United States Patent Office 2,843,612 Patented July 15, 1958

2,843,612

PROCESS FOR THE PREPARATION OF FATTY AMIDES

Louis Gene Ricciardi, Brooklyn, N. Y., and Joseph Philip Di Geronimo, Jersey City, N. J., assignors to Colgate-Palmolive Company, Jersey City, N. J., a corporation of Delaware

No Drawing. Application February 28, 1955 Serial No. 491,176

8 Claims. (Cl. 260—404)

The present invention relates to the production of fatty amides and has particular reference to an improved process for the manufacture of fatty amides from fatty triglycerides and an amidating agent.

Heretofore, it has been proposed to prepare fatty amides by reacting fatty triglycerides with hydroxy alkyl amine in the presence of an alkali metal alkoxide catalyst, preferably in the absence of aqueous medium. The fatty material and the amine form two separate phases, and in order to obtain a desirably rapid operation of such a process it has been necessary to subject the reactants to elevated temperatures, e. g. 100° C. For example, the prior art teaches the amidation of fats such as rape oil and hydrogenated castor oil with monoethanolamine containing sodium in solution by heating these reactants, with stirring, at 100° C. until the mixture becomes homogeneous. Once the mixture has become homogeneous an exothermic reaction occurs, going almost to completion within a few minutes to produce a solution of glycerine in the monoethanolamides of the fatty acids present. It has now been found that the achievement of such a homogeneous mass, as contrasted to the two substantially immiscible liquid phases previously present, is one of the controlling factors dictating the use of elevated temperatures in the previously proposed process, since operation at such elevated temperatures greatly diminishes the period of time required to obtain homogeneity, assuming other factors such as agitation and catalyst content to be constant.

The novel process of the present invention facilitates the rapid formation of a homogeneous mixture at a relatively low temperature thus enabling the use of lower temperatures for the ensuing exothermic amidation reaction. Operation of such an exothermic reaction at low temperatures is thermodynamically desirable in that it increases the equilibrium yield of the desired product and also results in the production of products of improved color and purity by virtue of reducing the extent of undesirable side reactions and thermal degradation of the reactants and products.

In accordance with the present invention fatty triglyceride and lower monohydric alcohol are commingled in the presence of alkali metal alkoxide and the resulting mixture of said triglyceride, alcohol and alkoxide is reacted with hydroxy alkyl amine. While the reaction may be carried out at higher temperatures, it is desirable to realize the advantages inherent in operating at relatively low temperatures such as from room temperature to about 80° C., and preferably at about 55° C. to 60° C. The reaction mixture rapidly become homogeneous and thereupon an exothermic amidation reaction ensues.

It will be understood that the alkali metal alkoxide may be added to the fatty triglyceride as such or in a manner such as to generate alkali metal alkoxide in situ. It is a preferred embodiment of the present invention to add the alkali metal alkoxide and lower monohydric alcohol as a unity to the fatty triglyceride, said unity having previously been prepared by reacting alkali metal with an

excess of lower monohydric alcohol. Obviously however, these materials may be added to the fatty triglyceride as separate entities, the order of addition being immaterial.

Although the fatty triglyceride may be in solid form at the time of the pretreatment with catalyst and alcohol, it is preferred to employ triglyceride which is in the liquid state. Naturally it is also desirable to perform this step at as low an operating temperature as possible so as to minimize deterioration and darkening of the reactants.

In carrying out the process of the present invention, the molar ratio of fatty triglyceride to lower monohydric alcohol must be within the range of 1:0.25 to 1:2, preferably about 1:1. If the ratio of triglyceride to alcohol is outside of these limits, the advantages of the present process are not fully realized. Normally the molar ratio of fatty triglyceride to alkali metal alkoxide is about 1:0.045 to 1:0.3, preferably about 1:0.2. The mixture of triglyceride, alcohol and alkoxide is reacted with the hereinafter defined hydroxy alkyl amine in proportions equal to or in slight molar excess of the fatty acids of the triglyceride, i. e. the molar ratio of fatty acids in said triglyceride to hydroxy alkyl amine is within the range of about 1:1 to 1:1.3.

It has been found that when fatty triglyceride is contacted, in the presence of a small amount of alkali metal alkoxide, with about 0.25 to 2 moles of lower monohydric alcohol per mole of said triglyceride, a rapid reaction occurs even at room temperature to produce a considerable quantity of fatty monoglycerides. The mixture normally also takes on a loose gel-like structure, possibly resulting from the formation of soaps by reaction between alkali metal and the fatty acid radicals released by the formation of the monoglyceride. The mechanisms of the gel formation and chemical reaction are not fully understood, however it is believed that the monoglyceride-containing loose gels are peculiarly subject to rapid diffusion by and chemical reaction with hydroxy alkyl amine, thus facilitating the rapid attainment of a homogeneous reaction mass at relatively low temperatures.

Fatty triglycerides suitable for amidation in accordance with the present invention are those containing fatty acid radicals predominantly of about 10 to 20 carbon atoms and preferably about 12 to 16 carbon atoms. Examples of preferred glycerides are those derived from lauric, myristic and palmitic acids, natural products such as coconut, palm kernel, and babassu oils being eminently suited for the present process. Other suitable triglycerides include lard, corn oil, cottonseed oil, tallow and soy bean oil.

The term hydroxy alkyl amine as used in the present specification and in the appended claims refers only to those hydroxy alkyl amines wherein an alkyl group joins at least one esterifiable hydroxy group to at least one nitrogen atom to which there is attached at least one replaceable hydrogen atom. Among the representative hydroxy alkyl amines which may be used are, for example, monoethanolamine, diethanolamine, monopropanolamine, dipropanolamine, isopropanolamine, dibutanolamine, monobutanolamine, monoisobutanolamine, mono- and dipentanolamine, mono- and dihexanolamine, mono- and dioctanolamine, monolaurylolamine, monohexadecylolamine, monoethyl ethanolamine, mono-octadecylolamine, monobutyl ethanolamine, cyclohexyl ethanolamine, ethanolaniline, 2-methylamine-propane-diol-1,3, 1 - phenol - amine - propane - diol - 2,3, 1 - hydroxy-ethylamino - 2 - methoxy-propan-ol-3, diglyceron monoamine, diglycerol diamine, and the like. It is a preferred embodiment of the invention, however, to use those hydroxy-alkyl amines having up to 4 carbon atoms in each alkyl radical, such as monoethanolamine, diethanolamine and monoisopropanolamine.

The lower monohydric alcohols to be used in the

process of the present invention are those aliphatic alcohols containing up to about 5 carbon atoms, examples thereof being methanol, ethanol, isopropanol, and butanol, methanol being preferred.

The alkali metal alkoxide catalyst referred to is well known to the art and is not a novel feature of the present invention. The catalyst is derived from lower monohydric alcohols having up to about 5 carbon atoms, such as methanol, ethanol, isopropanol and butanol, methanol being preferred. The catalyst may desirably be prepared by treating excess lower monohydric alcohol with alkali metal so as to produce a solution of alkali metal alkoxide in a lower monohydric alcohol suitable for direct addition to the fatty triglyceride as described previously. The catalyst may also be prepared in other manners using any material capable of reacting with lower monohydric alcohols to form alkali metal alkoxide. Suitable alkali metals include sodium, potassium and lithium.

It is understood, of course, that the term "catalyst" is used herein in reference to alkali metal alkoxides in the sense previously used in the amidation art. That is, it refers to a material which is employed in minor amounts to increase the rate of production of a desired product, and is not necessarily present in its original form at the end of the reaction.

In order to indicate even more fully the nature of the present invention the following examples are set forth. It will be understood that these examples are presented for illustrative purposes only and that it is not intended to limit the scope of the invention in any manner. It will be realized by those skilled in the art that the invention is not restricted to the examples except as indicated in the appended claims.

Example I

Approximately 0.2 gram moles of coconut oil at about 30° C. are placed in a 300 milliliter three necked spherical glass flask, the lower one-third of which is covered by an electrical heating mantle. An electrically driven glass stirrer continuously agitates the contents of the flask at about 500 R. P. M. A solution of 0.037 gram moles of sodium methoxide in about 0.18 gram moles of methanol is added to the flask and is allowed to interact with the coconut oil for approximately two minutes at about 30° C. During this period the contents of the vessel form a loose gel, and analysis of a sample of the contents of the flask indicates a monoglyceride content of approximately 15%.

At the end of the two minute pretreatment period, 0.67 gram moles of diethanolamine are added to the flask and form a separate liquid phase therein. The contents of the flask are then heated to about 60° C. by means of the previously described electric heating mantle. Within two minutes of reaching about 60° C., the contents of the flask become homogeneous and a typical exothermic amidation reaction occurs largely within about 2 minutes.

In contrast to the above example, if the same mixture of catalyst and lower monohydric alcohol is added to the diethanolamine, two and one-half times as much catalyst is required to achieve homogeneity within the same period of time under the same conditions of temperature and agitation, or as an alternative, the final mixture of reactants must be heated to a temperature of about 77° C.

Example II

Approximately 0.2 gram moles of coconut oil at about 30° C. are placed in a 300 milliliter three necked spherical glass flask, the lower one-third of which is covered by an electrical heating mantle. An electrically driven glass stirrer continuously agitates the contents of the flask at about 500 R. P. M. A solution of 0.018 gram moles of sodium methoxide in about 0.09 gram moles of methanol is added to the flask and is allowed to interact with the coconut oil for approximately two minutes at about 30° C. During this period the contents of the vessel form a loose gel.

At the end of the two minute pretreatment period, 0.67 gram moles of diethanolamine are added to the flask and form a separate liquid phase therein. The contents of the flask are then heated to about 78° C. by means of the previously described electric heating mantle. Within two minutes of reaching about 78° C., the contents of the flask become homogeneous and a typical exothermic amidation reaction occurs largely within about 2 minutes.

In contrast to this example, if the same mixture of catalyst and lower monohydric alcohol is added to the diethanolamine, approximately two times as much catalyst is required to achieve homogeneity within the same period of time under the same conditions of temperature and agitation, or as an alternative, the final mixture of reactants must be heated to a temperature of about 90° C.

Although the present invention has been described with reference to particular embodiments and examples, it will be apparent to those skilled in the art that variations and modifications of this invention can be made and that equivalents can be substituted therefor without departing from the principles and true spirit of the invention.

What is claimed is:

1. A process for the preparation of fatty acid hydroxy alkyl amides which comprises reacting fatty triglyceride with lower monohydric alcohol in the presence of alkali metal alkoxide having up to about 5 carbon atoms to form a reaction product containing fatty acid monoglyceride, the molar ratio of said fatty triglyceride to said monohydric alcohol being within the range of 1:0.25 to 1:2, and reacting the thus formed fatty acid monoglyceride-containing reaction product with hydroxy alkyl amine selected from the group consisting of hydroxy lower alkyl mono and di amines having up to 4 carbon atoms in each alkyl radical therein to form fatty acid hydroxy alkyl amide.

2. A process for the preparation of fatty acid hydroxy alkyl amides as set forth in claim 1 wherein said fatty acid monoglyceride-containing reaction product is reacted with said hydroxy alkyl amine at a temperature from room temperature to about 80° C.

3. A process for the preparation of fatty acid hydroxy alkyl amides as set forth in claim 1 wherein said fatty acid monoglyceride-containing reaction product is reacted with said hydroxy alkyl amine at a temperature of about 55° to 60° C.

4. A process for the preparation of fatty hydroxy amides which comprises reacting fatty triglyceride containing fatty acid radicals predominantly of about 10 to 20 carbon atoms with lower monohydric aliphatic alcohol containing up to about 5 carbon atoms in the presence of alkali metal alkoxide containing up to about 5 carbon atoms to form a reaction product containing fatty acid monoglyceride, the molar ratio of said triglyceride to alcohol being within the range of about 1:0.25 to 1:2, and reacting the resulting mixture of said monoglyceride, triglyceride, and alkoxide with hydroxy alkyl amine selected from the group consisting of hydroxy lower alkyl mono and di amines having up to 4 carbon atoms in each alkyl radical therein, said reaction with said hydroxy alkyl amine being carried out at a temperature from room temperature to about 80° C.

5. A process for the preparation of fatty hydroxy amides which comprises reacting fatty triglyceride containing fatty acid radicals predominantly of about 12 to 16 carbon atoms with lower monohydric alcohol in the presence of alkali metal alkoxide containing up to about 5 carbon atoms to form a reaction product containing fatty acid monoglyceride, the molar ratio of said triglyceride to alcohol being within the range of about 1:0.25

to 1:2 and the molar ratio of said triglyceride to alkoxide being within the range of about 1:0.045 to 1:0.3, and reacting the resulting mixture of said monoglyceride, triglyceride, alcohol and alkoxide with hydroxy alkyl amine in slight molar excess of said fatty acid of said mixed fatty monoglyceride and triglyceride, said hydroxy alkyl amine selected from the group consisting of hydroxy lower alkyl mono and di amines having up to 4 carbon atoms in each alkyl radical therein and said reaction with said hydroxy alkyl amine being carried out at a temperature from room temperature to about 80° C.

6. A process for the preparation of fatty hydroxy amides as set forth in claim 5 wherein the molar ratio of said fatty triglyceride to lower monohydric alcohol is about 1:1.

7. A process for the preparation of fatty hydroxy amides as set forth in claim 5 wherein the ratio of said

fatty triglyceride to hydroxy alkyl amine is within the range of about 1:1 to 1:1.3.

8. A process for the preparation of fatty hydroxy amides which comprises reacting coconut oil with methanol in the presence of sodium methoxide to form a reaction product containing coconut oil fatty acid monoglyceride, the molar ratio of said coconut oil to said methanol being within the range of 1:0.25 to 1:2, and reacting the resulting mixture of said monoglyceride, coconut oil, methanol and sodium methoxide with diethanolamine at a temperature from room temperature to about 80° C.

References Cited in the file of this patent

UNITED STATES PATENTS

2,464,094 Meade ---------- Mar. 8, 1949