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TREATMENT OF PROTEINS

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1

This invention relates to the treatment of proteins, and more particularly to a process for hydrolyzing proteins and for preparing a proteinaceous foam stabilizer. The invention also deals with a new hydrolysate product and the improved foam stabilizer. This case constitutes a continuation-in-part of our co-pending application, Serial No. 565,424 (abandoned), for Treatment of proteins.

Proteinaceous foam stabilizers for the extinguishing of fires are known to have many advantages. These materials produce a foam of fine bubble structure which is also stable to relatively intense heat. It is also known that by incorporating salts of heavy polyvalent metals in proteinaceous foam stabilizers, the bubble film of the foam may be further strengthened and the resistance of the foam to fire further increased. Difficulties, however, may be encountered in incorporating in the proteinaceous foam stabilizer the desired quantity of salts of heavy polyvalent metals since these salts tend to form insoluble complexes in the protein hydrolysate, and the solubility of such salts is subject to numerous limitations.

By the present process, a protein hydrolysate adapted for use as a foam stabilizer is formed with a minimum quantity of inorganic salts present in the hydrolysate. This permits the incorporation of larger quantities of salts of heavy polyvalent metals than would otherwise be possible. A protein hydrolysate produced in accordance with the invention may also be substantially free of mineral acids and the salts formed by neutralization of these acids which also permits the incorporation of additional quantities of heavy metal salts in the product. The enzyme hydrolysate may be produced from blood proteins which have heretofore not been economically and effectively hydrolyzed with enzymes. In addition, salts of the heavy polyvalent metals are used which permit a maximum incorporation of the metallic ions.

The invention contemplates the formation of a foam-stabilizing protein hydrolysate in which may be incorporated a maximum quantity of the salts of heavy polyvalent metals, and further contemplates the effective and efficient enzyme hydrolysis of blood proteins.

The invention is applicable to any suitable proteins, such as the histones, protamines, globins, globulins, albumins, keratins, casein, mucin, prolamines, and gluten. The invention, however, is particularly applicable to blood proteins.

The proteins are hydrolyzed by enzyme hydrolysis. Since blood proteins are not hydrolyzed by normal enzyme hydrolysis, these proteins in accordance with the invention are subjected to a pretreatment in which the proteins are conditioned for enzyme hydrolysis. It is believed that there are certain elements or factors present in the blood proteins which interfere with enzyme hydrolysis of these proteins. These elements are referred to herein as anti-enzymes, and the pretreatment is designed to destroy these anti-enzymes.

In the case of keratins, it is also necessary to destroy anti-enzymes before the hydrolysis can be effectively carried out.

In the case of proteins other than blood proteins and the keratins, it is possible to hydrolyze the proteins with enzymes without the pretreatment, but the alkali pretreatment of the invention has been found to condition the proteins for enzyme hydrolysis so as to make the hydrolysis easier, more economical and more effective.

The pretreatment of the proteins may involve heating the proteins in an alkaline medium by which is meant an aqueous solution of an alkaline earth metal or alkali metal oxide or hydroxide. Preferably, an alkali metal hydroxide, such as sodium hydroxide, is used. The quantity of the alkali metal hydroxide is preferably in the range of 3% to 9% by weight with respect to the dry protein. 7.5% has been found to be very satisfactory.

The alkali pretreatment may be carried on for a sufficient length of time to destroy the anti-enzymes. Normally, a period of time in the neighborhood of one hour has been found to be sufficient, but a somewhat longer period of time will usually permit more rapid action of the enzymes when the enzyme hydrolysis is carried out.

After the proteins have been treated with alkali to condition the proteins for enzyme hydrolysis, the excess alkali is neutralized with an acid, and preferably an organic acid. Such acids as acetic, citric, tartaric, oxalic, lactic, and formic acids, have been found to be suitable; and acetic acid is preferred. It is preferred that mineral acids not be used since the use of these acids tends to result in a precipitation of heavy metal salts in the form of protein complexes when the heavy metal salts are later added. In preparing a foam-stabilizing agent, organic acids are used rather than mineral acids in any neutralization, even if the protein is one which may be normally enzyme hydrolyzed.

The neutralized pretreated protein product is subjected to enzyme hydrolysis under conditions

of temperature and hydrogen ion concentration favorable to the quantity of the enzyme used. Any suitable hydrolyzing proteolytic enzyme may be used. For example, pancreatin or papain is suitable. In the case of these enzymes, a temperature in the neighborhood of 40° C. and a pH of about 5 to 8 have been found to be satisfactory.

The enzyme hydrolysis is carried on until a foam-form protein hydrolysate is formed. Preferably, the time of the enzyme hydrolysis is between 12 and 24 hours, but this time may vary considerably with the quantity of the enzyme used.

The enzyme hydrolyzed protein contains insoluble constituents and these materials are separated from the mixture by filtration or other suitable process.

To the protein hydrolysate may be added a salt of a heavy polyvalent metal, such as iron, chromium, nickel, aluminum, calcium, barium, copper, lead or arsenic. The metal is preferably one which exists in more than one state of valence, and in this case is preferably added in a form in which the metal is in a lower state of valence. For example, ferrous sulfate, ferrous chloride or other ferrous salts may be used. Preferably, the sulfate is used, as this has been found to be more readily incorporated than other ferrous salts, such as the chloride and acetate.

If a very large quantity of the salt of the heavy polyvalent metal is to be incorporated in the protein hydrolysate, the mixture may be adjusted to a pH of between 3 and 5.5, preferably between 4.5 and 4.8, and the precipitate formed separated by filtration. This operation is carried out after the enzyme hydrolysis and before the addition of the heavy metal salt. The precipitate apparently consists of high molecular weight protein degradation products which interfere with the incorporation of large quantities of the heavy metal salt. Without this action, between 4% and 8% of a heavy metal salt, such as ferrous metal sulfate, may be readily incorporated in a blood protein sulfate prepared in accordance with the invention. If, however, the heavy molecular weight protein degradation products are removed, as high as 12% by weight of the ferrous sulfate may be incorporated in the mixture.

After the enzyme hydrolysis, the mixture may be heated to inactivate the enzyme. The mixture may also be chemically treated in any conventional manner to inactivate the enzymes.

The solids content of the proteinaceous foam-stabilizing agent is preferably in the neighborhood of 30%. When the heavy molecular weight protein degradation products have not been removed, the viscosity of the solution will be relatively high as compared to the fractionated product from which the higher molecular weight degradation products have been removed. In either case, the viscosity of the solution may be adjusted by changing the concentration thereof. However, in the case of the mixture containing the high molecular weight protein degradation products, small changes in concentration produce a much greater change in viscosity than in the case of the fractionated product.

The enzyme hydrolyzed protein, whether blood protein or other protein, has been found to be particularly suitable for use as a foam-stabilizing agent since the enzyme hydrolysis does not destroy as many amino acids as does alkali or acid hydrolysis and the nitrogen content of the hydrolysate is higher.

In the pretreatment of the proteins in an alkaline solution, we prefer to employ a temperature of from 90 to 100° C. or higher. By bringing the proteins in the alkaline medium to a temperature within this range and preferably to the boiling temperature, we find that the anti-enzymes are rendered ineffective, and in the ensuing enzyme hydrolysis, the hydrolysis is effectively carried out.

The following are specific examples of the invention:

Example I

Liquid blood or dry blood mixed with approximately 7 times its own weight of water is mixed with approximately 7.5% of sodium hydroxide based on dry protein weight, and the mixture heated for a period of 1 to 5 hours. After heating, the solution is neutralized to a pH of about 8 by the addition of acetic acid. To the solution is then added approximately 3% of pancreatin, the proportion being based on the dry protein weight. The mixture is permitted to stand for a period of 12 to 24 hours at a temperature of 40° C. and a pH of 8 to carry out the enzyme hydrolysis.

The enzyme hydrolysate is adjusted in pH to approximately 7.5 and heated to boiling to inactivate the enzyme. The specific gravity of the solution is adjusted by evaporation or the addition of water to a solids content of approximately 30%. The solution is filtered to remove insoluble constituents and between 4% and 8% of ferrous sulfate is then added thereto. The final pH of the solution may be in the neighborhood of 6.3–6.7.

Example II

The enzyme hydrolysate prepared by the above method may, after heating to stop enzymic action, be acidified with sulfuric acid to a pH of 4.5 and heated to boiling. A heavy gummy precipitate separates out, and this precipitate is removed by decantation, filtration, or the like. The mixture is then neutralized to 7.5, using lime or calcium hydroxide to remove the sulfuric acid as calcium sulfate. The solution is again boiled and filtered free of a small precipitate. The concentration is then adjusted by evaporation or dilution until the solids content is approximately 30% and between 4% and 12% by weight of ferrous sulfate added to the solution.

In each of the above examples sodium carbonate and tri-sodium phosphate may be substituted for the sodium hydroxide, and satisfactory results will be obtained. We prefer, however, to use sodium hydroxide because it is unusually efficient in the process.

The invention is particularly applicable to blood proteins which have heretofore not been considered subject to normal enzyme hydrolysis. However, any suitable proteins may be treated in accordance with the invention to produce a desirable foam-stabilizing product.

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 of preparing a proteinaceous foam-stabilizing composition, comprising heating a blood protein in an aqueous solution of sodium hydroxide to a temperature of at least 90° C. to destroy anti-enzymes, subjecting the mixture to hydrolysis with a hydrolyzing proteolytic enzyme

under conditions of temperature and hydrogen ion concentration favorable to the enzyme action, and adding to the remaining solution from 4 to 8% of a water-soluble salt of a heavy polyvalent metal.

2. A process of preparing a proteinaceous foam-stabilizing composition, comprising heating to a temperature of about 90–100° C. a blood protein in an aqueous solution of sodium hydroxide to destroy anti-enzymes, subjecting the mixture to hydrolysis with a hydrolyzing proteolytic enzyme under conditions of temperature and hydrogen ion concentration favorable to the enzyme action, adjusting the pH to 3–5.5 to form a precipitate, removing the insoluble material, and adding to the remaining solution from 4 to 12% of a water-soluble salt of a heavy polyvalent metal.

3. A process of preparing a proteinaceous foam-stabilizing composition, comprising heating to a temperature of about 90–100° C. a blood protein in an aqueous solution of sodium hydroxide to destroy anti-enzymes, changing the pH of the mixture to that favorable to the action of a selected enzyme by the addition of an organic acid, subjecting the mixture to hydrolysis with said selected proteolytic enzyme under temperature conditions favorable to the enzyme action, adjusting the pH to 3–5.5 to form an insoluble precipitate, separating the insoluble material, and adding to the remaining solution from 4 to 12% of a water-soluble salt of a heavy polyvalent metal.

4. A process of preparing a proteinaceous foam-stabilizing composition, comprising heating to about boiling temperature a blood protein in an aqueous solution of sodium hydroxide to destroy anti-enzymes, changing the pH of the mixture to that favorable to the action of a selected enzyme, subjecting the mixture to hydrolysis with said selected proteolytic enzyme under temperature conditions favorable to the enzyme action, adjusting the pH to 3–5.5 to form a precipitate, removing the precipitate, and adding to the solution from 4 to 12% of a water-soluble salt of a heavy polyvalent metal.

5. A process of preparing a proteinaceous foam-stabilizing composition, comprising heating to about a boiling temperature blood in an aqueous solution of sodium hydroxide to destroy anti-enzymes, adding an organic acid and a selected proteolytic enzyme, subjecting the mixture to hydrolysis with said selected proteolytic enzyme and under temperature conditions favorable to the enzyme action to produce a foam-forming protein hydrolysate, removing the insoluble material, and adding to the hydrolysate from 4 to 8% of a water-soluble salt of a heavy polyvalent metal.

6. A process of preparing a proteinaceous foam-stabilizing composition, comprising heating to about a boiling temperature a blood protein in an aqueous solution of sodium hydroxide

to destroy anti-enzymes, subjecting the mixture to hydrolysis with a hydrolyzing proteolytic enzyme nder conditions of temperature and hydrogen ion concentration favorable to the enzyme action to produce a foam-forming protein hydrolysate, adjusting the pH to about the range of 4.5–4.8 to precipitate degradation products, removing the precipitate, and incorporating with the hydrolysate from 4 to 12% of a water-soluble salt of a heavy polyvalent metal.

7. A process of preparing a proteinaceous foam-stabilizing composition, comprising heating to about a boiling temperature blood in an aqueous solution of sodium hydroxide to destroy anti-enzymes, adjusting the pH through the use of an organic acid to that favorable to the action of a selected proteolytic enzyme, subjecting the mixture to hydrolysis with the selected proteolytic enzyme under temperature conditions favorable to the enzyme action to produce a foam-forming protein hydrolysate, adjusting the pH to about 4.5–4.8 to produce a precipitate of high molecular weight protein degradation products which interfere with the incorporation of large quantities of a heavy metal salt, removing the precipitate, and incorporating in the hydrolysate from 4 to 12% of a water-soluble salt of a heavy polyvalent metal.

8. A process of preparing a proteinaceous foam-stabilizing composition, comprising heating to about a boiling temperature a blood protein in an aqueous solution of sodium hydroxide to destroy anti-enzymes, subjecting the mixture to hydrolysis with a hydrolyzing proteolytic enzyme under conditions of temperature and hydrogen ion concentration favorable to the enzyme action to produce a foam-forming protein hydrolysate, adjusting the pH of the solution to between 3 and 5.5 to produce a precipitate of high molecular weight protein degradation products which interfere with the incorporation of a water-soluble salt of a heavy polyvalent metal, removing the precipitate, and incorporating in the hydrolysate from 4 to 12% of a water-soluble salt of a heavy polyvalent metal.

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