sodium sulfite concentration of from 10 to 15 percent by weight (6.75 to 10.1 percent SO_2) and was 79 percent compared with 65 percent for a typical thioglycolate solution.

Example III

A cold wave solution was made up and tested as in Example II, using 30 percent by weight of urea and varying weight percents of sodium sulfite. Maximum wet curl retention was obtained with sodium sulfite concentrations of from 10 to 12.5 percent by weight (6.15 to 7.7 percent SO_2) and was 82 percent.

Example IV

A cold wave solution of pH 6.5 (adjusted with NaOH) was made, using 40 percent by weight urea and 7.5 percent by weight of sodium bisulfite. Hair treated with this at 25° C. for one hour and neutralized with water for one half hour gave a wet curl retention of 75 percent.

Example V

A cold wave solution was made up of 30 percent formamide and 7.5 percent sodium bisulfite by weight. The pH was maintained at 6.8 and samples of hair were treated at 25° C. with this solution for varying lengths of time and then neutralized for one half hour with distilled water. At the end of 30 minutes of treatment, 48 percent curl retention was achieved, and at the end of one hour, 63 percent. This compares with 65 percent curl retention achieved by a typical thioglycolate solution under similar conditions.

Example VI

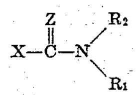
Hair was treated for one hour at 25° C. with a solution of 30 percent urethane (ethyl carbamate) and 5 percent sodium bisulfite by weight having a pH of 6.5. Neutralization was accomplished by immersion in water for one hour. A wet curl retention of 67 percent was achieved which compares with 65 percent for a typical thioglycolate solution.

Example VII

Hair was treated for one hour at 25° C. and 37° C. with a solution of 40 percent acetamide and 5 percent sodium bisulfite by weight over a range of pH from 5 to 8.5. Neutralization was accomplished by immersion in water for one half hour. The maximum wet curl retention was found at pH of 6.5, being 41 percent for the 25° C. treatment and 65 percent for the 37° C. treatment.

I claim:

1. The process of permanently setting hair in a predetermined configuration which comprises adjusting said hair to the desired configuration, imparting a controlled swelling to said hair by contacting said hair at a temperature not higher than 40° C. with a hair-swelling solution of a soluble bisulfite and a nitrogen-containing component having the formula



wherein X is a member selected from the group consisting of hydrogen, alkanol, and alkyl radicals containing not more than three carbon atoms, the radical

$$-(CH_2)_n-\overset{\overset{O}{\|}}{C}-NH_2$$

wherein n is an integer selected from 1 and 2, —OR wherein R is an alkyl radical containing not more than three carbon atoms, and $-NR_3R_4$, R_1, R_2, R_3, and R_4 being members of the class consisting of hydrogen, alkyl and alkanol radicals which when taken together shall contain not more than four carbon atoms, and Z is a member selected from the class consisting of oxygen and =NH, said soluble bisulfite being present in an amount equal to from about 2 to 10% by weight of said solution, and said nitrogen-containing component being present in an amount equal to from about 15 to 40% by weight of said solution, the combined solubility of said soluble bisulfite and said nitrogen-containing component being such that no appreciable salting out of components will occur on said hair at temperatures above about 20° C., said solution causing hair to swell at least 18% but not more than 80%, thereby not causing any substantial degree of hair damage at 40° C.; treating said hair with a mild oxidizing agent, and washing said hair with water.

2. The process in accordance with claim 1 wherein said solution is adjusted to a pH of between 6 and 7.

3. The process in accordance with claim 1 wherein said nitrogen-containing component is urea.

4. The process in accordance with claim 1 wherein said nitrogen-containing component is formamide.

References Cited in the file of this patent

UNITED STATES PATENTS

2,437,965	Michaels et al.	Mar. 16, 1948
2,445,028	Jones et al.	July 13, 1948

FOREIGN PATENTS

443,359	Great Britain	Feb. 20, 1936
449,073	Great Britain	June 19, 1936

OTHER REFERENCES

Jones et al: The Dispersion of Keratins. II Studies on the Dispersion of Keratins by Reduction in Neutral Solutions of Protein Denaturants, Archives of Biochemistry, vol. 3, Dec. 1943, No. 2, pp. 193–202.