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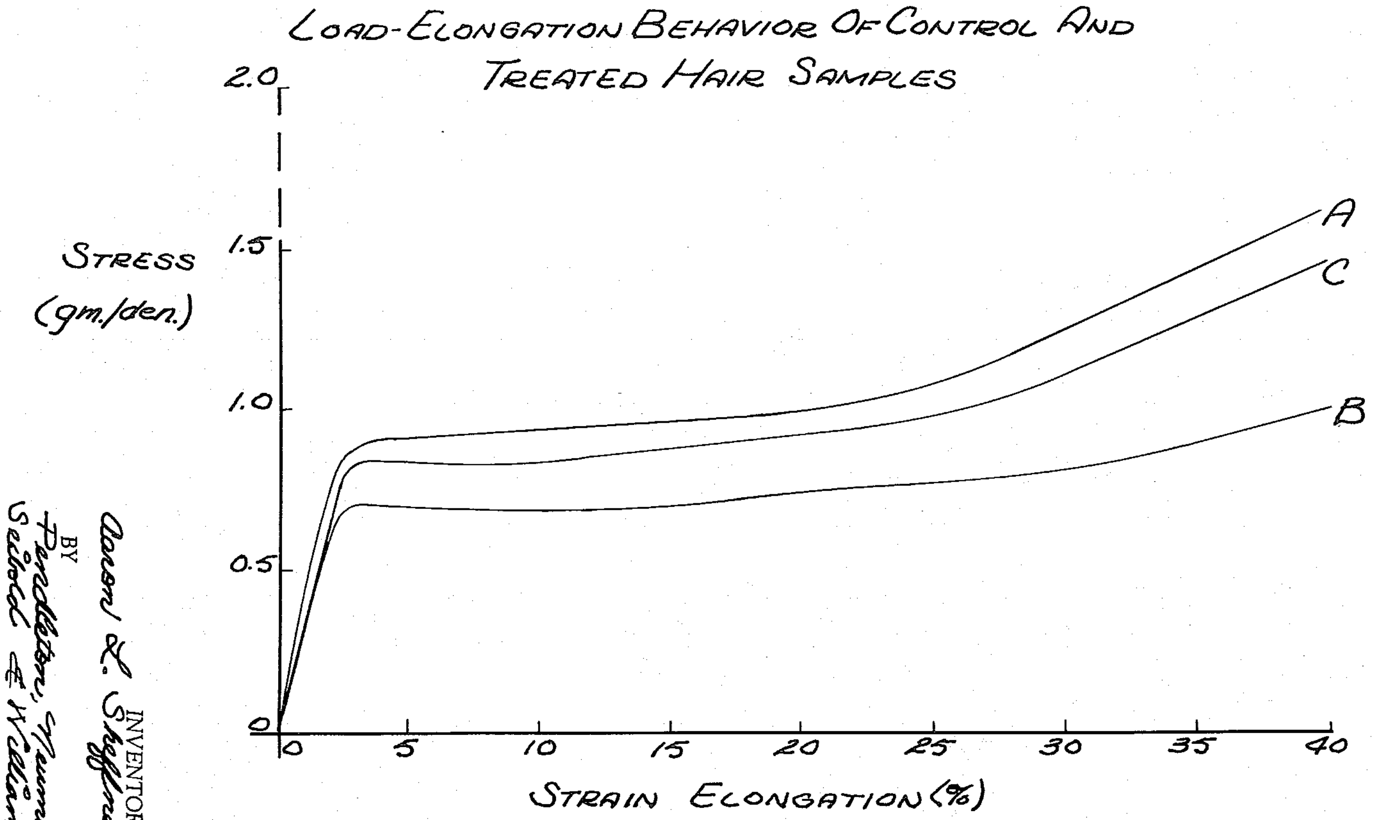
LOAD-ELONGATION BEHAVIOR OF CONTROL AND TREATED HAIR SAMPLES

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HAIR TREATMENT WITH N-ACYLCYSTEINES

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This application is a continuation-in-part of my copending patent application Serial No. 225,392, filed September 21, 1962, now abandoned.

This invention relates to processes and compositions for the permanent deformation of human hair which have substantial and unexpected advantages over currently available methods. These processes and compositions relate to the so-called permanent waving of hair as well as to the corollary processes and compositions of straightening naturally or artificially curled hair.

The most common processes now in use for the permanent waving of hair by chemical methods comprise a first step in which the hair is impregnated with an aqueous solution containing one or more sulfhydryl compounds as a reducing agent for the disulfide linkages of the keratin, in order to impart plasticity to the hair and permit reshaping. The sulfhydryl compound thioglycolic acid is the only member of the class that has achieved any substantial degree of practical application. It has come to the fore because of its low cost and because the undesirable properties of the thiols as a class are exhibited to a minimum extent by this compound.

Nevertheless, currently available permanent waving compositions possess substantial disadvantages. Most noteworthy is their foul odor and corrosiveness for the human skin and hair. Allergic reactions are sometimes encountered. Lack of universal applicability to the hair of all subjects, due to varying sensitivity thereof to thioglycolic acid also presents an unsolved problem to the art.

The corrosive nature of thioglycolate based waving lotions, which results in hair damage reflected in loss in tensile strength thereof is to an extent an inherent characteristic of the thioglycolate ingredient. Furthermore, such lotions are unstable on exposure to the air and large excesses of the material are frequently required. One of the reasons for the inapplicability of certain other thiol compounds having the desired inherent activity is that undesirable deposits are left thereby on treated hair or the hair otherwise acquires an undesirable appearance or odor.

The present invention, therefore, has along its objects:

(a) To provide processes for the permanent deformation of the hair as in permanent waving and hair straightening which employ innocuous, noncorrosive, and nonsensitizing compositions, substantially free of the undesirable odor usually associated with thioglycolates.

(b) To provide such processes which employ compositions having a convenient duration of storage stability.

(c) To provide such processes which have operating time cycles adapted to commercial or home use.

(d) To provide such processes which employ compositions having a wide margin of safety and yet which are effective for self-application or use in the home by unskilled operators.

(e) To provide compositions for use in the above processes, which have a diminished propensity to damage the hair when used therein.

These and other objects are achieved as a result of the present invention which involves the use of a compound selected from the group consisting of lower N-alkanoylcysteines having up to ten carbon atoms and N-aroylcysteines having up to twelve carbon atoms as thiol reducing

agents in hair plasticizing or waving processes. Their use in such processes is attended by a number of unexpected advantages, particularly when it is considered that cysteine itself is known to have very limited hair plasticizing capacity and is further limited in its applicability to such processes by its instability to air oxidation and propensity to leave a precipitate or deposit following oxidation thereof.

The cosmetic elegance of lower N-alkanoylcysteine and N-aroylcysteine hair preparations combined with the physiologically acceptable nature and keratin reducing capacity thereof, particularly adapts them for use in hair treatment processes. Furthermore, lower N-alkanoylcysteines and N-aroylcysteines yield only water soluble oxidation products and thus do not leave a film on the hair or otherwise impart an undesirable appearance after rinsing or oxidizing.

In one form the present invention relates to a process which includes contacting hair with a solution of N-alkanoylcysteine or N-aroylcysteine in order to form the hair into a predetermined configuration. In another form the present invention involves contacting clean human hair while confining it in the desired predetermined configuration with an aqueous solution of a lower N-alkanoylcysteine or an N-aroylcysteine having a pH within the range of about pH 7.0 to pH 9.5 and a concentration thereof of about 3% to about 20% by weight. A sufficient period of time of contact with the solution to result in permanent deformation of the hair is employed. This period ranges from about 10 min. to about 12 hrs., depending upon the characteristics of the hair being treated, the temperature, the pH of the solution, and the concentration and species of lower N-alkanoylcysteine or N-aroylcysteine. It is within the province of the skilled operator to ascertain the optimum time period in any given situation.

Preferred lower N-alkanoylcysteines include N-acetylcysteine, N-propionylcysteine, N-butyrylcysteine, N-valerylcysteine, N-caproylcysteine and N-heptanoylcysteine of either the D or L configuration or mixtures thereof. Preferred N-aroylcysteines include N-benzoylcysteine, N-toluoylcysteine, N-(ethylbenzoyl)cysteine, and N-(propylbenzoyl)cysteine. The preferred species of waving agent for use in the present process is N-acetyl-L-cysteine. The advantageous characteristics referred to herein are exhibited to an optimum degree by this member. The L-form is preferred on the basis of economic factors, L-cysteine from which it is made being commercially available from sources such as feathers, hoofs, etc. N-acetyl-DL-cysteine is equally effective and may be preferred where it can be obtained more cheaply, for instance, by total synthesis.

N-acetyl-L-cysteine has been found to possess a substantial advantage over thioglycolate preparations relative to hair damage. FIGURE 1 is a diagram of load elongation behavior of various hair samples treated according to the present invention and with a thioglycolate preparation as described in Example 9. This diagram shows that hair treated with a 10% (0.6 molar) aqueous solution of N-acetyl-L-cysteine having a pH of 9.3, sample C, is not significantly damaged relative to sample A, the untretated control tress. The sample treated with an 0.6 molar solution of thioglycolic acid having a pH 9.3 (sample B) was significantly damaged.

N-acetyl-L-cysteine has been shown to be essentially nontoxic on oral administration or by inhalation of an aerosol thereof. It is not harmful to the mucous membranes of the conjuctiva or the nasal passages, nor does it interfere with tracheal ciliary activity. It has been shown to lack sensitizing potential in both guinea pigs and human beings on repeated exposure thereto.

As is conventional in the hair-waving art, when contact of the hair with the N-alkanoylcysteine or N-aroylcysteine solution has achieved sufficient plasticization to permit it to assume the desired configuration, the hair is exposed to conditions of oxidation for the purpose of regenerating the cystine disulfide linkages of the keratin. This step has been referred to in the art variously as fixing or neutralizing. The former term is considered more appropriate in the present description, since the term neutralization also implies pH adjustment. When the term "fixing means" is employed in describing the present invention, it is intended to refer to the step of exposing the hair which has been plasticized by means of contact with a solution of a lower N-alkanoylcysteine or N-aroylcysteine to conditions of oxidation, permitting regeneration of the cystine disulfide bonds of the keratin.

Conventional fixing means known to the hair-waving art are applicable to the present process. These involve either exposure to the air for a prolonged period, or brief contact with a solution of an inorganic oxidizing agent. Oxidizing agents that have been employed and which are suitable in the present process include hydrogen peroxide, the alkali metal bromates and iodates, the alkali metal perborates, etc.

Since the described cysteine derivatives have an acid strength similar to that of acetic acid, neutralization of solutions thereof with a suitable base is preferably employed to adjust the pH to within the specified range for hair-waving action. The bases employed for pH adjustment should be sufficiently strong to neutralize the cysteine derivative, and should be cosmetically acceptable. Sodium hydroxide, ammonia or ammonium hydroxide meet both of these standards. Other materials that are applicable include the sodium, potassium, and ammonium salts of cosmetically acceptable acids having pK_a values in excess of 3.2. The cosmetically acceptable organic amines having basicities comparable to or greater than that of ammonia are suitable and in fact preferred. The pK_b values of such amines are less than 5.0.

The following list includes a sampling of suitable bases for pH adjustment of waving solutions employed in the present process: sodium hydroxide, potassium hydroxide, ammonia, methylamine, ethylamine, propylamine, butylamine, dimethylamine, diethylamine, monoethanolamine, ethylenediamine, piperazine, tetramethylenediamine, and sodium, potassium, or ammonium salts of the following acids: lactic acid, acetic acid, carbonic acid, citric acid, etc. Monoethanolamine is the preferred base for pH adjustment. The preferred pH range is pH 9.0 to 9.5. It will be noted that most of the bases listed above are water-soluble materials indicative of the preference herein for bases of that type.

The term cosmetically acceptable as applied to ingredients of the present composition is intended to refer to certain functional characteristics thereof. For example, cosmetically acceptable amines and salts are materials which are non-corrosive in the concentrations employed, which have low toxicities, and which lack irritating or sensitizing propensity. Furthermore, such ingredients should not have undue or irreversible softening effect on the hair. They should not react with the sulfhydryl group of either the lower N-alkanoylcysteine or N-aroylcysteine under conditions of storage and use in an irreversible or destructive fashion as by oxidation, condensation, or precipitation. Furthermore, they should not evoke undesirable color reactions to the detriment of the appearance of the composition as a whole or the hair treated therewith.

It is preferred in practicing the present invention to employ waving solutions in which the described cysteine derivative has a concentration in the range from about 7% to about 10% when the treatment is carried out at room temperature, e.g. cold waving. Solutions of up to 20% concentration have, however, been found to possess the excellent physiological tolerability referred to above. When elevated temperatures are employed in treating the hair with an N-alkanoylcysteine or N-aroylcysteine preparation, it may be desirable to use concentrations thereof of less than 7%.

Auxiliary materials of the sort employed in the hair-waving art are also suitable for use in the present processes. These include opacifiers and thickeners to impart a milky or creamy lotion-like consistency to the otherwise transparent solution of the described cysteine derivative. For this purpose, such ingredients are carboxymethyl cellulose, polyacrylates, polystyrene latex, emulsified oils, chlorinated hydrocarbons, pectins, gums, etc., can be employed. In addition, use may made of cosmetically acceptable perfumes and dyes if desired to lend elegance.

Additives of a functional nature can also be included, and in this regard it has been found that wetting agents and swelling agents can be incorporated to advantage into the compositions employed in the present process. Suitable wetting agents include the ionic and nonionic synthetic wetting agents and particularly detergents such as the sodium and potassium salts of the alkylsulfuric alkylsulfonic, and aralkylsulfonic acids having at least 12 carbon atoms, polyoxythylenes, polyoxypropylenes, and the ethers and esters thereof. Wetting agents are employed in concentrations of from about 0.1% to 1.0% by weight.

As materials which are known to swell the hair sheath on contact therewith in water, urea, thiourea, methylurea, ethylurea, and the mineral acid salts of guanidine may be mentioned. Such materials are included in the compositions in an amount of from about 1% to about 15% by weight of the waving solution as directed by properties affecting both function and elegance of the final product.

Other adjuvants that can be employed include agents to prevent overprocessing of the hair. Materials which are known in the art to be applicable for this purpose include ammonium chloride, ammonium sulfate, ammonium phosphate, and various other salts of weak bases and strong acids.

In order to more clearly illustrate the manner of practicing the present invention, several specific examples follow:

Example 1.—A highly curled tress of hair was submerged in a 7% aqueous solution of N-acetyl-L-cysteine, which had been adjusted to pH 9 with aqueous sodium hydroxide, for a period of 1 hr. at room temperature. The tress was then removed from the solution, weighted at its lower end with a small clamp, and suspended from a horizontal rod. It was kept suspended in this manner for a period of 5 min., during which time it was rinsed once with the N-acetyl-L-cysteine solution. The strands were then washed with tap water and allowed to air dry in suspended position. This treatment resulted in complete removal of the curl from the hair, providing a tress made up of straight, undamaged strands of hair.

Example 2.—The following waving solutions were compared in an experiment employing identical tresses of human hair. The compositions of these solutions are listed below as percent by weight of final solution. A fixing solution of 4.2 g. of sodium perborate monohydrate and 1.0 g. of sodium hexametaphosphate dissolved in 475 ml. of water was employed.

Solution No. 1—Water (serves as control)
Solution No. 2—7% N-acetyl-L-cysteine adjusted to pH 9.15 with ammonium hydroxide
Solution No. 3—7% N-acetyl-L-cysteine adjusted to pH 9.15 with sodium hydroxide
Solution No. 4—7% N-acetyl-L-cysteine and 15% urea, adjusted to pH 9.15 with sodium hydroxide
Solution No. 5—3% N-acetyl-L-cysteine and 15% urea, adjusted to pH 9.15 with sodium hydroxide

Five substantially identical tresses of hair were wound onto conventional home-permanent curlers and separately saturated with one of the waving solutions designated 1 through 5 above. After exposure for 10 min., excess waving solution was rinsed from the tresses with water. The curlers bearing the wet tresses were kept at room temperature for 30 min., and each wound tress was then saturated with the fixing solution. The tresses were then rinsed with warm water, removed from the curlers, and again rinsed with warm water. It was observed that on rinsing with water, the tress which had been treated with solution No. 1 (water) became straight, the remainder retained a curl, No. 5 somewhat less pronounced than Nos. 2, 3, and 4.

Results similar to those obtained with solution No. 4 are obtained when thiourea, methylurea, ethylurea, or guanidine acid addition salt such as the sulfate, phosphate, hydrochloride, or hydrobromide are substituted for urea on an equal weight basis.

Example 3.—Comparative experiments employing the waving solutions listed below and identical tresses of virgin human hair 6 inches in length and weighing approximately 1 g. each were conducted.

Solution No. 1—10% N-acetyl-L-cysteine adjusted to pH 9.3 with ammonium hydroxide

Solution No. 2—10% N-acetyl-L-cysteine adjusted to pH 9.3 with sodium hydroxide

Solution No. 3—10% N-acetyl-L-cysteine adjusted to pH 9.3 with monoethanolamine

The respective tresses were first moistened with the test solution, rolled onto conventional curling rods, remoistened with the same test solution, and held in this condition for 10 min. The tresses on the rods were then rinsed and carefully saturated with a fixing solution consisting of 1.5% aqueous hydrogen peroxide. Similar results are obtained if 1% sodium perborate or 1.5% sodium bromate aqueous solutions are substituted for the hydrogen peroxide as fixing solution. The tresses were then unwound, resaturated with the fixing solution, rinsed once more with warm water, and examined. Each was found to retain a definite curl in the wet condition. The tress that had been treated with Solution No. 3 had superior texture and a somewhat tighter curl.

Example 4.—A waving solution containing 10% N-acetyl-L-cysteine and 0.1% ethylene oxide-propylene oxide polymer having molecular weight 1750 (Pluronic F–68, Wyandotte Chemicals Corporation, Wyandotte, Michigan) was compared in effectiveness to a commercial waving lotion determined by analysis to contain 5.52% ammonium thioglycolate as waving agent and having pH 9.25. The experiment was conducted on separate tresses of virgin human hair as described in the preceding example, but using a processing time of 15 min. Curls of equivalent tightness were obtained in each instance but the tress curled by the N-acetylcysteine solution was softer and had a more natural texture. Similar results are obtained with an N-acetylcysteine solution containing the following wetting agents: 1% by weight of Pluronic F–68, 0.1% sodium lauryl sulfate, or 0.5% of polysorbate 80, and 1% of sodium dodecylbenzene sulfonate.

Example 5.—A further experiment on individual hair tresses as described in Example 3 was conducted. In this experiment three waving solutions having the following composition but adjusted respectively to pH 7, pH 8, and pH 9 were compared.

N-acetyl-L-cysteine	g	20.0
Urea	g	5.0
Polyoxyethylene-polyoxypropylene copolymer (Pluronic F–68)	g	1.0
Monoethanolamine, q.s. desired pH.		
Distilled water, q.s.	ml	100

Exposure times of 15 min. were employed. The tress treated at pH 7 had a weak curl, that at pH 8 was somewhat more pronounced, while that at pH 9 had a strong resilient curl.

Example 6.—A waving lotion having the composition given below is prepared. The mineral oil and liquid lanolin are included to provide a cream-like appearance for cosmetic elegance. The polyoxyethylene ingredients are non-ionic wetting agents included to improve waving efficiency and to assist in emulsification of the oils. The silicone antifoam is for manufacturing convenience and the disodium ethylene-diaminetetraacetic acid is a chelating agent which increases storage stability of the finished composition. N-acetyl-L-cysteine is the waving agent. Monoethanolamine is selected for pH adjustment since it has been observed that compositions containing it provide better-textured waves. Distilled water is the vehicle. A perfume ingredient may also be employed if desired.

A

Mineral oil	g	3.0
Liquid lanolin	g	0.75
Polyoxyethylene (4) lauryl ether	g	0.5
Polyoxyethylene (20) lauryl ether	g	0.5
Silicone antifoam agent	g	0.01

B

N-acetyl-L-cysteine	g	10.0
Disodium ethylenediaminetetraacetic acid	g	0.05
Monoethanolamine, q.s.	pH	9.3
Distilled water, q.s.	ml	100.0

Preparation of the composition includes the following steps. Solutions of the oil soluble and water soluble ingredients, designated by A and B above are prepared and warmed to 70° C. They are then combined and the silicone antifoam agent added. The pH of the mixture is then further adjusted if necessary and diluted to volume with water as a final step.

Example 7.—Permanent waves were applied to seven subjects in accordance with the usual technique involved in the use of permanent wave lotions including the steps of shampooing the hair, saturating with the waving solution, rolling the hair on curling rods, resaturating on the rods with waving solution, holding for a period of time which in the judgment of the operator is sufficient to impart a curl, rinsing, and neutralizing with a 1.5% hydrogen peroxide solution to serve as a fixing solution. The waving lotion of Example 6 with exposure periods as follows was employed:

	Min.
3 subjects	15
1 subject	17
1 subject	20
1 subject	30
1 subject	60

After saturation of the hair on the curling rods with the fixing solution, it was let down, resaturated with fixing solution, rinsed, set on rollers, and allowed to dry. On removing the rollers, waves were obtained which were considered satisfactory by the operator and each of the subjects.

Example 8.—A waving lotion similar to that of Example 6 was compared in effectiveness to a commercial waving lotion of the home permanent type having pH 9.25 which was determined by analysis to contain 5.52% ammonium thioglycolate as waving agent. The half head technique in which the permanent wave is applied using one lotion on the left-hand portion of the head and a second lotion on the right-hand portion of the head was employed on five subjects. The permanent waves were applied manually by a licensed beauty operator according to the usual technique as outlined in Example 7. The most striking difference between the two products which was observed by the operator in all cases was the greater ease with which the hair which had been treated with the lotion of Example 6 could be combed. There was a striking absence of tangled hair ends as was encountered with the commercial product.

Example 9.—Individual tresses of virgin human hair, 6 inches in length and weighing approximately 1 g. each were separately immersed in loose uncurled condition each in one of the following compositions for 30 min. The waving composition was then rinsed from the hair and the tresses saturated with a 1.5% solution of hydrogen peroxide as fixing solution. The tresses were again rinsed and dried.

A. Untreated control tress
B. Thioglycolic acid, 0.6 molar adjusted to pH 9.3 with monoethanolamine
C. N-acetyl-L-cysteine, 0.6 molar adjusted to pH 9.3 with monoethanolamine

Twenty-five to thirty individual hair filaments were selected from each tress and subjected to one-time loading to ultimate rupture on an Instron Tensile Testing Machine. This is a constant rate of extension machine with a load measuring system comprising a bonded strain gauge-type load cell and electronic amplifying equipment. The following Instron testing conditions were used:

Chart speed—10 inches per minute
Jaw speed—2 inches per minute
Gauge length—4 inches
Strain rate—50% per minute
Full scale load—100 and 200 g.
Temperature—70° F.
Relative humidity—65%

The values obtained for each filament from the various tresses were averaged and graphs of the average stress expressed in grams per denier and the average strain elongation expressed as percent of original length were prepared. These curves are shown in FIGURE 1. The post-yield slope for each tress was then determined from these curves according to the method of Harris and Brown, Textile Research Journal 17, 323 (1947). These authors have shown that as the number of disulfide bonds is reduced, post-yield slope is decreased accordingly. From the data contained in the following table, it was concluded that the post-yield slope for sample C, the N-acetyl-L-cysteine composition, was not statistically different from that of the untreated control sample, sample A. It was further concluded that sample B, the thioglycolate composition, was quite badly degraded by the treatment with the destruction of a number of cysteine linkages.

TABLE 1.—LOAD-ELONGATION POST-YIELD SLOPES FOR HAIR SAMPLES

Sample	Post-Yield Slope	Standard Deviation
A	3.50	0.40
B	1.91	0.56
C	3.31	0.42

Example 10.—Strain elongation work indices for the wet hair samples referred to in Example 9 were determined as a further measure of hair damage by the chemical treatment described. Approximately 10 filaments from each sample were subjected to load elongation studies in the apparatus referred to in Example 9 while immersed in water at 70° F. The same strain rates, 50% per minute, and gauge lengths, 4 in., were employed as in Example 9. An integrator was connected to the Instron testing dynamometer to automatically compute the area under the stress-strain diagram as a measure of the work done in straining each filament to strain levels of 20% and 30%. The work index (Speakman, Journal of the Textile Institute, vol. 37T, 102 (1947)) is the ratio of the work required to stretch the treated filament to a given strain value to the work required to stretch the untreated material to the same strain value. The results obtained are tabulated in Table 2.

TABLE 2.—STRAIN ELONGATION WORK INDEX RATIOS FOR TREATED HAIR SAMPLES (UNDER WATER AT 70° F.)

Sample Ratio	Index for 20% Strain	Index for 30% Strain
B/A	0.245	0.265
C/A	0.841	0.837

Sample B, the thioglycolate composition, was concluded to be substantially inferior to sample C, the N-acetyl-L-cysteine composition.

Example 11.—After shampooing and while saill moist, an adult woman's hair was wetted with a 7% aqueous solution of N-acetyl-L-cysteine having pH 7.0 (adjusted with sodium hydroxide), and put up in curlers. The hair on each curler was remoistened with the solution. This process was completed just before retiring and the curls remained moist during the night. The hair was then dried, the curlers removed, and the curls combed. The desired curly appearance was achieved and had a substantially greater degree of permanence than when water was used to wet the hair during the curling process. In addition, the hair appeared to have improved body and better sheen.

Examples 12 and 13.—The experiment described in Example 3 is repeated, substituting N-propionyl-L-cysteine and N-butyryl-L-cysteine for the N-acetyl-L-cysteine specified in that example. Substantially the same results are observed.

Example 14.—The experiment described in Example 3 is repeated, substituting N-benzoyl-L-cysteine for the N-acetyl-L-cysteine specified in that example. Substantially the same results are observed.

While several particular embodiments of this invention are shown above, it will be understood, of course, that the invention is not to be limited thereto, since many modifications may be made, and it is contemplated, therefore, by the appended claims to cover any such modifications as fall within the true spirit and scope of this invention.

What is claimed is:

1. In a process for imparting a predetermined configuration to human hair without substantial damage thereto by first plasticizing the hair by contacting a reducing agent therewith and thereafter subjecting it to oxidizing conditions, the step which comprises contacting therewith a cosmetically acceptable aqueous solution containing from about 3% to about 20% by weight of a compound selected from the group consisting of a lower N-alkanoylcysteine having up to ten carbon atoms and N-aroylcysteine having up to twelve carbon atoms for a period of from about 10 minutes to about 12 hours; said solution having a pH of from about pH 7 to about pH 9.5.

2. The process of claim 1 wherein said compound is N-acetyl-L-cysteine.

3. The process of claim 1 wherein said compound is N-acetyl-DL-cysteine.

4. The process of claim 1 wherein said solution has a concentration of from about 7% to about 10% by weight of a compound selected from the group consisting of said lower N-alkanoylcysteine having up to ten carbon atoms and N-aroylcysteine having up to twelve carbon atoms.

5. A process for permenently changing the configuration of hair without substantial damage to the hair structure which includes the step of contacting the hair while in desired configuration with an aqueous solution containing from about 3% to about 20% by weight of a compound selected from the group consisting of a lower

N-alkanoylcysteine having up to ten carbon atoms and N-aroylcysteine having up to twelve carbon atoms for a period of time sufficient to achieve plasticization thereof, said solution having a pH of from about pH 7.0 to about pH 9.5.

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LEWIS GOTTS, *Primary Examiner.*