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METHOD FOR SETTING KERATINOUS FIBERS

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This invention relates to a method for treating keratinous fibers and filaments, both hereinafter referred to as "fibers." More specifically, it relates to an improved method for treating said fibers so as to impart and maintain a desired configuration therein.

While being adapted to treat keratinous fibers in general, such as hair, wool, and the various furs and epidermal fibers in general, this invention is of particular interest in the field of permanently waving or permanently straightening human hair, and will be particularly described in connection therewith.

Many methods have been proposed for imparting and maintaining the set of human hair, ranging from the mere application of heat to treatment with complex organic and inorganic chemical agents in various combinations. These known methods have in general, however, suffered from one or more of a number of serious disadvantages. Among these disadvantages may be mentioned undesirable bleaching or denaturing (deadening) effects on the hair itself, lack of permanency, and most commonly and seriously, the employment of toxic or otherwise hazardous treating agents.

It is with the "permanent" type of wave that this invention is concerned. Permanent waving methods in general are chemical treatments which involve subjecting the hair, which has been previously set to a desired configuration, to the action of an agent which "de-stabilizes" it, so that it becomes relaxed in the desired configuration, and subsequently restabilizing it, for example by means of a neutralizing solution, so that it is permanently set in said configuration.

Although the exact mechanism of the reactions involved in destabilization and restabilization remains the subject of considerable controversy, it appears that one type of destabilization involves the cleavage of a cystine disulfide (—C—S—S—C) linkage in the hair structure, and the compounds which have been found most effective are those which are capable of cleaving this linkage. Among such compounds are alkalis in 5 to 10% solution, alkali sulfites, ammonium hydrosulfide and more recently, organic sulfur-containing compounds, such as thioglycolic acid and its derivatives.

In most of the known processes, particularly in the various cold-wave and home-permanent processes, it was subsequently necessary to employ an arresting solution or neutralizer to prevent the destabilization from going too far, which would damage or destroy the hair, and also to reconstitute or regenerate as many as possible of the disulfide linkages which had been disrupted by the destabilization (or to form similar linkages with equivalent effects). Among the arresting solutions that have been employed are solutions of divalent metal salts, to form —S—M—S— linkages (M being barium, copper, nickel, etc.), phosgene, and alkalis such as NaOH which regenerate the disrupted —C—S—S—C— linkage as a stable —C—S—C— linkage. In all of these methods, the object was to first disrupt the disulfide linkage and then, the hair being in a relaxed condition and disposed in the desired configuration, to regenerate the broken linkage either in its former state or as a modified

—C—S—M—S—C—

or —C—S—C— linkage.

More recently, it has been proposed to use mercaptans

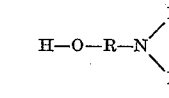
of various types as destabilizing agents. Among the advantages professed for these agents was the fact that certain of the mercaptans were capable of imparting a permanent set without the necessity of employing an arresting agent since they were capable of being sufficiently removed by thorough water-washing. The effectiveness of these agents apparently resulted from the fact that when a destabilizing solution of this type is removed, the ruptured disulfide linkages are left in a sufficiently reactive condition to reconstitute themselves spontaneously.

While the above-described type of destabilization involving cleavage of a disulfide linkage is the one which has been most extensively studied, there are other methods of destabilizing the hair molecule. Among these may be mentioned the cleavage of the hydrogen bond cross-linkages between the amide and the carbonyl groups of the polypeptide chains by such agents as urea and guanidine hydrochloride and cleavage of the "salt bridges" between charged free amino and carboxylic groups by the action of acids, bases, and salts. Destabilization techniques employing these mechanisms are not as fully developed as those involving cleavage of the disulfide linkage, perhaps because it has not heretofore been possible to reconstitute the structure of hair destabilized by these methods. In the practice of the present invention, however, destabilization by these mechanisms appears to function fully as well as disulfide destabilization for the purpose of rendering the hair amenable to waving. Superheated steam is used as a destabilizing agent in some fields of industry, for example in wool treatment. Although not applicable to the waving of human hair in vivo, this destabilizer is also useful, where it is applicable, in the practice of the present invention.

In application Serial No. 302,994, filed August 6, 1952, and now abandoned, a new and improved type of hair-waving process was disclosed, which is basically a "one-solution" process, since the air is waved or curled merely by tensioning it in the desired configuration, applying the agent, which is an aminoalcohol titanate, and subsequently removing the titanate from the hair, for example by washing with water. The action of the aminoalcohol titanates is apparently the result of a coordination between the aminoalcohol titanate and the protein molecule as a whole (not necessarily involving the disulfide or any other particular linkage as such). However, it has also been discovered that this coordination is greatly facilitated if the hair is first destabilized, for example, by one of the known destabilizing agents, such as alkali sulfites, bisulfites and the like, and the degree of wave and ease of waving are thereby enhanced.

An object of this invention, therefore, is to provide an improved method for setting keratinous fibers. A further object is to provide a method for setting keratinous fibers which will impart a greater degree of waving action than previously known methods. Other objects and advantages will become apparent from the following more complete description and claims.

In its broadest aspects this invention contemplates a method for imparting a desired configuration to keratinous fibers which comprises imparting said configuration to said fibers, destabilizing said fibers, and treating said fibers with an aminoalcohol titanate or zirconate. The particular aminoalcoholtitanates and zirconates which are preferred for use in this invention are the titanate and zirconate esters of aminoalcohols having the formula:



in which R is selected from the group consisting of ethylene and alkyl-substituted ethylene radicals, R′ is selected from the group consisting of β-hydroxyalkyl and β-amino-

alkyl radicals and R'' is selected from the group consisting of hydrogen, alkyl hydrocarbon groups containing from 1 to 3 carbon atoms and β-hydroxyalkyl and β-aminoalkyl radicals.

The destabilizing agents adaptable for use in the process of this invention include all the well-known reducing destabilizers, such as alkali sulfides, thioglycolates, and the like, but it is preferred to employ alkali sulfites or bisulfites since these are among the most convenient and effective agents to employ. Non-reducing destabilizers such as urea, guanidine hydrochloride, oxidizing agents, acids, bases, or neutral salts may also be used in place of or in conjunction with the reducing destabilizers (except where they are chemically incompatible). The reason for the effectiveness of these agents and the mechanism whereby the destabilization assists the subsequent coordination of the protein molecule with the aminoalcohol titanate are not completely understood. The titanium values which remain in the hair apparently react with the hair or else are very strongly adsorbed, but the cystine linkage or other linkages which may be cleaved apparently are regenerated as such and not, for example, as a —C—S—C— or C—S—Ti—S—C— bond to any substantial extent. Apparently the cleavage of a linkage leaves the entire protein molecule in an activated state, so that it coordinates more readily with the aminoalcohol titanate even though the linkage itself is apparently not involved in the coordination reaction.

The method of carrying out the process of this invention is simple and may be varied considerably to suit the convenience of the operator. The hair must be destabilized, which is accomplished by applying the destabilizing agent at suitable concentration and temperature. Concentration and temperature depend somewhat upon the nature of the particular destabilizer employed, but in general, most of the destabilizers, including the alkali sulfites and bisulfites, are effective when used in 5 to 10% aqueous solution at room temperature. At higher temperatures, it is frequently possible to use lower concentrations, e.g. about 1%. Application of the destabilizer to the hair may be accomplished in almost any desired way, and either before or after the desired configuration is imparted to the hair, but a preferred and very convenient method is to wind a tress on a curling rod or mandrel and apply the destabilizer as an aqueous solution, using a sponge or the like.

The aminoalcohol titanate solution is also preferably applied to the hair as an aqueous solution. Concentration may be varied within wide limits, however, and those of the aminoalcohol titanates which are liquids may be employed without the addition of any water. In general, it is preferred to maintain the concentration of the aminoalcohol titanate below 75 percent in aqueous solution, to prevent difficulties occasioned by excessive viscosity, and it is even more desirable to have the concentration no higher than about 25%, to avoid wasting the titanate. On the other hand, it is preferred to maintain an aminoalcohol titanate concentration of at least 1 percent in the solution, because solutions having less than this concentration may in some cases give less pronounced waving action on hair which is difficult to wave.

As to the particular titanate chosen, any of the aminoalcohol titanates falling within the scope of the above description may be used but it has been found especially advantageous to use triethanolamine titanate, which is relatively inexpensive and easily prepared.

The exact composition of the aminoalcohol titanate used, with respect to the ratio of aminoalcohol groups to titanium atoms, may be varied between wide limits, but it is preferred to use titanates which contain at least two and a half aminoalcoholic hydroxyl groups for each titanium atom. Examples of compounds meeting this requirement would be the mixed titanate produced by reaction of three mols of diethanolamine with two mols of a suitable titanium ester, such as butyl titanate, or

that produced by reaction of three mols of β-aminoethylethanolamine (which has only one aminoalcoholic hydroxyl group) with one mol of such a titanium ester. Moreover, it is preferred to have from three to eight such hydroxyl groups for each titanium atom. The number of aminoalcohol hydroxyl groups as just described includes all such groups in the aminoalcohol molecule whether they are esterified with the titanium or remain as free hydroxyls. The product produced by the ester interchange reaction of one mol of a titanium ester with two mols of triethanolamine, for example, would be considered to have six aminoalcoholic groups per titanium atom, despite the fact that substantially four of these hydroxyl groups are esterified to form R—O—Ti— linkages.

The duration and temperature of the aminoalcohol titanate treatment are not critical. It has been found that the time required to apply the titanate to the fiber and then remove it is sufficient to effect the desired action, while on the other hand, no undesirable effects accrue if the titanate is allowed to remain in contact with the fiber for extended periods. Similarly, the treatment is most conveniently carried out at room temperature, but may be effected at lower or higher temperatures, even in the neighborhood of the boiling point, without affecting the results produced.

In most cases, it is preferred to remove the destabilizer by rinsing thoroughly with water before application of the titanate solution. In some cases, however, particularly when the sulfite or bisulfite destabilizers are employed, it is possible to omit this step if so desired.

As pointed out above a convenient way of treating keratinous fibers, such as hair, with a destabilizer and aminoalcohol titanate is to first apply the destabilizer to the hair, thereafter remove the destabilizer by thoroughly rinsing the hair with water, and then treating the rinsed hair with an aminoalcohol titanate.

As an alternative procedure the destabilizer and the aminoalcohol titanate may be mixed with water and applied as an aqueous solution to the hair. In this connection when the destabilizing agent is admixed with an aminoalcohol titanate to form a solution for treating hair it is desirable that the pH of the solution be above 6 and and preferably about 9, adjustment of the pH value of the solution within this range being done by the addition of ammonium hydroxide, ammonium carbonate, ammonia and the like. It is also desirable to add a stabilizing agent to the solution to prevent hydrolysis of the titanium values which tend to hydrolyze if the solution is acid or if the pH is above 9. Suitable titanium stabilizing agents are sorbitol and gluconic acid.

Thus by way of illustration a hair waving solution may be prepared first by admixing a thiol, such as thioglycerol or thioglycolic acid, with an aminoalcohol titanate, such as triethanolamine titanate, and to this solution may be added sorbitol and/or gluconic acid to stabilize the titanium values against hydrolysis, and ammonium hydroxide to adjust the pH of the solution to about 9. This solution is then applied to the hair and allowed to remain thereon for a predetermined length of time after which the hair is treated with an oxidizing solution (neutralizer) such as $KBrO_3$ for setting the hair; or the latter step may be dispensed with altogether and a suitable oxidation catalytic agent, such as a manganese salt, added to the hair-treating solution to promote oxidation of the solution upon exposure to the air. It has been found that curls of comparable tightness and permanence may be obtained by either of these two procedures; and that the curls were equally as tight as curls obtained using conventional oxidizing or reducing agents alone. As for other properties it was found that the color, lustre, manageability and odor of curls formed by treating the hair with a solution of an aminoalcohol titanate and a thioglycolate were noticeably superior to curls treated with conventional hair waving agents. Further in this same vein it is com-

monly recognized that a definite deterioration of hair flexibility occurs with the use of conventional hair waving agents. To the contrary it was noted that in no case was the hair embrittled by treatment with a destabilizing agent in the presence of an aminoalcohol titanate.

The treated keratinous fibers produced in accordance with the present invention are well-waved or tightly curled, depending on the vigor and effectiveness of the destabilizing treatment employed, and have a natural appearance indistinguishable from naturally curly or wavy fibers. The treatment is permanent and resistant to washing. When employed for the waving of human hair, the method produces a waved or curled condition that persists until the treated hair "grows out." The treatment is, moreover, easy, inexpensive, and safe to apply, even for the unskilled operator.

This invention has been described with particular reference to the waving of human hair. However, it is pointed out that the novel treating agents and methods of treatment of this invention are equally applicable to other animal epidermal fibers in general such as wool, horse hair and the like. Moreover, the term "waving" is to be broadly construed as including the imparting of any desired configuration to the fiber including the straightening of previously waved or curled fibers. The following examples are presented to further illustrate the nature and use of the treating agents of the present invention.

Example I

A destabilizing solution was prepared from 6.2 parts of sodium metabisulfite, 4.4 parts of sodium sulfite, 10 parts of isopropyl alcohol and sufficient water to make 100 parts by weight of solution. The completed solution had a pH of 6.

A sample of very fine straight hair was curled upon a mandrel and treated with the above solution for 3½ hours at room temperature, and then rinsed in water. A 5% solution of normal triethanolamine titanate, prepared by reaction of 1⅓ mols of triethanolamine with 1 mol of butyl titanate, was applied to the hair by squeezing the solution into the curl from a sponge. The squeezing-in operation was carried out three times at 5 minute intervals, after which the hair was unwound from the mandrel and immersed once more in the same titanate solution. The treated hair was then combed out, styled and dried. The appearance and lustre of the hair were enhanced by the treatment, and the treated hair was found to be more easily styled than similar hair samples treated with the same waving solution but neutralized with the well-known oxidizing neutralizers such as potassium bromate, sodium persulfate solutions, etc.

Example II

A destabilizing solution was prepared containing 2% sodium sulfite and 2% sodium bisulfite in aqueous solution. The pH of the solution was slightly over 6. This solution was used for treating a medium-fine bleached hair by winding the hair upon a mandrel and saturating it for ten minutes at 50° C. with the solution. No rinse was used after the sulfite treatment in this case, but instead, the hair was directly treated with a 2% solution of normal triisopropanolamine titanate which was applied as above to give a total contact time of 15 minutes at room temperature. The treated hair was then rinsed, combed, styled and dried as before. The results were similar to those obtained in Example I.

Example III

The procedure of Example I was repeated using, in place of the sodium metabisulfite-sodium sulfite solution there described, an aqueous solution containing 10% sodium sulfite and 2% ammonium carbonate. This solution had a pH of 9. The aminoalkyl titanate solution used in this case was a 5% solution of tetra (β-aminoethylethanolamine) titanate instead of the triethanolamine titanate used in Example I. Results were substantially identical with those above described.

Example IV

A destabilizing solution was prepared by dissolving thioglycerol in water, adjusting the pH to 9 with ammonia, and adjusting the concentration to 0.6 N. A sample of coarse straight hair was wound upon a mandrel and treated for 45 minutes at room temperature with this solution. The hair was then rinsed thoroughly with water and subsequently treated according to the procedure above described with a 5% solution of normal triethanolamine titanate and ½% H_2O_2. The H_2O_2 in this case helped to destroy the mercaptan odor. The results were similar to those obtained in the previous examples, and no odor was detectable in the treated hair.

Example V

A sample of wool flannel cloth was stretched over a roll in a pleated condition, and destabilized by treating it with 1% solution of hydrogen peroxide which had been adjusted to a pH of 4 with acetic acid. The peroxide was allowed to remain in contact with the wool for 4 hours at room temperature, after which the cloth was rinsed 15 minutes in water, and finally treated for 10 minutes with a 10% solution of triethanolamine titanate at pH of 8.9. The cloth was then removed from the roll, washed and dried. The treated cloth was found to be permanently pleated but otherwise unchanged in appearance, texture or tensile strength.

Example VI

A destabilizing solution was prepared by dissolving thioglycolic acid in water, adjusting the pH to 9 with ammonia and then adjusting the concentration to 0.6 N. This solution was used to treat a sample of fine straight hair wound upon a mandrel. The treatment was continued for one hour at room temperature, after which the hair was rinsed thoroughly with water and subsequently treated according to the procedure previously described with a solution containing 5% normal triethanolamine titanate, 1% sorbitol and 0.5% hydrogen peroxide. The results were similar to those obtained in Examples I–IV.

Example VII

A destabilizing solution was prepared containing 15% sodium metabisulfite and 12% guanidine carbonate. The resulting solution was a clear yellow color and had a pH of about 5 to 6. This solution was used to treat a sample of fine straight hair, the treatment being carried out in the usual way for one hour at room temperature. The hair was then rinsed and set with a 5% solution of normal triethanolamine titanate according to the procedure described above. An excellent wave, permanent to washing, was produced.

Example VIII

The procedure of Example II was repeated, substituting for the triisopropanolamine titanate an equal quantity of triisopropanolamine zirconate. The results obtained were similar to those obtained in Example II.

Example IX

A hair waving solution was prepared by admixing thioglycerol and triethanolamine titanate with water to form an aqueous solution consisting of 0.6 N thioglycerol and 0.1 N TiO_2. This aqueous solution was stabilized with sorbitol in a mole ratio of 1:1:0.5 triethanolamine to titanium to sorbitol and adjusted to a pH of 9 by the addition of ammonium hydroxide. The solution was applied to a fine brown hair tress and the hair then tightly wound on a plastic curling rod for 1 hour. At the end of this time the tress was treated with a setting solution consisting of 10 g.p.l. $KBrO_3$ by means of a syringe. Three treatments were given at 5 minute intervals. The

tress was removed from the rod, rinsed in tap water, combed and dried. The appearance and lustre of the hair were enhanced and the hair was found to be more easily styled than similar hair samples treated with conventional destabilizer solutions.

Example X

A hair waving solution was prepared by admixing thioglycerol with triethanolamine titanate and water to form a solution consisting of 0.6 N thioglycerol and 0.1 N TiO_2. The solution was adjusted to a pH of 9 by the addition of ammonium hydroxide and stabilized by the addition of sorbitol and gluconic acid in a mole ratio of 1:1:0.2:0.2 triethanolamine to titanium to sorbitol to gluconic acid. To this solution was added $KMnO_4$ in a concentration of 0.004 g.p.l. as Mn to catalyze oxidation of the solution on exposure to air. This solution was applied to a hair tress and the hair wound on the curling rod. After 15 minutes a tress was resaturated with the solution and allowed to reduce 30 minutes at room temperature. Thereafter the tress was sponged free of excess solution and allowed to dry slowly on the rod for 6 hours. When dried the tress was removed from the rod, rinsed, combed and brushed. The tress had substantially the same superior qualities as the tress described in the foregoing examples.

While this invention has been described and illustrated by the examples shown, it is not intended to be strictly limited thereto and other modifications and variations may be employed within the scope of the following claims.

We claim:

1. Method for imparting a desired configuration to keratinous fibers which comprises imparting said configuration to said fibers, and treating said fibers while held in said configuration with an aqueous solution consisting essentially of from 1–10% of thioglycerol, at least 1% of triethanolamine titanate, and a stabilizing agent selected from the group consisting of sorbitol, gluconic acid and mixtures thereof.

2. Method for imparting a desired configuration to keratinous fibers which comprises imparting said configuration to said fibers and treating said fibers while held in said configuration with an aqueous solution having a pH within the range of from 6 to 9 said aqueous solution consisting essentially of from 1–10% of thioglycerol, at least 1% of triethanolamine titanate, a stabilizing agent selected from the group consisting of sorbitol, gluconic acid and mixtures thereof and a manganese salt.

3. An aqueous solution for imparting a desired configuration to keratinous fibers, said aqueous solution having a pH within the range of from 6 to 9 and consisting essentially of from 1–10% of thioglycerol, at least 1% of triethanolamine titanate, and a stabilizing agent selected from the group consisting of sorbitol, gluconic acid and mixtures thereof.

References Cited in the file of this patent

UNITED STATES PATENTS

2,540,980	Den Beste et al.	Feb. 6, 1951
2,569,414	Boyd	Dec. 18, 1951
2,643,375	Gant	June 23, 1953
2,689,858	Boyd	Sept. 21, 1954
2,787,274	Gant	Apr. 2, 1957
2,824,114	Bostwick	Feb. 18, 1958

FOREIGN PATENTS

941,430	Germany	Apr. 12, 1956
150,690	Sweden	July 12, 1955
27,851	Finland	Dec. 31, 1955
756,002	Great Britain	Aug. 29, 1956

OTHER REFERENCES

Speer: "Org. Compounds of Titanium," Ind. and Eng. Chem., February 1950, pp. 251–3.

Grant: Transcript of Record (CCPA) Pat. App. Docket No. 5241, December 27, 1945, p. 17.

Schimmel Briefs, No. 176, November 1949, (1 p.).