

UNITED STATES PATENT OFFICE

2,521,582

TREATMENT OF KERATINACEOUS MATERIALS

Havard L. Keil, Clarendon Hills, and Joseph Sterling Ingraham, Chicago, Ill., assignors to Armour and Company, Chicago, Ill., a corporation of Illinois

No Drawing. Application November 27, 1944,
Serial No. 565,425

10 Claims. (Cl. 195—29)

1

This invention relates to the treatment of keratinaceous materials, and more particularly to the preparation of a foam-stabilizing protein hydrolysate from keratinaceous materials, such as hoofs, horns, and hair.

In the preparation of foam-stabilizing protein hydrolysates, it has been found that the addition of salts of heavy polyvalent metals, such as iron, aluminum, and chromium, react with the proteinaceous materials and toughen the bubble films of the foam. The addition of such heavy metal salts substantially improves the fire-extinguishing characteristics of the foam and also enables the obtaining of a stiffer foam. However, the incorporation of the heavy metal salts in protein hydrolysates is greatly limited if there is any substantial quantity of inorganic salts present in the mixture. When proteins are hydrolyzed with acid and to a lesser extent when hydrolyzed with alkali, inorganic salts are found in the resultant product, and the product is not as suitable for the incorporation of heavy metal salts as a similar product prepared by enzyme hydrolysis.

In the case of the proteins found in hoofs, horn, and hair referred to generically as the keratins, enzyme hydrolysis may not be carried out with the untreated proteins, apparently because the proteins contain an anti-enzyme element which prevents enzyme hydrolysis, and also because certain enzymes are not effective in the presence of sulfides which are contained in the proteins.

An object of the present invention is to provide for the enzyme hydrolysis of keratinaceous materials. Another object is to form a foam-stabilizing composition of hydrolyzed keratinaceous materials in which a salt of a heavy polyvalent metal is incorporated in the composition for increasing fire resistance and stiffness of the mixture. Still another object is to provide a pretreatment for the keratinaceous materials in which the anti-enzymes are destroyed. A further object is to remove or fix the sulfides present in the keratinaceous materials without deleteriously affecting the ability of the materials to take up salts of heavy polyvalent metals. Still another object is to provide a pretreatment for keratinaceous materials as a result of which the materials may be readily hydrolyzed with enzymes.

The invention contemplates the pretreatment of keratinaceous materials to condition the materials for enzyme hydrolysis, enzyme hydrolysis of the materials, and the preparation of a foam-

2

stabilizing protein hydrolysate containing an iron of a heavy polyvalent metal.

Broadly, the steps of the treatment include the heating of the materials with alkali to destroy anti-enzymes, acidifying the materials and heating them to remove the hydrogen sulfide, and adding an ion of an alkaline earth metal to fix in the precipitated un-ionized form any sulfides remaining in the mixture. These steps constitute the pretreatment, after which the material is ready for enzyme hydrolysis. The enzyme hydrolysis may be carried out in the conventional manner with a proteolytic enzyme and the insoluble constituents separated from the hydrolysate. The mixture may be heated to inactivate the enzyme, and a salt of a heavy polyvalent metal, such as ferrous sulfate, added to the mixture to obtain the final product.

The invention is applicable to keratinaceous materials, by which is meant protein-bearing materials containing the protein keratin and characterized by resistance to normal enzyme hydrolysis. The resistance of these materials to normal enzyme hydrolysis is attributed to anti-enzyme elements which are destroyed in the pretreatment of the invention. Of the nature, character, and action of the anti-enzyme elements, very little is known, but this term is used herein to describe generically elements or factors which prevent normal hydrolysis of keratinaceous materials with proteolytic enzymes.

In the pretreatment of the keratinaceous material, the material is treated with an alkali and heated for a substantial period of time in the presence of the alkali. For example, the mass may be heated with an alkali at a temperature of 80° C. for a period of 24 hours and then boiled for 30 minutes to remove free ammonia. By alkali is meant a hydroxide of an alkali metal or alkaline earth metal. Since the oxides of the alkaline earth metals form hydroxides in solution, these substances are also included in the definition of the term "alkali."

After treating the keratinaceous material with alkali and boiling to remove free ammonia, the mixture is acidified, preferably with an organic acid, such as acetic acid, formic acid, lactic acid, oxalic acid or citric acid. Mineral acids, such as hydrochloric or sulfuric acids, may be used, but are not as desirable as the organic acids. In acidification, the solution is brought to a slightly acid pH, such as a pH of 6.5, and then boiled for a period of time to remove hydrogen sulfide which has been formed from the acidification of sulfide present in the solution. An alkaline earth

3

metal ion, such as calcium in the form of the oxide or hydroxide, is added to neutralize the mixture and, if desired, to raise the pH slightly above neutrality. This alkaline earth metal ion reacts with any sulfides remaining in the solution to form calcium sulfide which is insoluble and also slightly ionized.

After the pretreatment which conditions the keratinaceous materials for enzyme hydrolysis, the solution is brought to a temperature within the active range of the enzyme being used, and similarly is brought to a pH within the active range of the enzyme employed. The pH and temperature ranges within which the particular enzymes are active are well known to the art. The enzyme is added to the solution and left to act for a substantial period of time, such as for 24 hours or more. The insoluble constituents of the mixture may then be removed by filtration or otherwise, and if desired the solution adjusted to approximate neutrality, as by the addition of an organic acid. In this way we obtain a hydrolyzed keratinous product, the hydrolysis being accomplished through enzyme action.

The filtered neutralized solution may be heated to inactivate the enzyme, and cooled. When the product is to be employed in the preparation of a fire-extinguishing composition, an ion of a heavy polyvalent metal, such as iron, chromium, nickel, aluminum, calcium, barium, copper, lead or arsenic, may desirably be added. The ion may be added in the form of a water-soluble salt, such as a sulfate. When the metal is one which is characterized by a plurality of valences, the form in which it is added to the mixture is preferably one of the lower valences. As a specific example, ferrous sulfate may be added to the mixture. The proportion of the ferrous sulfate or other heavy polyvalent metal salt added may be in the neighborhood of 1% to 4% by weight with respect to the solution.

A specific example of the invention in the preparation of a fire-extinguishing composition is as follows:

Whole animal hoofs are covered with water in an autoclave and heated under 50 pounds of steam pressure for 5 hours at a temperature of about 138° C. The hoofs swell and take up water. They are then ground to form a meal or paste. To this hoof meal or paste is added 5 parts by weight of water and 8% of sodium hydroxide based on the dry protein material weight. The mixture is heated at 80° C. for 24 hours and then brought up to boiling temperature for a period of 30 minutes to remove free ammonia which has been liberated from the protein. The mixture is then neutralized and acidified with acetic acid, the pH preferably being adjusted to approximately 6.5 and the mixture boiled for 30 minutes to liberate hydrogen sulfide. Lime is then added to the mixture until a pH of approximately 8 is obtained. This completes the pretreatment of the material.

The pretreated mixture is cooled to 40° C. and 3% of pancreatin or papain added thereto for the enzyme hydrolysis. The hydrolysis is permitted to proceed for a substantial period of time, such as 24 hours. At the end of this time, the insoluble constituents are separated from the mixture by filtration and the pH adjusted to approximately 7 by the addition of acetic acid. The mixture is then boiled to inactivate the enzyme, and after cooling 1% to 4% by weight of ferrous sulfate is added to obtain the final product.

By means of the process of the invention,

4

keratinaceous materials are readily hydrolyzed with conventional proteolytic enzymes, the pretreatment being effective to destroy anti-enzymes and to fix or remove sulfides which might otherwise interfere with the enzyme action. The enzyme hydrolysis of the keratinaceous materials produces a protein hydrolysate which contains a minimum quantity of inorganic salts, and the hydrolysate is therefore adapted to receive and support without precipitation the salts of the heavy polyvalent metals which increase the fire resistant qualities and the stiffness of the fire-extinguishing foam produced from the material. The final product differs from hydrolysates of keratinaceous materials which have heretofore been prepared in that it is an enzyme hydrolyzed product, by which is meant a product in which the hydrolysis is carried out primarily with enzymes and in which the inorganic salt content is maintained at a minimum.

Although the invention has been illustrated in connection with certain specific embodiments, it will be apparent that modifications and changes may be made without departing from the spirit and scope of the invention.

We claim:

1. A process for the treatment of the proteins of hoofs, horns, and hair, comprising heating the protein-bearing material in an aqueous alkaline medium to destroy anti-enzymes present therein, acidifying the mixture, heating the acidified mixture to liberate hydrogen sulfide therefrom, and treating the mixture while still water insoluble with a hydrolyzing proteolytic enzyme under conditions favorable to enzyme activity to form a protein hydrolysate.

2. A process for the treatment of the proteins of hoofs, horns, and hair, comprising heating the protein-bearing material in a water solution of an alkaline metal hydroxide to destroy anti-enzymes present therein, acidifying the mixture, heating the acidified mixture to liberate hydrogen sulfide therefrom, treating the mixture while still water-insoluble with a hydrolyzing proteolytic enzyme under conditions of temperature and hydrogen ion concentration within the active range of the enzyme to form a keratinaceous hydrolysate, and separating the insoluble constituents from the mixture.

3. A process for the treatment of the proteins of hoofs, horns, and hair, comprising heating the protein-bearing material in a water solution of an alkali metal hydroxide to destroy anti-enzymes present therein, acidifying the mixture, heating the acidified mixture to liberate hydrogen sulfide therefrom, adding to the mixture a hydrolysate of an alkaline earth metal to substantially remove from the ionic form any sulfides remaining in the mixture, and treating the mixture while still water-insoluble with a hydrolyzing proteolytic enzyme to form a protein hydrolysate.

4. A process as set forth in claim 3 wherein the mixture is acidified with a water-soluble organic acid.

5. A process for the treatment of the proteins of hoofs, horns, and hair, comprising heating the protein-bearing material in a water solution of an alkali metal hydroxide for an extended period of time to destroy anti-enzymes therein, boiling the solution to remove free ammonia therefrom, acidifying the mixture with an organic acid, heating the acidified mixture to liberate hydrogen sulfide therefrom, adding to the mixture a sufficient quantity of an alkaline earth metal

5

hydroxide to render the solution alkaline and to substantially remove from the ionic form any sulfides remaining in the mixture, and treating the mixture while still water-insoluble with a hydrolyzing proteolytic enzyme under conditions of temperature and hydrogen ion concentration within the active range of the enzyme to form a protein hydrolysate.

6. A process for the treatment of the proteins of hoofs, horns, and hair, comprising heating the protein-bearing material in an aqueous alkaline medium to destroy anti-enzymes therein, acidifying the mixture, heating the acidified mixture to liberate hydrogen sulfides therefrom, treating the mixture while still water-insoluble with a hydrolyzing proteolytic enzyme under conditions favorable to enzyme activity to form a protein hydrolysate, and separating the insoluble constituents from the mixture.

7. A process for the treatment of the proteins of hoofs and horns comprising autoclaving the protein-bearing material at a temperature sufficiently high to cause the material to swell and take up water, disintegrating the material and heating the same in an alkaline medium, acidifying and heating the mixture to liberate hydrogen sulfide, and treating the mixture with a hydrolyzing proteolytic concentration under conditions of temperature and hydrogen ion concentration favorable to the activity of the enzyme.

8. A process for the treatment of the proteins of hoofs and horns comprising heating the protein-bearing material under pressure at a temperature generally about 138° C. for a sufficient period to cause the material to swell and take up water, disintegrating the material and heating the same in an alkaline medium, acidifying to adjust the pH to about 6.5, heating the mixture to liberate hydrogen sulfide, and treating the mixture with a hydrolyzing proteolytic enzyme under conditions of temperature and hydrogen ion concentration favorable to the activity of the enzyme.

6

9. A process for the treatment of the proteins of hoofs and horns comprising autoclaving the protein-bearing material at a temperature sufficient to cause the material to swell and take up water, disintegrating the material, heating the material in an aqueous alkaline medium, acidifying the mixture, heating the acidified mixture to liberate hydrogen sulfide therefrom, and treating the mixture with a hydrolyzing proteolytic enzyme under conditions of temperature and hydrogen ion concentration favorable to the activity of the enzyme.

10. A process for the treatment of the proteins of hoofs, comprising heating the protein-bearing material under pressure at a temperature generally about 130° C. for a sufficient period to cause the material to swell and take up water, grinding the material, heating the material in an aqueous alkaline medium, acidifying the mixture to bring the pH to about 6.5, heating the acidified mixture to liberate hydrogen sulfide therefrom, and treating the mixture with a hydrolyzing proteolytic enzyme under conditions of temperature and hydrogen ion concentration favorable to the activity of the enzyme.

HAVARD L. KEIL.

JOSEPH STERLING INGRAHAM.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,284,740	McKee	Nov. 12, 1918
1,489,181	Weidner	Apr. 1, 1924
1,495,308	Jennings	May 27, 1924
1,754,825	Heuser	Apr. 15, 1930
1,921,398	Sturm	Aug. 8, 1933
2,151,398	Weissenborn	Mar. 21, 1939
2,158,499	Grassman	May 16, 1939
2,212,470	Friedrich	Aug. 20, 1940
2,324,951	Ratzer	July 20, 1943