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[54] TREATMENT OF KERATIN FIBERS

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[56] **References Cited**

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[57] **ABSTRACT**

Keratin fibers are softened by sulfitolysis which forms S-sulfo groups or a mixture of S-sulfo groups with thiol groups in the fibers, then changed in configuration and maintained in the new configuration while restoring the fibers by treating with an aqueous solution containing at pH 5 to 11 from 0.02 to 0.3 mole per liter of an alkali metal, ammonium or lower alkanolamine sulfide or hydrosulfide, an aliphatic mercaptan, or mixtures thereof with each other or with an aliphatic disulfide. An aliphatic disulfide may be used alone when the ratio of S-sulfo groups to thiol groups in the sulfitolyzed keratin fibers is from 4:1 to 1:4.

8 Claims, No Drawings

TREATMENT OF KERATIN FIBERS

This invention relates to the treatment of keratin fibers and pertains more specifically to the restoration of sulfitolyzed keratin fibers.

The disulfide crosslinkages of keratin are ruptured during chemical setting processes such as the permanent waving of hair, or the permanent creasing or pleating of wool fabrics or garments. Such processes may be considered as consisting of three steps:

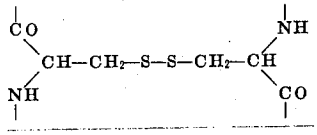
1. The rupture of disulfide bonds between the polypeptide macromolecular chains of the keratin fiber structure, to soften the fiber and permit relative movement of the molecules into a new configuration.

2. The imposition of a new mechanical configuration on the structure; for example, a curl in the case of human hair, a crease or a pleat in the case of wool fabric.

3. The restoration of disulfide bonds between the polypeptide chains to stabilize or set the structure in the newly imparted configuration.

The order in which the first two steps are performed can be reversed if desired.

The most important bonds ruptured in the first step are the disulfide crosslinkages between the polypeptide chains, resulting from the incorporation of the diamino-dicarboxylic acid cystine in the structure:



In order to restore the mechanical and physical properties of the material in the third step, it is desirable to rebuild most or all of these disulfide linkages. When the keratin disulfide linkage (K-S-S-K) is ruptured by reduction, for example by means of a mercaptan ($R\text{-}S^-$ or R-SH), the rebuilding is conveniently accomplished by oxidation. Many common oxidants, such as hydrogen peroxide, potassium bromate, sodium perborate, or aerial oxygen, are effective for this purpose. In certain situations, however, rupture of the keratin disulfide linkage by sulfitolysis, using a sulfite or a bisulfite as the rupturing agent, is preferable to reduction, on account of the freedom of these reagents from odor and from metal staining problems, and of the greater stability in storage of the ruptured keratin made in this way. The sulfitolysis is believed to occur according to the following equations, with the generation of one S-sulfo group ($K\text{-}S\text{-}SO_3^-$) and one thiol group (K-SH or $K\text{-}S^-$) from each disulfide linkage:

$$K\text{-}S\text{-}S\text{-}K+SO_3^{=} \rightleftharpoons K\text{-}S\text{-}SO_3^-+K\text{-}S^-$$

or

$$K\text{-}S\text{-}S\text{-}K+HSO_3^- \rightleftharpoons K\text{-}S\text{-}SO_3^-+K\text{-}SH \quad (1)$$

Practical use of these reactions has been impeded by the lack of effective and convenient means of rebuilding disulfide bonds in sulfitolyzed keratin. This difficulty is particularly bothersome in low-temperature processes (below 60° C.), in which case it is necessary to rupture a larger portion of the disulfide bonds in the keratin than at higher temperatures in order to accomplish the setting; consequently, a failure to rebuild most of the rupture disulfide linkages leaves a fiber with impaired properties. The problem is of less consequence in processes in which the setting is performed at high temperatures, for example in boiling solution or in steam. In this case only a few disulfide bonds need to be broken, and imperfect restoration does not have serious consequences. Furthermore, under the influence of heat, there may be extensive formation of other bonds which stabilize the configuration and strengthen the fiber, principally secondary bonds such as hydrogen bonds.

Three ways have been employed in the art, individually or in combination, to restore disulfide crosslinkages in sulfitolyzed keratin:

The first consists of the use of an oxidant, such as any of those commonly employed for rebuilding reduced keratin. Under normal reaction conditions, these oxidants do not react with S-sulfo groups. Consequently, only the thiol groups are relinked to form disulfide crosslinkages. The S-sulfo groups, which are retained in the rebuilt keratin, tend to swell and weaken the structure by virtue of their hydration and ionization over the whole pH range from pH 1 upward. Hence, the physical and mechanical properties of the fiber are not completely restored, the fiber being weak and rubbery when wet, and brittle and hard in the dry state.

The second way of rebuilding disulfide linkages in sulfitolyzed keratin consists in reversing the sulfitolysis reactions, which are equilibrium reactions, by removal of sulfite or bisulfite reactant, for example by rinsing the keratin fiber with water. This process is inefficient because the sulfite and bisulfite ions are strongly sorbed by keratin, so that their complete removal by rinsing is difficult; unfortunately, the presence of only a small quantity of either ion suffices to maintain a substantial extent of disulfide bond rupture.

The third method by which partial rebuilding can be accomplished consists in changing the pH of the keratin fiber. Because the extent to which the sulfitolysis reactions proceed before reaching equilibrium varies depending upon the pH of the reaction, reaching a maximum at about pH 6, if the sulfitolysis is carried out at this pH and is allowed to approach equilibrium, some disulfide linkages can be restored by appropriate change in pH, usually upward from 6. The second and the third methods just described are frequently employed in conjunction.

It has now been found that more complete restoration of the disulfide linkages may be achieved and damage to the fibers, as evidenced by increased susceptibility to breakage and changed response to bleaching and dyeing agents, which occurs during sulfitolysis, can be greatly reduced by employing during the restoration step an aqueous solution of certain sulfur-containing compounds, namely the alkali metal, ammonium, and lower alkanol-amine sulfides; alkali metal, ammonium, and lower alkanolamine hydrosulfides; aliphatic mercaptans; aliphatic disulfides; or mixtures of any of these.

The ability of mercaptans, sulfides, and hydrosulfides to restore disulfide linkages in keratin is quite unexpected, since these materials are normally considered to be disulfide-bond rupturing agents, and are extensively employed for this purpose in hair waving and similar processes.

It is generally understood that Bunte salts ($R\text{-}S\text{-}SO_3^-$) not made from keratin react with mercaptans ($R'\text{-}S^-$) to form a disulfide:

$$R\text{-}S\text{-}SO_3^-+R'\text{-}S^- \rightleftharpoons R\text{-}S\text{-}S\text{-}R'+SO_3^{=} \quad (2)$$

One would therefore expect that the addition of a mercaptan to S-Sulfo keratin would result in the formation of the mixed disulfide:

$$K\text{-}S\text{-}SO_3^-+R\text{-}S^- \rightleftharpoons K\text{-}S\text{-}S\text{-}R+SO_3^{=} \quad (3)$$

This reaction would not restore disulfide crosslinkages in the keratin. However, we have discovered that the product of this reaction is not the mixed disulfide, but the symmetrical keratin disulfide, K-S-S-K. The exact reaction mechanism is not understood, but it appears that 1 mole of disulfide crosslinkages is generated per mole of mercaptan employed, and the reaction is believed to be as shown in the following equations:

$$2K\text{-}S\text{-}SO_3^-+R\text{-}S^- \rightleftharpoons K\text{-}S\text{-}S\text{-}K+R\text{-}S\text{-}SO_3^-+SO_3^{=}$$

or

$$2K\text{-}S\text{-}SO_3^-+R\text{-}SH \rightleftharpoons K\text{-}S\text{-}S\text{-}K+R\text{-}S\text{-}SO_3^-+HSO_3^- \quad (4)$$

As indicated above, certain sulfides and hydrosulfides similarly cause the restoration of keratin disulfide crosslinkages; these reactions are believed to proceed as follows:

$$2K\text{-}S\text{-}SO_3^-+S \rightleftharpoons K\text{-}S\text{-}S\text{-}K+S_2O_3 \quad +SO_3^{=}$$

or

$$2K\text{-}S\text{-}SO_3^-+HS^- \rightleftharpoons K\text{-}S\text{-}S\text{-}K+S_2O_3 \quad +HSO_3^- \quad (5)$$

As is apparent from these equations, lowering of the concentration of the soluble reaction derivatives of the mercaptan employed, the sulfite and the S-sulfo products and the

thiosulfate, by dilution or rinsing, drives the reaction to the right and so promotes the rebuilding of disulfide crosslinkages.

The sulfitolysis of keratin fibers during the process of the present invention can be carried out in any conventional manner. For example, the fibers may be brought into contact with an aqueous solution of such sulfitolyzing agents as water-soluble sulfites, bisulfites or hydrosulfites, for example the alkali metal or ammonium or lower alkanolamine salts. Solutions containing 0.1 to 4.0 moles or more of the sulfitolysis ingredient per liter may be used. In this case the ratio of S-sulfo groups to thiol groups in the sulfitolyzed hair is approximately 1:1, as indicated by equations (1).

There may also be used solutions containing in addition an oxidizing agent such as a transition metal ion in the higher oxidation state such as cupric of ferric ion, or such as a water-soluble polythionate as described in the copending application of Wolfram, Ser. No. 488,759 filed Sept. 20, 1965 now abandoned. Such polythionates include the alkali metal, ammonium, or lower alkanolamine trithionates, tetrathionates, pentathionates and hexathionates; they may be present in amounts from 0.05 to 2 moles or more per liter. When sulfitolyzation is carried out in the presence of such an oxidizing agent the ratio of S-sulfo groups to thiol groups in the sulfitolyzed hair is greater than 1:1, if sufficient oxidizing agent is employed the ratio is greatly increased, approaching the point where the sulfitolyzed hair contains only S-sulfo groups and no thiol groups.

Finally, sulfitolyzation may be carried out by using solutions containing in addition to sulfites, bisulfites or hydrosulfites a reducing agent such as a water-soluble mercaptan, including any of those hereinafter described for use in restoring the disulfide linkages. The ratio of S-sulfo groups to thiol groups in hair sulfitolyzed in the presence of such a reducing agent is less than 1:1, depending upon the relative proportions of sulfitolyzing agent and reducing agent.

Such sulfitolyzing solutions may have a pH from 4.5 to 11, the pH being adjusted by the addition of ammonia or other alkaline material or of conventional buffer salts. It will be understood that there may also be present in the sulfitolyzing composition conventional protein swelling agents such as urea, isopropanol, lithium bromide, phenol and the like in amounts up to 8 moles per liter, or deswelling agents such as various inert water-soluble salts, e.g., sodium chloride, potassium chloride, sodium sulfate, magnesium sulfate and the like, in amounts up to 1 mole per liter.

In treating hair, the sulfitolytic solution may be applied to hair on the human head in the same ways as waving or straightening lotions are conventionally applied. In treating wool the fibers or fabric may simply be immersed in the solution, or the solution may be applied by various other conventional methods such as by padding. In the case of wool the temperature of the solution may be from room temperature (20° C.) to as high as the boiling point (ca. 100° C.), but when the solution is used as a waving lotion on the human head the temperature of the solution normally does not exceed about 50° C. The time required to effect substantial sulfitolysis varies depending upon the temperature and concentration of the solution, as is well known; usually the solution should be left on the hair for at least 10 minutes at room temperature but at a temperature as high as the boiling point, which may be used in the case of wool, substantial sulfitolysis occurs during treatment which lasts only a few seconds.

The relative proportion of S-sulfo groups and of thiol groups in sulfitolyzed hair can readily be determined by analysis of three fresh samples, each weighing about 0.1–0.2 gram, by the following methods. The first sample, after blotting with a towel, is washed by immersion in three successive 25 ml. portions of 6 normal sulfuric acid at room temperature for periods of 1 minute, 1 minute, and 14 minutes successively, then hydrolyzed by heating for 17 hours at 95° C. in approximately 85 ml. of 6 normal sulfuric acid. The hydrolysis converts each mole of S-sulfo keratin to 1 mole of cysteine. The mixture is then cooled to room temperature, diluted with water to 100 ml. and the amount of cysteine present is determined by titration. This includes both the cysteine formed by acid hydrolysis of the S-sulfo keratin and the cysteine formed along with the S-sulfo keratin in the sulfitolysis process of equation (1). The aliquot of acid hydrolysate to be titrated is first alkalized with an excess of sodium carbonate and then titrated with an aqueous solution which is 0.1 N in salyrganic acid and 1.0 N in sodium chloride, using a 1 percent aqueous solution of sodium nitroprusside as the indicator. The results are expressed as millimoles/gram of hair sample of the total of both S-sulfo and thiol groups, designated MNP_1.

The second sample, after the initial three sulfuric acid immersions, is blotted with a towel and then washed by immersion in two successive 25 ml. portions of deaerated distilled water in a nitrogen atmosphere (to prevent oxidation of thiol groups) for periods of 1 minute and 4 minutes respectively. The sample is blotted with a towel, then immersed in two successive 25 ml. portions of 0.2 molar sodium sesquicarbonate (pH about 9.5) in a nitrogen atmosphere for periods of 1 minute and 9 minutes respectively, after which it is washed by immersion in 25 ml. of deaerated distilled water in a nitrogen atmosphere. This treatment causes reversal of the reaction of equation (1); as pointed out above, the extent of reversal is somewhat less than 100 percent. The sample is then subjected to 17-hour sulfuric acid hydrolysis and titration as in the case of the first sample. The results are expressed as millimoles per gram of sample of residual S-sulfo and thiol groups, after reversal, designated MNP_2.

The third sample is treated in the same way as the second except that the sulfuric acid hydrolysis is preceded by the step of immersion for 30 minutes in 100 times the sample weight of a 5 percent by volume solution of acrylonitrile in aqueous sodium borate (pH 9.2) at 32° C. After this step, which renders the thiol groups inactive by blocking, the sample is subjected to the 17-hour sulfuric acid hydrolysis step and to titration as in the case of the first two samples. The results are expressed as millimoles per gram of sample of residual S-sulfo groups after reversal, designated MNP_3.

From the foregoing, the millimoles of S-sulfo group per gram of original sample can be calculated as follows:

$$\text{Millimoles S-sulfo groups per gram of sample} = \frac{MNP - MNP_2}{2} + MNP_3$$

The difference between MNP_1 and the foregoing gives the millimoles of thiol groups per gram of sample, from which the ratio can be computed.

Following sulfitolysis of the keratin fibers, in the practice of the present invention, the excess sulfitolysis solution is removed from the fibers as by rinsing with water and there is then applied to the fibers an aqueous solution comprising the desired sulfur-containing compounds. The water-soluble compounds which may be used include the alkali metal, ammonium, and lower alkanolamine sulfides and hydrosulfides as well as the water-soluble aliphatic mercaptans and aliphatic disulfides as well as mixtures. By the term "lower alkanolamines" is meant mono-, di-, and triethanolamine, and mono-, di-, and tri-isopropanolamine. Among satisfactory water-soluble mercaptans are cysteine, thio-glycolic acid, dimercaptoadipic acid, thiolactic acid, beta-mercaptopropionic acid, thioglycol, thioglycerol, and mercaptoethyl sulfonate; in general open chain aliphatic mercaptans containing not over six carbon atoms and containing one or more hydroxyl groups, amino groups or acidic groups, such as carboxylic or sulfonic are satisfactory. The useful disulfides include those corresponding to the foregoing mercaptans, for example, cysteine, dithiodiglycolic acid, the cyclic disulfide of dimercaptoadipic acid, the disulfide of thiolactic acid, the disulfide of beta-mercaptopropionic acid, and the like.

The process of the present invention is concerned only with sulfitolyzed hair in which the ratio of S-sulfo groups to thiol groups is 1:4 or greater, up to and including such hair in which no thiol groups but only S-sulfo groups are present.

The sulfides or hydrosulfides or mercaptans or mixtures thereof can be used in regenerating sulfitolyzed hair which contains only S-sulfo groups and no thiol groups as well as sulfitolyzed hair containing mixtures of S-sulfo groups with thiol groups in ratios down to as low as 1:4. These compounds have optimum effectiveness, however, when the ratio is above 4:1.

The aliphatic disulfides can be used as the sole sulfur-containing compound in practicing the regeneration step when the ratio of S-sulfo groups to thiol groups in the sulfitolyzed hair ranges from 4:1 to 1:4. When the aliphatic disulfide is used in admixture with the sulfides or hydrosulfides or mercaptans, however, the mixture may be used over the entire range from 100 percent S-sulfo groups down to as low as a ratio of 1:4 S-sulfo:thiol groups.

The sequence of reaction steps involved in rebuilding with a soluble disulfide is believed to be as follows:

Firstly, it is believed that the disulfide reacts with a keratin thiol group to generate mixed disulfide and a mercaptan:

$$K\text{-}S^- + R\text{-}S\text{-}S\text{-}R \rightleftharpoons K\text{-}S\text{-}S\text{-}R + R\text{-}S^- \quad (6)$$

The mercaptan so generated is available to reform one disulfide crosslinkage from two keratin S-sulfo groups, and to form 1 mole of sulfite, as explained above in reaction (4); the sulfite then reacts with the unstable mixed disulfide arising from reaction (6), either a keratin thiol group or a keratin S-sulfo group being liberated; it is believed, according to the following reactions:

$$K\text{—}S\text{—}S\text{—}R + SO_3{=} \begin{cases} \rightarrow K\text{—}S^- + R\text{—}S\text{—}SO_3^- \\ \rightarrow K\text{—}S\text{—}SO_3^- + R\text{—}S^- \end{cases} \quad (7)$$

Rebuilding of disulfide crosslinkages then proceeds according to the reverse of reaction (1). The rebuilding may be promoted by removal of the sulfite from reaction (1). In addition, elevation of pH is helpful, as the higher the pH, the farther to the left lies the equilibrium in reaction (1).

Consideration of the mechanism of the disulfide rebuilding postulated above makes it evident that there is no upper limit to the reagent concentration above which the rebuilding becomes less effective. The reagent concentration may be selected in any given case on the basis of extent and rate of rebuilding desired, economics, and similar factors. In general, there is no advantage in using a concentration of disulfide above 1.0 molar. When a disulfide is present, it is usually desirable that it amount to at least 0.02 'molar.

The pH of the solution of sulfur-containing compounds may vary from 5 to 11, although it is preferred that it be maintained from 6 to 10 for solutions to be used in restoring sulfitolyzed wool, and that it be maintained from 5 to 9 in solutions to be used on hair. For best results the pH of the solution should be maintained from 7 to 9 in every case. The carboxylic groups present in certain aliphatic mercaptans and disulfides may be in the form of carboxylate groups, e.g., ammonium carboxylate, in the case of those solutions in the higher pH range. The amount of sulfur-containing compound present in the aqueous solution, exclusive of disulfide present, may vary over a wide range from 0.02 to about 0.3 mole per liter.

The aqueous solution of the sulfur-containing compound may be applied to the keratin fibers in the same manner as the sulfitolyzing solution is conventionally applied. While the temperature of the solution may be above 35° C., even as high as 50° C., in some cases as for example in the case of wool, it is generally preferred to maintain the temperature no higher than 35° C., particularly in applying the solution to hair on a human head. For effective restoration of sulfitolyzed hair, the solution of the sulfur-containing compound must be maintained in contact with the hair fibers for at least about 5 minutes at room temperature. While a period of 30 minutes usually suffices to ensure complete restoration of the hair fibers, there are no adverse effects from maintaining the solution in contact with the hair for longer periods of time. In the case of wool, the fibers of which are usually smaller in cross section than hair fibers, as little as 2 minutes contact of the wool with the solution of sulfur-containing compound suffices to produce substantial restoration of the sulfitolyzed fibers and complete restoration is ensured with less than 30 minutes contact, but longer contact does no harm.

Following treatment of the fibers with aqueous solution of sulfur-containing compound, the fibers may simply be washed with water and dried. When the sulfur-containing compound is an aliphatic mercaptan, it may be desirable in some cases to include an additional step, either in place of or in addition to the water rinsing, namely, contacting the hair with a solution of a conventional neutralizing agent of the type used in hair waving. Such solutions contain conventional oxidizing agents such as peroxides, bromates, perborates, percarbonates, and the like which serve to oxidize any excess mercaptan sorbed in the fibers or incompletely removed during the rinsing step.

The following specific examples are intended to illustrate more fully the nature of the present invention without serving as a limitation upon its scope.

EXAMPLE 1

Bundles of brown European hair fibers 10 inches long were immersed in water at 30° C. for 1 hour. The modulus of the hair was measured by stretching the bundle of hair between two supports so that the bundle was extended by 1 percent of its length, then measuring the force required to produce an additional extension of 0.2 percent of the length of the bundle.

Following the measurement, the water in which each bundle was immersed was replaced by an aqueous solution of 1M ammonium bisulfite and 0.5M potassium tetrathionate adjusted to pH 9.5 with ammonium hydroxide. After maintaining the solution in contact with the hair bundle for 1 hour at 30° C., this solution was replaced with water. At this point analysis showed the ratio of S-sulfo groups to thiol groups to be 19:1. After 20 minutes the water was in turn replaced by a solution of a sulfur-containing compound as identified in the following table, a different solution being used for each hair bundle. After each hair bundle had been exposed for 20 minutes to the selected solution, the solution was replaced by water, with which the bundle remained in contact for a further 20 minute period. The modulus of the hair bundle was measured, following the same procedure described above, at various stages of the treatment. The results reported as a percentage of the value determined initially, before sulfitolysis (relative modulus), are given in the following table for measurements made immediately before exposure of the hair bundle to the solution of the sulfur-containing compound and again made after the final water wash.

Solution of sulfur-containing compound (all at pH 8)	Relative modulus, percent: After sulfitolysis and washing	Relative modulus, percent: After final washing
0.1M ammonium thioglycolate	42	75
0.1M Cysteine	43	78

When an aqueous solution of ammonium hydroxide or of hydrogen peroxide was substituted for the solution of the sulfur-containing compound, there was no substantial increase in relative modulus from the value determined after sulfitolysis and washing. A low value of relative modulus indicates weakness or inferior physical properties of the hair.

EXAMPLE 2

The same procedure was employed as in Example 1 except that the sulfitolyzing solution was adjusted to pH 6 with ammonia rather than to pH 9.5, which produced approximately

the same ratio of S-sulfo groups to thiol groups. The aqueous solutions of sulfur-containing compounds contained only ammonium thioglycolate adjusted to pH 8 at varying concentrations. The effectiveness of these solutions in restoring the keratin is shown by the measurement of relative modulus as set forth in the following table.

Solution of ammonium thioglycolate (at pH 8)	Relative modulus, percent: After sulfitolysis and washing	After final washing
0.2 M	49	73
0.1 M	47	79
0.05M	47	51

Measurements of extent of swelling of the hair fibers and analysis of the hair fibers for cysteine content also show the great effectiveness of the method of the present invention for restoring the fibers after sulfitolysis to a condition similar to that of untreated hair.

EXAMPLE 3

Samples of brown European hair, 1 gram in weight, were immersed in an aqueous solution 1M in ammonium bisulfite and 0.2M in potassium trithionate, adjusted to pH 7 by means of ammonia, at 35° C. for 30 minutes. They were then rinsed for 1 minute in deionized water at which point they contained S-sulfo groups and thiol groups in a ratio of about 19:1. Each of the samples was immersed for 15 minutes in one of several different rebuilding solutions, all of which were adjusted to pH 7, at 35° C. The rebuilding solutions used included cysteine at concentrations of 0.004M, 0.016M, and 0.1M, and sodium hydrosulfide at 0.1M. The samples were then rinsed with water.

Portions of the samples were equilibrated with an atmosphere of 65 percent relative humidity; one portion was analyzed for thiol content, and another for total sulfur content.

The data showed that even as low a concentration of cysteine as 0.004 mole per liter effects a significant amount of restoration, as judged by reduction in thiol content, the effectiveness increasing with concentration to 0.1 mole per liter. As judged by both the residual thiol content and the fiber swelling, sodium hydrosulfide is highly effective.

EXAMPLE 4

Tresses of brown European human hair, 5 inches long, weighing 1 g. each, and having the fibers glued to plastic tabs at their rootward ends, were shampooed, and then saturated with a solution 1M in ammonium bisulfite, 3M in urea, which had its pH adjusted to 7.0 by means of ammonia. The tresses were then wound on waving rods, placed on a flat surface maintained at 35° C., and covered with a plastic sheet. After 15 minutes, the tresses were resaturated with the same solution, and the treatment was allowed to continue for a further 15 minutes; the wound tresses were then rinsed with warm-running tap water for 2 minutes. Analysis showed the ratio of S-sulfo groups to thiol groups in the sulfitolyzed hair to be approximately 1:1. The tresses were then saturated with the various solutions listed in the table below, and allowed to react for 10 minutes, after which time they were unwound from the rods, and resaturated with the solution. Ten minutes later they were thoroughly rinsed with water and air dried.

The tresses were wetted out and rated for degree of curl impartation by comparison with a graded series of photographs on which grade 1 represents completely straight hair, and grade 10 an excessive amount of curl; they were then wound on setting rollers of ¾-inch diameter, and allowed to dry at room temperature overnight. At this point they were unwound, suspended in an atmosphere of 65 percent relative humidity, and the increase in the hanging length with time, which is a measure of the set-holding effectiveness of the process, was determined. In the table below, the hanging length after 24 hours, in centimeters, is recorded in the column labeled "Set-Holding." (The lower the values, the better the set-holding.)

Solution	Wet Curl	Set-Holding, cm.
0.375M hydrogen peroxide	5	5½
0.10M cysteine, pH 7	3½	5½
0.10M ammonium dithiodiglycolate, pH 9	4	5
Untreated hair	2	8½

Although the set-holding characteristics of the hair treated with a solution of cysteine were the same as those treated with a solution of hydrogen peroxide, as shown by the results set forth in the table, nevertheless all of the S-sulfo groups present in the hair fibers were eliminated by the cysteine treatment but were not eliminated by the treatment with hydrogen peroxide. Consequently the physico-chemical characteristics of the hair treated in accordance with the present invention, such as its solubility in aqueous alkali solutions and the extent to which it swells in aqueous thioglycolate solutions, are greatly superior to the characteristics of hair treated with hydrogen peroxide solution. Since the sulfitolysis procedure employed in the present example, using ammonium bisulfite without any oxidizing agent or polythionate, produced a ratio of S-sulfo groups to mercapto groups of about 1:1 in the keratin molecules of the hair, an aliphatic disulfide, viz: ammonium dithiodiglycolate, is effective as the sulfur-containing compound used for restoring the keratin as shown by the results set forth in the table. Hair treated with the solution of the disulfide not only displayed set-holding characteristics superior to the hair treated with hydrogen peroxide but also displayed superior resistance to dissolution in alkali and to swelling in thioglycolate solution.

EXAMPLE 5

Tresses about 3 inches long were prepared from Negro hair from female heads in the manner described in Example 3. After thorough shampooing with a solution of nonionic detergent, each tress was saturated with a solution 1M in ammonium bisulfite and 3M in urea, adjusted to pH 7.0 by means of ammonia, and thickened by the addition of 1 percent of a guar gum thickener.

The tresses were then placed on a flat surface maintained at 33° C., and covered with a plastic sheet. After 15 minutes, the plastic sheet was removed, the tresses were resaturated with the solution, and then periodically combed for the next 15 minutes. The treatment was concluded by a 2-minute running tap water rinse, resulting in a ratio of S-sulfo groups to thiol groups in the hair of approximately 1:1. Thereafter, duplicate tresses were saturated, by combing on, with the solutions shown in the table below, which were allowed to remain in contact with the hair for 5 minutes before rinsing, shampooing and air-drying.

The hair was then rated for degree of curl removal, using a subjective scale on which "5" represents complete straightening, and "0" no straightening, by three skilled observers.

Solution	Straightening
0.375M hydrogen peroxide	4.0
0.10M cysteine, pH 7	2.7
0.10M dithiodiglycolate, pH 9	4.7
Untreated hair	0

Although the treatment with the solution of cysteine was less effective for straightening than was treatment with a

hydrogen peroxide solution, nevertheless the hair possessed superior physicoechemical characteristics as described in Example 4.

EXAMPLE 6

An undyed wool-worsted flannel, of plain weave construction, weighing 5 oz./sq. yd., was cut into rectangular swatches 5 inches long in the filling and 25 inches long in the warp direction.

The swatches were immersed for 5 minutes, at 25° C., in an aqueous solution 0.2M in sodium bisulfite, 1M in urea, adjusted to pH 7 by means of sodium hydroxide and containing 0.01 percent of a nonionic wetting agent. The ratio of weight of fabric to volume of reagent solution was 20:1.

Excess solution was removed from the swatches by a passage between rubber-covered squeeze rolls at a pressure of 50 lbs./sq. in., and they were then allowed to dry and condition by an overnight exposure to an atmosphere of 65 percent relative humidity at 70° F. The sulfitolyzed wool fibers contained S-sulfo groups and thiol groups in a ratio of approximately 1:1.

Each sample was then folded in half along the warp direction and pressed in a Hoffman press using a 15-second steaming, 45-second baking cycle.

Some of the swatches were then subjected to the various treatments listed in the table below; the treatments consisted of a 5-minute immersion in the appropriate solution at room temperature, with the crease closed.

Samples of each swatch were then taken for the determination of alkali-solubility. The remainder of each swatch was then immersed for 30 minutes, with the crease open, in a dilute pH 7 buffer at 35° C., to evaluate the stability of the crease. The samples were then air-dried while hanging with the crease in a vertical position, and the sharpness of the residual crease was assessed, under oblique lighting conditions, by three skilled observers. The creases were rated on a scale on which 5 = perfect crease, and 1 = no crease.

Solution	Alkali Solubility, %	Residual Crease
None	15.1	2¾
Water	13.7	4
0.375M hydrogen peroxide	10.1	5
0.10M cysteine, pH 7	9.8	5
0.10M ammonium dithiodiglycolate, pH 9	9.1	5
Untreated fabric	9.3	1

The data show that the mercaptan and the disulfide are equivalent to the oxidant, hydrogen peroxide, in the stabilization of the crease but superior in the restoration of the chemical condition of the wool, as indicated by the alkali solubility value.

Although specific embodiments of the invention have been described herein, it is not intended to limit the invention solely thereto but to include all of the variations and modifications which suggest themselves to one skilled in the art.

What is claimed is:

1. The method of treating keratin fibers which comprises first reacting the fibers with a first aqueous solution containing a member of the group consisting of water-soluble sulfites, bisulfites, and hydrosulfites to form S-sulfo groups and thiol groups in a ratio of at least 1:4 in the keratin or to form S-sulfo groups alone in the keratin, removing the excess of said first solution changing the configuration of the fibers, and subsequently bringing said keratin fibers while maintained in changed configuration into contact with a second aqueous solution comprising from 0.02 to about 0.3 mole per liter of a water-soluble sulfur-containing compound selected from the group consisting of alkali metal, ammonium, and lower alkanolamine sulfides; alkali metal, ammonium and lower alkanolamine hydrosulfides; aliphatic mercaptans; and mixtures thereof with each other and with aliphatic disulfides; at a pH of 5 to 11.

2. The method of treating keratin fibers which comprises first reacting the fibers with a first aqueous solution containing a member of the group consisting of water-soluble sulfites, bisulfites, and hydrosulfites to form a mixture of S-sulfo groups and thiol groups in a ratio of 4:1 to 1:4 in the keratin, removing the excess of said first solution, and changing the configuration of the fibers, and subsequently bringing said keratin fibers while maintained in changed configuration into contact with a second aqueous solution comprising from 0.02 to about 0.3 mole per liter of a water-soluble aliphatic disulfide at a pH of 5 to 11.

3. The method as claimed in claim 2 in which the keratin fibers comprise human hair, the aliphatic disulfide is present in an amount of at least 0.02 mole per liter, the pH of said second solution is 7 to 9, and the temperature of said second solution is from room temperature to 35° C.

4. The method as claimed in claim 1 in which the keratin fibers comprise human hair, the sulfur-containing compound comprises an aliphatic mercaptan in an amount from 0.02 to 0.3 mole per liter, the pH of said second solution is 7 to 8, and the temperature of said second solution is from room temperature to 35° C.

5. The method as claimed in claim 4 in which said mercaptan is ammonium thioglycolate.

6. The method as claimed in claim 4 in which said mercaptan is the ammonium salt of cysteine.

7. The method as claimed in claim 1 in which the keratin fibers comprise wool, the pH of said second solution is 7 to 8, and the temperature of said second solution is from room temperature to 50° C.

8. The method as claimed in claim 2 in which the keratin fibers comprise wool, the pH of said second solution is 7 to 9, and the temperature of said second solution is from room temperature to 50° C.

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