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MODIFICATION OF KERATIN TO THE S-SULFO FORM

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ABSTRACT OF THE DISCLOSURE

A composition in the form of a particulate mixture of reducing agent including water-soluble sulfite, bisulfite or hydrosulfite with oxidizing agent including water-soluble trithionate, tetrathionate, pentathionate or hexathionate, the composition being useful, when in water solution at pH 4.5–11, for treating hair or wool.

This application is a continuation-in-part of copending application Ser. No. 488,759 filed Sept. 20, 1965, now abandoned.

This invention relates to a composition and method for the chemical modification of keratin-containing fibers and to the use of such modification in depilation of hair or in imparting to wool resistance to felting and shrinkage during laundering or in increasing the ease with which such fibers may be dyed.

The keratin-containing fibers to which the present invention relates include both human hair and animal hair, such as wool.

One object of the present invention is to provide a composition and method for modifying keratin-containing fibers to permit them to be softened or dissolved under mild conditions, i.e. at moderate temperatures without the necessity for using strong alkali.

Another object is to provide a composition and method for producing a high proportion of S-sulfo groups (—S—SO_3^- groups) in keratin-containing fibers in a single step without use of a metal catalyst.

Another object is to provide a stable dry keratin fiber, substantially free from metal, having its chemical composition modified by the rupture of disulfide linkages and formation of S-sulfo groups to enhance its dye receptivity and to improve its set-holding characteristics.

Still another object is to provide a stable wool textile fabric having enhanced resistance to felting or laundering shrinkage.

Other and further objects will be apparent from the description which follows.

It has now been found that dry (i.e. substantially free from water) finely-divided particulate solid mixtures of water soluble reducing agents which are sulfites, bisulfites, or hydrosulfites, with water soluble oxidizing agents which are trithionates, tetrathionates, pentathionates, or hexathionates are effective, when dissolved in an aqueous medium, to react with keratin-containing fibers at room temperature or elevated temperature to convert the disulfide linkages of the keratin into the S-sulfo form with concomitant swelling and softening of the fiber.

Among the materials which may be used are the ammonium and alkali metal and mono-, di-, or tri-lower alkanolamine salts of the foregoing anions. The mixture may contain compounds having different cations as well as the same cations. By means of the present invention the extent to which the fibers may be reacted is much greater than can be achieved when the reducing agent alone is used to react with the hair. The compositions in either dry form or in the form of aqueous dispersion or solution are nontoxic when applied to the skin. The compositions in dry form are very stable and may be stored over long periods of time. After the addition of water to form a solution or slurry, however, the composition is relatively unstable and should not be stored for an extended period of time before use.

While the mechanism of the reactions may not be fully understood and we do not wish to be bound by the following theory, it is believed that tetrathionate, pentathionate and hexathionate react with the reducing agent to form a trithionate; in the case of tetrathionate, one mole of sulfite reducing agent reacts with each mole of tetrathionate to form the trithionate; in the case of pentathionate, two moles of sulfite react to form trithionate; and in the case of hexathionate, three moles of sulfite react to form trithionate. The general equation for such reactions is:

$$S_nO_6^{--}+(n-3)SO_3^{--}\rightleftharpoons S_3O_6^{--}+(n-3)S_2O_3^{--}$$

where n is an integer from 4 to 6. It is also believed that no rapid reaction occurs between the trithionate and the reducing agent but that the reducing agent reacts with the disulfide linkages in the keratin to form an S-sulfo group and a thiol group from each such linkage, and that the trithionate oxidizes each thiol group thus produced back to the disulfide form. The present invention makes it possible to produce considerably more than the one milliequivalent of S-sulfo group from each milliequivalent of disulfide linkages, as shown in greater detail below, because, it is believed, some of the disulfide linkages thus formed again are again ruptured in a continuing series of reactions.

The relative proportions of reducing agent and of oxidizing agent may vary over a considerable range; when only sulfite and trithionate are present, for example, any mole excess of trithionate over the sulfite performs no useful function; an excess of sulfite over trithionate, however, is available for reacting with the keratin as pointed out above. When sulfite and tetrathionate or higher polythionates are in the mixture some of the sulfite reacts with the polythionate leaving only the balance to react with the keratin; under these circumstances an excess of the reducing agent is preferred. In general, from 0.05 to 2 moles of oxidizing agent should be present for each mole of reducing agent for best results, subject to the foregoing provision that excess reducing agent should be present when a noxidizing agent other than trithionate is used.

The concentration of reducing agent and oxidizing agent in the aqueous solution or slurry may vary widely. In general, the composition may contain from 0.1 to 4 moles per liter of reducing agent, together with from 0.05 to 2 moles of oxidizing agent for each mole of reducing agent. The eqeuous composition may have a pH

from 4.5 to 11, but the reaction proceeds most rapidly at pH 6–7. When the invention is employed to shrink-proof wool or to render it more susceptible to dyeing, it is preferred to employ a short treatment of the keratin fiber with the aqueous composition at a pH value above 8 so as to obtain maximum conversion of the disulfide linkages in the surface portion of the keratin fibers with minimum conversion of the disulfide linkages in the interior of the fiber. On the other hand, when uniform modification of the entire keratin fiber is desired the best results are obtained using longer treatment of the fibers with the composition at a pH value of 8 or below. While any conevntional alkaline material may be used for adjusting the pH if desired, ammonium hydroxide is usually preferred. If desired, any of the conventional buffer salts may be used to maintain the pH within desired range.

There may also be incorporated in the composition protein swelling agents such as urea, isopropanol, lithium bromide, phenol, and the like. These swelling agents increase the rate of formation of S-sulfo groups as well as enhance the swelling of the keratin fibers. When used, such swelling agents generally may be present in amounts up to 8 moles per mole of reducing agent, preferably from 1 to 8 moles per mole of reducing agent, the exact amount present depending upon the identity of the particular swelling agent employed and upon the effect desired. If excessive amounts are present they may be insoluble, or may cause salting out of other ingredients. When the composition is to be used for dehairing hides, or for depilation of the human skin, the presence of such swelling agents is particularly desirable.

When it is desired to confine the effect of the composition to the surface of the keratin fiber and to minimize swelling, as for example in the process of shrink-proofing wool, there may be included in the composition a deswelling agent such as an inert water soluble salt such as sodium chloride, potassium chloride, sodium sulfate, magnesium sulfate, etc., generally in amounts up to 4 moles per mole of reducing agent, preferably from 0.5 to 4 moles per mole of reducing agent, the precise amount present depending upon the identity of the salt and the effect desired, as in the case of swelling agents.

Upon using the composition it is first mixed into an aqueous medium then applied to the keratin fibers either at room temperature or at elevated temperatures which may be as high as the boiling point of the solution when it is used for dehairing hides or for shrink-proofing wool. However, in general, it is preferred to use temperatures from room temperature up to about 40° C.

In making use of the compositions of the present invention for dehairing hides or for depilation the aqueous composition is simply left in contact with the keratin fibers for a sufficient period of time to swell and soften the fibers so that they may readily be removed from the skin or hide by gentle rubbing or scraping. As little as 5 minutes contact provides rupture of a susbtantial portion of the disulfide linkages in the hair, at least half of the side chain end groups resulting from the rupture being S-sulfo groups which are not removed by rinsing with water. In dehairing cattle hides or other animal hides, it is possible to permit the reaction to proceed until virtually all of the disulfide linkages in the hair fibers are ruptured, but the fibers are so weakened when about half of the disulfide linkages have been ruptured that the fibers may be readily removed mechanically.

The following specific examples are intended to illustate more clearly the nature of the present invention without limiting the scope thereof.

EXAMPLE 1

There were prepared a series of aqueous solutions each containing 1 molar ammonium bisulfite and containing sodium tetrathionate in varying concentrations as set forth in the table below. Each solution was adjusted to pH 7 by ammonium hydroxide. There was immersed for 30 minutes in a 50 ml. portion of each solution at 35° C. a 1 gram sample of brown European human hair. Each hair sample was then removed from the solution and rinsed in running water for 5 minutes, during which time most remaining pairs of thiol groups and S-sulfo groups recombined to form disulfide linkages. The hair samples originally contained 0.75 milliequivalent of disulfide linkages per gram of hair. The extent to which S-sulfo groups remained in the keratin fiber without being reconverted to the disulfide linkage was then determined by first alkylating any remaining thiol groups by immersing the hair for 15 minutes in a 1 molar aqueous solution of acrylonitrile at pH 9.2, then hydrolyzing the hair by immersing for 2 hours at 105° C. in 25 ml. of 30 percent sulfuric acid to convert the remaining S-sulfo groups into thiol groups, the concentration of which was then determined by titration with an organomercurial (salyrganic acid) using sodium nitroprusside as an indicator. The titer is reported in the following table as milliequivalents of irreversible (i.e. irreversible by dilution of the solution) S-sulfo groups per gram of hair.

Concentration of sodium tetrathionate, molarity:	Irreversible S-sulfo groups
0.0	0.08
0.2	0.65
0.4	0.68
0.6	0.63
0.8	0.42
1.0	0.22

The results set forth in the table clearly show that the presence of even a small proportion of sodium tetrathionate in the solution leads to a remarkable increase in the number of irreversible S-sulfo groups present in the keratin fiber and that the effectiveness of the mixture decreases when the amount of sodium tetrathionate approaches the amount of ammonium bisulfite present. Even when the molar concentration of reducing agent and oxidizing agent in the solution is the same, however, the effectiveness of the solution of the mixture is very much greater than that of a solution of the reducing agent alone because the reaction between the sodium tetrathionate and the ammonium bisulfite is an equilibrium reaction, leaving some ammonium bisulfite available to react with the hair keratin.

EXAMPLE 2

The same procedure was followed as in Example 1 above except that sodium trithionate was substituted for sodium tetrathionate. The results obtained are set forth in the following table.

Concentration of sodium trithionate, molarity:	Irreversible S-sulfo groups
0.0	0.08
0.1	0.56
0.2	0.77
0.3	0.81
0.4	0.84
0.5	0.86
0.75	0.89
1.0	0.88

The results clearly show that the presence of a small amount of sodium trithionate in the aqueous solution produces a very large increase in the proportion of irreversible S-sulfo groups formed in the keratin fiber and also show that the effectiveness of the mixture does not decrease when the amount of sodium trithionate approaches the amount of reducing agent.

EXAMPLE 3

The procedure of Example 1 was followed but sodium pentathionate was substituted for sodium tetrathionate. The results were as set forth in the following table.

Concentration of sodium pentathionate, molarity:	Irreversible S-sulfo groups
0.0	0.08
0.2	0.50
0.5	0.65

These results also demonstrate the superior effectiveness of the aqueous solution of the mixture as compared with an aqueous solution of the reducing agent alone.

EXAMPLE 4

A solution was prepared by dissolving in water a mixture of sodium hydrosulfite and sodium trithionate, the concentration of the hydrosulfite being 0.6 molar and that of the trithionate being 0.2 molar, so that the mole ratio of oxidizing agent to reducing agent was approximately 0.33:1. The pH of the solution was adjusted to 7 by means of ammonium hydroxide. There was immersed in a 50 ml. portion of this solution maintained at 35° C. 1 gram of brown European human hair for 6 hours. The hair samples originally contained 0.75 milliequivalent of disulfde linkages per gram of hair. The hair was then removed, rinsed in water and the concentration of irreversible S-sulfo groups was determined as described in Example 1 and found to be 0.69 milliequivalent per gram.

EXAMPLE 5

A mixture of 13.5 g. sodium tetrathionate (50 millimoles), 6.1 g. of sodium sulfite (50 millimoles), and 5.4 g. of sodium bisulfite (50 millimoles) was triturated and stored in a loosely covered container. This particulate solid mixture was then dissolved in water to make 100 ml. of solution having a pH of 7. One gram of brown European human hair was immersed in the solution maintained at 35° C. for 30 minutes. The hair samples originally contained 0.75 milliequivalent of disulfide linkages per gram of hair. After removal from the solution and rinsing the irreversible S-sulfo group content of the treated hair was found to be 0.33 milliequivalent per gram.

A composition was prepared as described above except that there was substituted for the tetrathionate 12.0 g. of sodium trithionate (50 millimoles). Hair treated with a solution prepared from this composition as described above had an irreversible S-sulfo group content of 0.72 milliequivalent per gram.

EXAMPLE 6

An aqueous solution was prepared containing 0.6 molar ammonium bisulfite, 0.2 molar sodium tetrathionate, and 3 molar urea. Several different 50 ml. portions of the solution were adjusted to various pH values by means of ammonium hydroxide as set forth in the following table. One gram of brown European human hair was immersed in each of the 50 ml. portions maintained at 35° C. for 10 minutes, and the concentration of irreversible S-sulfo groups was determined as described in Example 1 above. The hair samples originally contained 0.75 milliequivalent of disulfide linkages per gram of hair. The results obtained are set forth in the following table.

pH:	Irreversible S-sulfo groups
7.0	0.24
8.0	0.29
9.0	0.26
9.7	0.25

While the extent of formation of irreversible S-sulfo groups was approximately the same in each solution, microscopic examination of the keratin fibers showed that the solutions having higher pH values penetrated more slowly into the interior of the fibers.

EXAMPLE 7

An aqueous solution was prepared containing 1 molar ammonium bisulfite and 0.5 molar sodium tetrathionate. To several different 50 ml. portions of this solution there were added various quantities of keratin swelling agents as set forth in the following table and the pH of each portion was adjusted to 7 with ammonium hydroxide. One gram of brown European human hair was immersed in each portion maintained at 35° C. for 30 minutes. The hair was then removed from each portion of solution and the number of irreversible S-sulfo groups was determined as described in Example 1 above. In addition, the extent of swelling of the hair in a buffer at pH 7 was determined by means of a standard procedure. The results are set forth in the table below.

Swelling agent	Irreversible S-sulfo groups	Swelling
Untreated hair		31
None	0.68	131
2 molar urea	0.84	172
4 molar urea	0.84	340
2 molar isopropanol	0.83	177
4 molar isopropanol	0.84	213

It is clear from the results set forth that the swelling agents increase the extent of formation of irreversible S-sulfo groups as well as increasing the disruption of the keratin protein structure as shown by the increased swelling capability.

EXAMPLE 8

An aqueous solution was prepared containing 0.6 molar ammonium bisulfite, 0.3 molar sodium trithionate, and 3 molar urea. The pH of the soluton was adjusted to 7 by means of ammonium hydroxide. A piece of salted steer hide measuring 3 inches by 3 inches was rinsed in water to remove the salt and then immersed in the solution maintained at 35° C. for 45 minutes. After this immersion the hair was sufficiently loosened to be readily removed by means of a wooden scraper. This contrasts with conventional dehairing methods which require several hours to several days to achieve the same extent of loosening of the hair fibers. Similar results are obtained when treating cow hide, the process being applicable to cattle hair generally as well as to other animal hair.

EXAMPLE 9

An aqueous solution was prepared containing 1 molar ammonium bisulfite and 0.8 molar potassium trithionate, and the pH was adjusted to 7 by means of ammonium hydroxide. A piece of cotton gauze was saturated with the solution, applied to the skin of a woman's forearm, and covered with a plastic wrap. After 20 minutes the hair fibers on the portion of the arm so treated could be pulled out with very little effort.

EXAMPLE 10

Four different aqueous solutions were prepared containing ingredients in the concentrations given in the following table, the pH of all four solutions being 9.6. Small squares of undyed woolen flannel were immersed in portions of each of the solutions, 50 ml. of solution being used for each gram of fabric. After immersion for 15 minutes while maintaining the temperature of the solution at 35° C. the samples were removed, thoroughly rinsed with water, and then with an aqueous solution containing 0.1 molar borax to cause any remaining thiol groups in the keratin fiber to combine with the S-sulfo groups. The dimensions of the flannel squares were then measured and each was hand-milled with a 5 percent aqueous solution of sodium oleate soap and the dimensions were measured again to determine the extent of shrinkage. The results obtained are set forth in the following table.

	Solution composition, molarity				
	Sodium sulfite	Sodium thithionate	Sodium tetrathionate	Potassium chloride	Area shrinkage, percent
A	0.5	0.2	None	None	8.8
B	1.0	0.2	None	None	0.6
C	1.0	0.2	None	3	0.6
D	1.0	None	0.2	None	0.7
	Untreated				29.2

All of the specimens had a satisfactory hand and appearance after the treatment, sample C being the best.

EXAMPLE 11

There was prepared an aqueous solution containing 1 molar ammonium bisulfite and 0.2 molar sodium trithionate, and it was adjusted to pH 7 by adding ammonium hydroxide. Several different swatches of undyed wool flannel measuring 6 inches by 6 inches were immersed in individual 100 ml. portions of the solution, some for 10 minutes at 35° C., others for 30 minutes at 25° C. The swatches were then removed, rinsed thoroughly with water, and then with an aqueous solution containing 0.05 molar borax to cause any residual thiol groups in the keratin fiber to recombine with the S-sulfo groups.

Portions of the treated swatches along with an untreated swatch as control were then dyed by immersion in solutions of basic dyes and acid dyes. In all cases the treated swatch was markedly more deeply dyed than was the untreated control.

EXAMPLE 12

There were prepared 50 ml. portions of aqueous solution containing 0.6 molar ammonium bisulfite, 0.3 molar sodium tetrathionate, and 0.3 molar urea, adjusted with aqueous ammonia to pH 6. A one gram sample of brown European hair was immersed in each portion while maintained at 35° C. Pairs of samples were withdrawn from the solution after predetermined times. One of these was immediately rinsed with hydrochloric acid (1 normal) to stop the rupture reaction from proceeding further, and then hydrolyzed and analysed for thiol content; the value so obtained is considered to represent the total rupture level of disulfide linkages existing in the keratin at the time of immersion in acid, reflecting both the thiol and S-sulfo groups present; the other sample was rinsed with water, and treated with acrylonitrile as described in Example 1, prior to hydrolysis and analysis to determine the quantity of irreversible S-sulfo groups present. The results are recorded in the following table.

Treatment time	Total rupture [1]	Irreversible S-sulfo groups [1]
Minutes:		
5	0.29	0.09
10	0.49	0.18
15	0.58	0.28
22½	0.68	0.37
30	0.74	0.54

[1] Milliequivalents per gram.

It is evident that under the conditions used here, the total rupture proceeds more rapidly in the initial stages than the formation of irreversible S-sulfo groups. However, the rate of rupture slows down after the first 10–15 minutes, whereas irreversible S-sulfo groups continue to be generated at a constant rate; consequently, after 30 minutes, almost three quarters of the rupture is in the form of irreversible S-sulfo groups.

EXAMPLE 13

One-gram samples of brown European hair were each immersed for 10 minutes at 35° C. in 50 ml. portions of solutions of the following composiiton: 0.6 molar ammonium bisulfite, 0.2 molar sodium tetrathionate, and 3 molar urea, the pH being adjusted to various values by means of aqueous ammonia. The total rupture level and the irreversible S-sulfo group content were determined by the methods described in Examples 1 and 4. The following results were obtained.

pH	Total rupture [1]	Irreversible S-sulfo groups [1]
7.0	0.44	0.24
8.0	0.36	0.29
9.0	0.30	0.26
9.7	0.25	0.25

[1] Milliequivalents per gram.

These data demonstrate that the amount of irreversible S-sulfo groups generated as a proportion of the total extent of rupture, in a short treatment, may be varied by appropriate selection of pH of the reaction medium. As the pH is raised, the rate of total rupture decreases, but the proportion of irreversible S-sulfo groups increases.

Microscopic examination of the course of the reaction between keratin fibers and sulfite solutions has shown that the slower rate of reaction at high pH is associated with a slow rate of penetration of the reagent into the fiber.

EXAMPLE 14

An aqueous solution was prepared containing 1 molar ammonium bisulfite, 4 molar urea, and 0.4 molar potassium tetrathionate, and adjusted to pH 8 by means of ammonia. A tress of European human hair, weighing ½ g., was immersed in 10 ml. of this solution, at 32° C. After one hour, the tress was thoroughly rinsed with water and shampooed. Two additional similar tresses were treated with media of the same composition but diluted with one or two volumes of water per volume of solution respectively.

Single fibers were removed from the tresses and cut in half to provide duplicate fiber specimens. The radius of curvature of each piece was determined; it was then placed, wet, in a circular form ⅝" diameter. Knowing the original radius of curvature of each specimen, and the diameter of the form, the level of strain imposed on each sample could be calculated.

The forms containing the fibers were then maintained at 100% relative humidity for one hour and subsequently at 32% relative humidity for 18 hours to give the fibers a set. The fibers were then taken out of the forms and placed in an atmosphere of 65% relative humidity; the subsequent increase in radius of curvature of the fiber arc was followed over a period of two hours. The "strain ratio," reported in the table below, represents the strain retained by the fiber after two hours relaxation divided by the imposed strain. The higher the strain ratio, the greater the extent to which the hair fiber retained the strain imposed upon it in the ⅝" circular form.

Concentration of solution	Irreversible S-sulfo groups	Strain ratio
Full strength	0.84	0.98
0.5	0.44	0.52
0.33	0.24	0.40
Untreated control fiber		0.34

It is evident that, as the irreversible S-sulfo group content increases, the strain ratio increases also; in other words, the set-holding ability of the hair is improved.

EXAMPLE 15

There was prepared a slurry containing 13.5 g. of sodium tetrathionate (50 millimoles), 6.1 g. of sodium sulfite (50 millimoles), 5.4 g. of sodium bisulfite, and 30.6 milliliters of isopropropanol (400 millimoles). The slurry was found to be stable upon storage in a stoppered container. Shortly before use, sufficient water was added to make 100 milliliters of total composition, having a pH of 6.7.

Two grams of brown European hair were immersed in this solution, maintained at 35° C., for 30 minutes, to

form S-sulfo groups. The hair was then rinsed; the extent of its swelling in a buffer at pH 7 was determined, and found to be 167%.

Keratin fibers and textile fabrics treated in accordance with the present invention may be rinsed with water and dried without loss of the irreversible S-sulfo groups. The fibers and fabrics retain their increased dye receptivity, set-holding ability, and felting resistance indefinitely. When such fibers and fabrics are treated with an aqueous solution of sulfite alone, however, they lose their S-sulfo groups when in contact with wash water, reverting to the properties of untreated materials.

Such stable keratin fibers are those having from 10% to 70% of their disulfide linkages ruptured, at least half of the side chain end groups resulting from the rupture being irreversible S-sulfo groups, i.e. S-sulfo groups which do not recombine with thiol groups in the molecule when the fibers are rinsed with water. Such fibers are free from metal since no metal catalyst is used in the process of the present invention.

What is claimed is:

1. The method of treating keratin-containing fibers selected from the class consisting of human hair, cattle hair and wool which comprises contacting said fibers with an aqueous composition containing in solution a reducing agent selected from the class consisting of water-soluble ammonium, alkali metal, and mono-, di-, or tri-lower alkanolamine sulfites, bisulfites and hydrosulfites and also in solution an oxidizing agent selected from the class consisting of water-soluble ammonium, alkali metal, and mono-, di-, or tri-lower alkanolamine trithionates, tetrathionates, pentathionates, and hexathionates, the concentration of said reducing agent being from 0.1 to 4 moles per liter of said composition, the molar ratio of oxidizing agent to reducing agent being from 0.05:1 to 2:1, said reducing agent being present in molar excess when said oxidizing agent is tetrathionate, pentathionate or hexathionate, the pH of the composition being from 4.5 to 11 and the temperature of said composition being from room temperature to the boiling point thereof, for a period of time of at least 5 minutes, and rinsing with water.

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