Patented Apr. 12, 1938

2,113,819

UNITED STATES PATENT OFFICE

2,113,819

PROCESS OF PREPARING FATTY ACID CONDENSATION PRODUCTS

Nathaniel Beverley Tucker, Glendale, Ohio, assignor to The Procter & Gamble Company, Cincinnati, Ohio, a corporation of Ohio

No Drawing. Application November 2, 1936, Serial No. 108,811

11 Claims. (Cl. 260—9)

This invention relates to the production of wetting, sudsing, emulsifying and detergent agents by the condensation of peptides with fatty acids of high molecular weight.

It has already been proposed to make wetting, sudsing, emulsifying and detergent agents suitable for use, particularly as textile assistants, by first digesting protein matter such as leather scraps, etc., with aqueous solutions of sodium hydroxide or calcium hydroxide to convert the proteins into peptides, and then treating this aqueous solution with fatty acid chlorides of high molecular weight in the presence or absence of organic solvents such as alcohols or aromatic hydrocarbons to cause a condensation and thereby form the desired product in aqueous solution. It has further been proposed to evaporate the water from this solution after carrying out this reaction and thereby obtain a product in substantially dry form. A hard water solution subsequently prepared from the dry product thus formed, however, possesses markedly poorer sudsing and detergent properties than the solution of the product before evaporation.

It is an object of the present invention to provide in substantially dry form a compound of the above type of superior value and particularly of greatly improved detergent and sudsing power.

I have discovered that condensation products in dry form and possessing greatly increased sudsing and detergent power over those products heretofore prepared are obtained by first hydrolyzing the proteins to peptides with an aqueous alkaline solution, evaporating the peptide solution substantially to dryness, then treating the residue with a fatty acid halide in the presence of an inert organic solvent for the fatty acid halide. The condensation product is obtained in dry form by removal of the solvent by distillation or otherwise.

It has been found in the course of my experimental work that the presence of soap in the type of condensation product herein concerned is detrimental to the sudsing and detergent efficiencies in hard water and I believe that this fact offers an explanation of why the product obtained by my process is more efficient than similar products obtained by prior art methods. When the process is carried out in an aqueous solution throughout, including both the hydrolysis of the protein and condensation of the peptides and acid halides, and the solution containing the reaction product is then evaporated to obtain the solid material, some soap is formed. Apparently some hydrolysis of the condensation product occurs during the evaporation step thereby forming peptides and free fatty acids, which acids react with the alkali present to form soap. The presence of the soap thus formed, as previously stated, has a distinctly deleterious effect on sudsing and detergency in hard water.

In my process, on the other hand, there is no opportunity for these valuable characteristics to be affected in this manner since in the substantial absence of water during condensation and subsequent evaporation of the organic solvent no harmful hydrolysis and soap forming reactions can occur to any noticeable extent. My product therefore in dry form is distinguished from those of the prior art by the relative absence of fatty acid soaps.

My invention will be readily understood from a comparison of the following tests in which Examples 1 and 2 describe the preparation of superior condensation products in accordance with my invention and the check test describes a method of preparing products in accordance with a customary prior art procedure.

Example 1.—Fifty grams of gelatin were treated with a solution of 15 grams of sodium hydroxide in 500 c. c. of water at substantially boiling temperature for 24 hours. The solution was then filtered to remove insoluble humin and the water evaporated with the use of the steam bath, thereby obtaining the peptides in substantially dry form. To this residue were added 200 c. c. of dioxane. To this mixture while mechanically stirred were added gradually 25 grams of the chlorides of fatty acids derived from coconut oil. The reaction began at once with considerable evolution of heat. The temperature of the mixture was allowed to rise to 60–70° C. during the addition of the fatty acid chloride and then maintained within that temperature range for 20 minutes after the addition was completed, agitation being continued throughout. With the aid of the steam bath the dioxane was evaporated from the mixture and the product subsequently dried at 150° C. The color darkened somewhat but the detergent properties were excellent. A one per cent solution in water containing 21 grains of hardness was perfectly clear at room temperature and showed a pH value of 7.0. The expression "21 grains hardness" is a common expression generally used in reference to water, the hardness of which is equivalent to 21 grains calcium carbonate per U. S. gallon.

Example 2.—The procedure described in Example 1 was repeated employing benzol in place

of dioxane as the solvent in the condensation reaction.

Check test of prior art method.—Fifty grams of the same gelatin used in Example 1 were treated with a solution of 15 grams of sodium hydroxide in 500 c. c. of water at substantially boiling temperature for 24 hours. After this treatment the solution was filtered to remove the insoluble humin, then cooled to about 50° C. To the mechanically agitated, cooled solution were added gradually 25 grams of the fatty acid chlorides derived from coconut oil. Reaction was apparent at once as indicated by the evolution of heat. The temperature of the reaction mixture was allowed to rise to 60–70° C. during the addition of the fatty acid chloride and then maintained at about that temperature range for 20 minutes after the addition was completed, agitation being continued throughout. With the use of the steam bath, most of the water was then evaporated from the mixture so formed, the residue being finally reduced to substantially dry form in an oven at 150° C. A one per cent solution of the product in water containing 21 grains of hardness was cloudy and showed a pH value of 7.0.

The efficiency of these products was then determined with the use of a test which consists essentially in agitating or washing uniformly soiled fabric under standardized laundering conditions with an aqueous solution of the detergent for a fixed time at a fixed temperature. Various concentrations are used in these tests. The washed fabric after thorough rinsing and drying is examined for whiteness by a photoelectric apparatus, thus eliminating any human element. Sudsing tests are conducted along with the detergency tests, the amount of suds in the container being noted at the end of the washing period. In determining the stability or lasting property of the suds formed, the amount of suds present in the washing container five minutes after the end of the washing period is recorded.

The results of such tests conducted on the products prepared in accordance with the examples given above are recorded in the following table.

Product of solvent		Detergency conc. of deterg.		Suds formed in c. c. conc. of deterg.		Suds stability in c. c. conc. of deterg.	
Example	Used	0.15%	0.27%	0.15%	0.27%	0.15%	0.27%
1	Dioxane	19	33	105	310	80	305
2	Benzol	15	29	90	310	35	305
Check test water		5	11	5	15	None	5

In the above table the detergency is expressed in arbitrary units of measurement of the current generated by the photoelectric cell when activated by the light reflected from the surface of the washed cloth, which units show the relative whiteness of the soiled cloth after washing; the greater the number of units, of course, the greater the efficiency of the detergent. The figures for suds formed are the total cubic centimeters of suds produced during the detergency test with 200 c. c. of solution. The figures under suds stability represent the cubic centimeters of suds remaining five minutes after the detergency test was completed.

Tests at two concentrations are shown in the above table, that is, 0.15% and 0.27%. These tests were made in water of 21 grains per gallon hardness at a temperature of 100° F. Tests made at other temperatures and in water of different hardnesses, however, showed substantially the same differences.

It will be clear from the table that the materials prepared in accordance with this invention, using either dioxane or benzol, solvents in which the fatty acid halide is soluble but the peptide substantially insoluble, have greatly superior detergency and sudsing characteristics at either concentration than the material prepared in accordance with prior art procedure in aqueous solution.

Practically any material consisting largely of protein matter such as, for example, leather scraps, gelatin, casein, and many other materials can be used in the practice of my invention. Protein matter extracted from cottonseed meal, soybean meal and the like may also be employed.

The fatty acids which can be used are preferably those derived from coconut oil or similar oils of the so-called coconut oil group, such as palm kernel oil, corozo nut oil, and others characterized by their relatively high content of lauric acid and similar fatty acids and by their relatively high saponification number, but other fatty acids containing from about ten to about twenty carbon atoms such as those derived from others fats and fatty oils may also be used. Synthetic fatty acids such as those obtained by the oxidation of paraffin may be used likewise, fractions having saponification numbers falling in the range of about 210 to about 270 being especially useful.

The fatty acids are preferably used in the form of their chlorides, but other halides such as the bromides and iodides may also be used.

The solvents which can be used in my process include any inert organic solvent which will dissolve the fatty acid halides but which will not dissolve the peptides. Among the solvents which may be employed are dioxane, benzol, petroleum ether, chloroform, carbon tetrachloride and other chlorinated hydrocarbons.

The condensation reaction between the fatty acid halides and peptides must be effected in an alkaline medium, that is, in the presence of an acid binding reagent. This is most simply accomplished by using in the original protein hydrolysis reaction a sufficient amount of a water-soluble alkali or alkaline earth metal hydroxide such as sodium, potassium, calcium hydroxide or the like to react with the hydrohalic acid liberated in the subsequent condensation reaction. If desired, however, the hydrolysis of the protein may be carried out in the presence of a smaller amount of alkali or alkaline earth metal hydroxide than would be necessary to neutralize the hydrohalic acid, in which case, additional metal hydroxide, or carbonate, or tertiary nitrogen base such as pyridine, quinoline, triamyl amine or the like may be added just prior to the addition of the fatty acid halide for neutralization of the hydrohalic acid liberated.

Having thus described my invention, what I claim and desire to secure by Letters Patent is:—

1. Process of making wetting, sudsing, emulsifying and detergent agents in substantially dry form which comprises hydrolyzing material consisting predominantly of proteins by treatment with an aqueous alkaline solution, evaporating substantially all of the water, reacting the residue thus formed under alkaline conditions with a

fatty acid halide in the presence of a solvent in which the fatty acid halide is soluble but in which the hydrolyzed protein is substantially insoluble, and removing said solvent, said fatty acid halides containing from about ten to about twenty carbon atoms in the molecule.

2. Process of making wetting, sudsing, emulsifying and detergent agents in substantially dry form which comprises hydrolyzing material consisting predominantly of proteins by treatment with an aqueous alkaline solution, evaporating substantially all of the water, reacting the residue thus formed under alkaline conditions with a fatty acid halide in the presence of a solvent in which the fatty acid halide is soluble but in which the hydrolyzed protein is substantially insoluble, and removing said solvent, said fatty acid halides being derived from an oil of the coconut oil group.

3. Process of making wetting, sudsing, emulsifying and detergent agents in substantially dry form which comprises hydrolyzing material consisting predominantly of proteins by treatment with an aqueous alkaline solution, evaporating substantially all of the water, reacting the residue thus formed under alkaline conditions with a fatty acid halide in the presence of a solvent in which the fatty acid halide is soluble but in which the hydrolyzed protein is substantially insoluble, and removing said solvent, said fatty acid halides being derived from coconut oil.

4. Process of making wetting, sudsing, emulsifying and detergent agents in substantially dry form which comprises hydrolyzing material consisting predominantly of proteins by treatment with an aqueous alkaline solution, evaporating substantially all of the water, reacting the residue thus formed under alkaline conditions with a fatty acid halide in the presence of a solvent in which the fatty acid halide is soluble but in which the hydrolyzed protein is substantially insoluble, and removing said solvent, said fatty acid halides being derived from palm kernel oil.

5. Process of making wetting, sudsing, emulsifying and detergent agents in substantially dry form which comprises hydrolyzing material consisting predominantly of proteins by treatment with an aqueous alkaline solution, evaporating substantially all of the water, reacting the residue thus formed under alkaline conditions with a fatty acid halide in the presence of a solvent in which the fatty acid halide is soluble but in which the hydrolyzed protein is substantially insoluble, and removing said solvent, said fatty acid halides being derived from the high molecular weight fatty acids obtained by the oxidation of paraffin hydrocarbons.

6. Process of making wetting, sudsing, emulsifying and detergent agents in substantially dry form which comprises hydrolyzing material consisting predominantly of proteins by treatment with an aqueous alkaline solution, evaporating substantially all of the water, reacting the residue thus formed under alkaline conditions with a fatty acid halide in the presence of a solvent in which the fatty acid halide is soluble but in which the hydrolyzed protein is substantially insoluble, and removing said solvent, said fatty acid halides being derived from the fatty acids obtained by the oxidation of paraffin hydrocarbons and having an apparent saponification number from about 210 to about 270.

7. The process of preparing wetting, sudsing, emulsifying and detergent agents in substantially dry form which comprises hydrolyzing material consisting predominantly of proteins by treatment with an aqueous solution of an alkali metal hydroxide, evaporating substantially all of the water, reacting the residue thus formed with a fatty acid chloride in the presence of dioxane, and removing the dioxane, said fatty acid chloride being derived from coconut oil.

8. The process of preparing wetting, sudsing, emulsifying and detergent agents in substantially dry form which comprises hydrolyzing material consisting predominantly of proteins by treatment with an aqueous solution of sodium hydroxide, evaporating substantially all of the water, reacting the residue thus formed with a fatty acid chloride in the presence of dioxane, and removing the dioxane, said fatty acid chloride being derived from coconut oil.

9. The process of preparing wetting, sudsing, emulsifying and detergent agents in substantially dry form which comprises hydrolyzing material consisting predominantly of proteins by treatment with an aqueous solution of an alkali metal hydroxide, evaporating substantially all of the water, reacting the residue thus formed with a fatty acid chloride in the presence of benzol, and removing the benzol, said fatty acid chloride being derived from palm kernel oil.

10. Process of making wetting, sudsing, emulsifying and detergent agents in substantially dry form which comprises hydrolyzing material consisting predominantly of proteins by treatment with an aqueous alkaline solution, evaporating substantially all of the water, reacting the residue thus formed under alkaline conditions with a fatty acid halide in the presence of an inert solvent for the fatty acid halide, and removing said solvent, said fatty acid halides containing from about ten to about twenty carbon atoms in the molecule.

11. In the reaction of a higher molecular fatty acid halide with a substantially dry hydrolysis product of a protein to form a wetting, emulsifying, sudsing and detergent agent, the step which comprises carrying out the reaction in the absence of substantial amounts of water and the presence of an acid-neutralizing agent and a solvent which is chemically inert to said fatty acid halide.

NATHANIEL BEVERLEY TUCKER.

Certificate of Correction

Patent No. 2,113,819. April 12, 1938.

NATHANIEL BEVERLEY TUCKER

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, lines 50 to 58 inclusive, strike out the table and insert instead the following:

Product of example	Solvent used	Detergency		Suds formed in c. c.		Suds stability in c. c.	
		Conc. of deterg.		Conc. of deterg.		Conc. of deterg.	
		0.15%	0.27%	0.15%	0.27%	0.15%	0.27%
1	Dioxane	19	33	105	310	80	305
2	Benzol	15	29	90	310	35	305
Check test	Water	5	11	5	15	None	5

and second column, line 30, for the word "others" read *other*, and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 28th day of June, A. D. 1938.

[SEAL]

HENRY VAN ARSDALE,
Acting Commissioner of Patents.