

UNITED STATES PATENT OFFICE

2,434,688

REGENERATED KERATIN

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No Drawing. Application November 3, 1942,
Serial No. 464,428

14 Claims. (Cl. 18—47.5)

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This invention relates to processes for preparing regenerated keratin and the products thereof. It relates particularly to improved methods for dissolving keratin without substantially changing the polypeptide linkages thereof. Certain embodiments relate to chemical derivatives of regenerated keratin.

Keratin is found in certain varieties of horn. Of greater importance is the fact that keratin is found in fibrous form in wool, fur, mohair and the like. The physics and chemistry of keratin is of particular interest in connection with the art of reshaping wool for making artificial Persian lamb fur coats and the like.

For many years the prior art has known: That proteins are made up of amino acids; that the carboxyl ($-\text{CO}_2\text{H}$) group of one amine acid is chemically bound to the amino ($-\text{NH}_2$) group of another amino acid molecule in the protein; that said carboxyl-amino or peptide ($-\text{CONH}-$) linkages are easily hydrolyzed or split by water under suitable reaction conditions such as high temperature, pH, etc.; that a great number of amino acid molecules are united to form a polypeptide chain; that the polypeptide chains of keratin are normally folded in a generally random manner; that the polypeptide chains of keratin, although not as orderly arranged as ions in an inorganic crystal, are generally axially oriented in the fiber; and that keratin fibers are characterized by cross linkages of cystine. For many decades it has been known that keratin contains cystine $\text{HO}_2\text{CCHNH}_2\text{CH}_2-\text{SS}-\text{CH}_2\text{CHNH}_2\text{CO}_2\text{H}$ which is rather easily reduced to two molecules of cysteine $\text{HO}_2\text{CCHNH}_2\text{CH}_2\text{SH}$. Cysteine is in turn rather easily oxidized to cystine; however, unless the reaction conditions are properly controlled, the oxidation may proceed to the formation of 2-amino, 2-carboxylic ethanesulfonic acid, $\text{HO}_2\text{CCHNH}_2\text{CH}_2\text{SO}_3\text{H}$ which can be reduced only with such extreme difficulty as to be economically infeasible.

A cysteine unit is furnished by each of the two long polypeptide chains which are united by a cystine linkage. Thus, the $-\text{SS}-$ portion of a cystine cross link is at the middle thereof. It is sometimes helpful to think of a molecule in a keratin fiber as analogous to a ladder having rope rungs characterized by centrally disposed snap connectors easily engaged or disengaged. Reshaping of animal textile fibers is believed to involve a disconnection of the cross rungs, a stretching and reshaping of the fiber to relatively and axially shift the long polypeptide units, and a reconnection of the cross rungs to stabilize the long

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polypeptide units in their new relationship and shape. Chemically, such fiber reshaping is believed to involve: a reduction of some of the cystine to cysteine; pressure phenomena; and an oxidation of some of the cysteine to cystine to restore the original chemical and essential structure of the keratin fiber. For convenience, a single cross linkage between two chains has been explained. However, it should be understood that a keratin fiber contains thousands of long polypeptide chains, and that a cross-section of such a fiber might cut through hundreds of chains. Moreover, a chain may be connected to each of a dozen or so adjacent parallel chains by means of cystine cross-linkages.

A pound of wool has about 1.42×10^{23} cross-linkages. Although, substantially all of the cystine of keratin probably provides cross linkages between parallel polypeptide chains, it is possible: that some of the cysteine units are chemically united with cysteine units in the same polypeptide chain to form heterocyclic units characterized by the disulfide $-\text{SS}-$ linkage; that some of the cysteine units are chemically united to other cysteine units of a relatively independent branch of a long chain; and/or that some of the cysteine units are in some other relationship distinguishable from the cross linkages.

Wool contains approximately 12.4% cystine. Cystine contains approximately 25% sulfur. Thus, it has been calculated that wool contains approximately 3.34% of cystine sulfur and that 959 grams of wool contain about 1 mole of cystine sulfur.

It is an important object of the present invention to prepare regenerated keratin without injuriously affecting the chemical or physical characteristics of the keratin material. It is an object of the present invention to dissolve keratin without breaking any of the polypeptide linkages. Further objects of certain embodiments are to prepare keratin like material having improved characteristics, to prepare synthetic keratin fibers at a minimized cost, and to provide protein containing plastics of unusual strength and water resistance.

A feature of the present invention is the utilization of a process of dissolving keratin at a lower pH than has heretofore been used. Features of certain embodiments include: the provision of chemical derivatives of keratin; the provision of synthetic fibers having unique physical characteristics; and the utilization of effective reducing agents prior to and/or simultaneously with the dissolving of the keratin.

In describing the present invention in detail, reference may be made to examples. The terminology of these examples are for a purpose of illustration and not for limitation. Although certain of the steps of the present invention can be conveniently described in terms of liquid treatment, it should be understood that gaseous reagents, paste reagents, and/or powdered reagents may be used satisfactorily.

In the preparation of regenerated keratin, two important steps are involved. The keratin must be dissolved and subsequently precipitated. In certain embodiments of the present invention, additional steps are provided.

Particular importance is placed upon the step of dissolving keratin in accordance with the present invention. Heretofore, keratin has been dissolved by means of strong alkaline solutions of a sulfide salt. However, damage is done to the keratin material by the high alkalinity of such a solution. Moreover, the odor of the alkaline sulfide is very objectionable because of its resemblance to the odor of rotten eggs. Because the damage to keratin by such methods is so extensive, and because the odor is so objectionable, there have been substantially no efforts to commercialize regenerated keratin processes.

It should be especially noted that, according to the present invention, keratin is dissolved at a relatively low pH. The keratin is first reduced by means of a non-sulfide reducing agent capable of effecting such reduction at a pH lower than 13.5. Particularly satisfactory results are obtained by the use of an alkanthiol as a reducing agent. Benzylthiol, furfurylthiol, hydroxyalkanthiols, thioglycolic acid, other methanthiol derivatives, and numerous other related materials, whether in acid, basic or neutral media, are included within the term alkanthiol. Alkanthiols having no additional functional groups can be effectively used as reducing agents for this step if suitable ventilating means are used to remove the offensive odor incident thereto. The use of alkanthiols having additional functional groups ordinarily avoids the objectionable odor. Derivatives having strong polar groups, such as thioglycolic acid, are quite effective. However, by reason of the fact that polar groups ionize when dissolved, whereas non-polar groups do not, even more satisfactory results can be obtained by the use of alkanthiol derivatives having additional functional groups of a relatively non-polar nature. For example, thioglycerol is a very effective reducing agent for the preparation of regenerated keratin. Thiosorbitol, thiomannitol and other polyhydroxyalkanthiols are very satisfactory.

The molal concentration of the alkanthiol and/or alkanthiol derivative should be at least .2 and should desirably be about .5. It is ordinarily not necessary to increase the molal concentration of alkanthiol above 1.5. However, it should be understood that an effective reduction of keratin can be achieved at molal concentrations of alkanthiol as low as .1 and substantially higher than 1.5.

The temperature of the reduction influences the speed of the reaction. However, the speed of the hydrolysis of the polypeptide linkages is also increased at high temperatures. In order to avoid undue hydrolysis and in order to avoid the expense of maintaining high temperatures, it is ordinarily desirable to reduce keratin at a temperature below 55° C. to 60° C. The pH of the reducing solution should be above 3 and below

13.5. In order to dissolve the reduced keratin, a solution having a pH between 9 and 13.5 should be used. Although the reducing and dissolving can be conveniently described separately, it should be understood that such terminology is intended to generically define not only the two step but also the one step reducing and dissolving operations.

Examples of the step of reducing and dissolving keratin in accordance with the present invention follow:

Example 1.—50 grams of horn, human hair waste, wool waste, and/or cowhair clippings are dissolved in 1 liter of .5 molal thioglycolic acid containing $\text{Ca}(\text{OH})_2$ to bring the solution to a pH of 12.5. The reaction is carried on at 50° C. for 20 minutes, by which time the keratin is substantially dissolved.

Example 2.—1,000 grams of human hair waste are dissolved in 50 liters of .2 molal ethylmercaptan containing NaOH to bring the pH to 13.4. The reaction is carried on at 45° C. for 25 minutes, by which time the keratin is substantially dissolved.

Example 3.—150 grams of wool waste are dissolved in 1 liter of 1.5 molal thioglycerol containing NaOH to produce a pH of 13.3. The reaction mixture will dissolve the keratin after 3 hours at room temperature.

While the keratin is in its reduced state, it may be subjected to any of several treatments.

Example 4.—Methylchloride is reacted with a solution of dissolved keratin to produce a methyl derivative of keratin. Instead of methylchloride, aliphatic homologues or any aryl compounds, such as benzylchloride, $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$, may be used. Instead of any alkylchloride, there may be used an alkylbromide, an alkyl iodide, or other compound having a functional group capable of reacting with cysteine sulfur to attach an organic group to the cysteine sulfur.

Example 5.—Ethylene chloride is reacted with a solution of reduced keratin to form bishioether cross linkages in the keratin. Other dichloro compounds, or other reagents (e. g. ketene, acetaldehyde and the like) capable of reacting to attach an organic group to two cysteine sulfur units may be used instead of ethylene-chloride.

Example 6.—Ketene, formaldehyde, benzaldehyde, or the like can be reacted with a solution of reduced keratin to produce material having organic groups attached not only to the cysteine sulfur but also to NH_2 and other reactive groups of the keratin.

Although it is ordinarily not desirable, the keratin can be precipitated by controlling the reaction conditions in the above Examples 4, 5 and 6.

It is ordinarily desirable to precipitate the keratin as a separate step. The precipitation of the keratin may be conveniently achieved by the addition of sufficient acid to decrease the pH of the solution to about 4.5. The keratin can be prepared by centrifuging, drying, or other suitable methods.

Example 7.—The solution prepared according to Example 3 is treated with 21 ml. of 10 normal H_2SO_4 to precipitate the keratin material.

Example 8.—A solution of reduced keratin is spun into an acid (pH5) precipitating solution containing an oxidizing agent such as H_2O_2 adapted to reform cystine cross linkages.

Important advantages of the regenerated fibers of the present invention are that they are very strong and may have a tensile strength greater

than 85% of the average tensile strength of wool. Moreover, they have polypeptide chains substantially as long as those in wool.

As previously explained, the solution of reduced keratin is not necessarily treated according to Examples 4, 5 or 6. After the keratin has been precipitated, the non-fibrous mass may, if desired, be treated with any of the reagents mentioned in Examples 4, 5, and 6. The precipitated keratin can be utilized in any one of several ways. If it is desired to make a thermo-setting material therefrom, condensing reagents such as formaldehyde, crotonaldehyde, or the like, can be mixed with the precipitated mass, which can then be molded in conventional molding machines. The heat of the mold will accelerate the reaction between the reduced keratin and condensing reagent, and convert the material to a thermo-setting plastic. The material thus formed possesses less hygroscopicity than other plastics derived from proteins. The hygroscopicity and tendency to swell in water can be minimized by reacting the reduced keratin with a long chain reagent capable of attaching to the cysteine sulfur and utilizing a condensing reagent of high molecular weight, such as benzaldehyde.

Synthetic fibers may be formed from the dough-like plastic mass prepared as above, by extruding it in fibrous form. The initially prepared solution of reduced keratin may be extruded through spinnerettes into an acid precipitating bath. Particularly satisfactory results are obtained by: dissolving the keratin with an alkanthiol derivative reducing agent of pH 9-12.5; precipitating the keratin by decreasing the pH to about 4.5; treating the precipitated mass with just enough alkaline solution (pH about 12.5) to form a gel; working and aging the gel to improve its physical characteristics; and extruding the gel through fine spinnerettes into a precipitating medium.

After the initial formation of the fiber, it is desirably stretched, relaxed, and restretched in order to axially orient the polypeptide chains. The fiber is desirably prepared as a reduced keratin fiber. After stretching and other physical treatment, the reduced keratin is chemically modified in order to permanently retain the physical characteristics thus achieved. H_2O_2 or other suitable oxidizing agent may be used to oxidize the cysteine and to form new cystine cross linkages. However, particularly satisfactory results are obtained by reacting the reduced keratin with ethylene-chloride or other reagents capable of forming bishioether cross linkages. After suitable thiol cross linkages have been formed, the fiber may be reacted with a suitable condensation reagent such as ketene or formaldehyde to harden the fiber.

I claim:

1. The method of preparing a modified keratin comprising reducing the keratin with a non-polar mercaptan in an aqueous solution having a pH above 3 and below 13.5, dissolving the reduced keratin in an aqueous alkaline solution having a pH between 9 and 13.5 and precipitating the modified keratin in an acid precipitating bath.

2. The method of preparing a modified keratin comprising reducing the keratin with a non-polar hydroxyalkanthiol in an aqueous solution having a pH above 3 and below 13.5, dissolving the reduced keratin in an aqueous alkaline solution having a pH between 9 and 13.5 and precipitating the modified keratin in an acid precipitating bath.

3. The method of preparing a modified keratin

comprising reducing the keratin with a non-polar mercaptan in an aqueous solution having a pH above 3 and below 13.5, dissolving the reduced keratin in an aqueous alkaline solution having a pH between 9 and 13.5 and precipitating the modified keratin with an acid bath containing an oxidizing agent.

4. A new composition of matter comprising a modified keratin prepared by reducing keratin with a non-polar mercaptan in an aqueous solution having a pH above 3 and below 13.5, dissolving the reduced keratin in an aqueous alkaline solution having a pH between 9 and 13.5 and precipitating the modified keratin in an acid precipitating bath.

5. A new composition of matter comprising a modified keratin prepared by reducing keratin with a non-polar hydroxyalkanthiol in an aqueous solution having a pH above 3 and below 13.5, dissolving the reduced keratin in an aqueous alkaline solution having a pH between 9 and 13.5 and precipitating the modified keratin in an acid precipitating bath.

6. A new composition of matter comprising a modified keratin prepared by reducing keratin with a non-polar mercaptan in an aqueous solution having a pH above 3 and below 13.5, dissolving the reduced keratin in an aqueous alkaline solution having a pH between 9 and 13.5 and precipitating the modified keratin with an acid bath containing an oxidizing agent.

7. The method which includes: treating and dissolving keratin with an aqueous alkaline solution having a pH between 9 and 13.5 and containing a non-polar hydroxyalkanthiol reducing agent between 0.1 and 1.5 molarity to reduce the keratin without materially hydrolyzing its amide linkages; and subsequently precipitating the modified reduced keratin with an acid.

8. The method which includes: treating keratin with an aqueous alkaline solution having a pH between 9 and 13.5 and containing a non-polar mercaptan reducing agent of about 0.5 molarity to dissolve the keratin without materially hydrolyzing its amide linkages; and subsequently precipitating the modified keratin with an acid.

9. The method which includes: treatment of keratin with an aqueous alkaline solution having a pH between 9 and 13.5 and containing at least 0.1 M non-polar hydroxyalkanthiol reducing agent to dissolve the keratin without materially hydrolyzing its amide linkages; forming a fiber by spinning the solution into an acid precipitating bath and stretching the so-formed fiber.

10. In the treatment of keratin the method which comprises; reducing at least some of the cross linkages or —SS— bonds by treatment with an aqueous alkaline solution having a pH between 9 and 13.5 and containing a non-polar mercaptan; precipitating with acid to produce a modified keratin mass; and treating the mass with an aldehyde.

11. The process comprising the steps of: treating keratin with an aqueous alkaline solution having a pH between 9 and 13.5 and containing a non-polar mercaptan to reduce at least some of the cystine —SS— linkages and to form a solution of reduced keratin; extruding the reduced keratin material into an acid bath to form fibers from the reduced keratin; stretching said fibers to orient keratin chains parallel to the fiber axes; and treating the reshaped modified keratin with an aldehyde.

12. The process comprising treating keratin with an aqueous alkaline solution having a pH

between 9 and 13.5 and containing a non-polar mercaptan to reduce at least some of the cystine —SS— linkages to form a solution of reduced keratin, extruding the solution into an acid precipitating bath to form fibers from the reduced keratin; stretching; relaxing; and restretching said fibers to orient keratin chains parallel to the fiber axes, and treating the reshaped keratin with an aldehyde.

13. A new composition of matter comprising a modified keratin prepared by treating keratin with an aqueous alkaline solution having a pH between 9 and 13.5 and containing a non-polar mercaptan to reduce at least some of the —SS— linkages to form a solution of the reduced keratin; subjecting the reduced keratin to an acid bath and treating this modified keratin with an aldehyde.

14. The process which includes the step of dissolving keratin in an aqueous alkaline solution containing a non-polar hydroxyalkanethiol and having a pH between 9 and 13.5; precipitating the keratin by decreasing the pH to its acid range and dissolving the precipitated mass with just sufficient alkaline solution to form a gel; working and aging the gel; extruding the gel through fine spinnerettes into an acid precipitating bath to

form fibers; and treating the fibers with an aldehyde.

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