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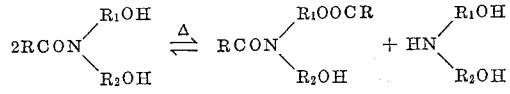
PROCESS FOR THE PREPARATION OF AMIDES

Vincent Lamberti, Teaneck, N.J., assignor to Lever Brothers Company, New York, N.Y., a corporation of Maine

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This invention relates to a method of making amides and more particularly to an improved process for the preparation of amides from fatty acid esters of glycerol and secondary alkylolamines.

Fatty acid dihydroxyalkyl amides are frequently employed as additives in liquid detergent compositions. In the reaction between esters of higher fatty acids and dihydroxyalkyl amines to form fatty acid dihydroxyalkyl amides, there is a tendency toward the formation of an amide-ester by the following equilibrium:



where R—CO— is a higher fatty acyl radical and R_1 and R_2 are alkylene radicals. Since the presence of the amide-ester is deleterious to the foaming properties of detergent compositions containing the fatty acid dihydroxyalkyl amide, it is desirable to prepare the amide under conditions to suppress the formation of the undesirable amide-ester.

For example, one method disclosed in the prior art to produce fatty acid dihydroxyalkyl amides essentially free of amide-ester is to hold the final reaction mixture containing the amide and substantial amounts of the amide-ester for at least two days at temperatures below 55° C. in the presence of an alkali metal catalyst. During this holding period, much of the amide-ester by-product is converted to the dihydroxyalkyl amide. The use of an aging period is time-consuming and therefore uneconomical.

Another method developed to produce fatty acid dihydroxyalkyl amides free of deleterious amounts of amide-ester is to condense fatty acid esters with secondary amines in the presence of a catalyst selected from the group of alkali metals, their amides and alkoxides at temperatures of 200°–280° F. and thereafter slowly cool the reaction mixture to storage temperatures. At the end of the slow cooling step the amide-ester is at a level which is insufficient to interfere with the foaming properties of the amide.

An object of the present invention is to provide a rapid and efficient method of preparing substantially colorless and odorless fatty acid dihydroxyalkyl amides from fatty acid esters of glycerol.

Another object is the preparation of dihydroxyalkyl amides without using holding periods or a slow cooling step.

Still another object of the invention is to provide a process for the production of dihydroxyalkyl amides free of substantial amounts of by-products which tend to inhibit the foaming properties of the amides.

These and other objects and advantages of the invention are attained by reacting a fatty acid ester of glycerol with an excess of a dihydroxyalkyl amine at temperatures of about 65° C. to about 100° C. in the presence of at least about 0.02 mole of an alkali metal hydroxide catalyst per mole of ester group. In a preferred embodiment, the glyceride is added gradually to the heated mixture of the catalyst and the amine under conditions such that at all times during the reaction there is maintained an excess of free amine relative to the glyceride.

The formation of the amide-ester is largely suppressed under the conditions of the present process thereby yielding a product having a relatively low level of this impurity without the necessity of using a holding period or a slow cooling step. The product is also substantially free of undesirable odors, has an acceptable color and is admirably suited for use in formulating detergent compositions.

The glycerol esters used in the process are mono-, di- or triglycerides derived from higher fatty acids and mixtures of these acids. The fatty acid radical generally contains about 8 to about 18 carbon atoms and may be derived from acids including palmitic, stearic, lauric and myristic. Thus, glycerol monostearate, glycerol distearate, mixed mono- and diglycerides of stearic acid or stearic-lauric acids can all be utilized in the invention. Preferably, the esters employed are naturally occurring triglycerides fats and oils such as coconut oil, palm kernel oil, lard, tallow, soy bean oil, etc. Refined coconut oil is a particularly preferred triglyceride. Mixtures of the mono-, di- and triglycerol esters may also be employed.

The secondary amine is a dihydroxyalkyl amine such as diethanolamine, dipropanolamine, diisopropanolamine, dibutanolamine, diisobutanolamine, etc. which are dihydroxy lower alkyl amines. These amines have two alkyl radicals each joining a hydroxyl group to the same nitrogen atom which contains a replaceable hydrogen. It is vitally important to the successful operation of the present process that the amine be present in excess during the reaction. At least 1.1 moles of amine per mole of ester group is necessary, and it is preferred to utilize a ratio of about 1.3 moles of amine for each mole of ester group. Higher levels can also be used, if desired.

As an aid in maintaining a relatively large excess of amine when the process is carried out as a batch operation, the fatty acid ester of glycerol is preferably added gradually to the reaction mixture. When the reaction is complete, the reaction mixture may be cooled to storage temperatures.

The catalyst used in the process of the invention is an alkali metal hydroxide. While sodium hydroxide is preferred, other alkali metal hydroxides such as potassium hydroxide and lithium hydroxide can also be utilized. An important advantage in the use of alkali metal hydroxides as catalysts is that selected species of these reagents are relatively inexpensive in comparison to catalysts such as the sodium alkoxides conventionally used in preparing fatty acid alkanolamides. In addition, the hydroxide catalysts are unexpectedly superior in terms of providing a substantially odorfree, colorless product with a low amide-ester content.

A level of hydroxide catalyst of at least about 0.02 mole per mole of ester group is necessary to provide a product having an acceptable amide-ester content. A preferred amount of catalyst is about 0.06 mole per mole of ester group. The maximum amount of catalyst depends upon a number of factors. Thus, at any given reaction temperature the hydroxide has a limited solubility in the reaction medium. Undissolved catalyst is not only inefficient from an economical standpoint but may also cause plugging of lines and equipment and lead to soap formation which has a deleterious effect upon the foam stabilizing properties of the amide product. In general, the upper limit on the level of catalyst is about 0.2 mole per mole of ester group. If free fatty acids are present in the glycerol ester, the proportion of catalyst present in the reaction medium as discussed above would be in addition to the amount required to neutralize the fatty acids.

Reaction temperatures ranging from about 65° C. to about 100° C. should be employed. A preferred temperature range is 80° C. to 90° C. Temperatures above about 100° C. are undesirable since high levels of amide-ester are obtained and the product exhibits a darker color as the reaction temperature increases.

The following examples are illustrative of the present invention.

EXAMPLE 1

Refined, bleached and deodorized coconut oil, 658 parts, was added gradually to a mixture of 405 parts of diethanolamine (molar ratio of amine to oil=3.85) and 4.95 parts of powdered sodium hydroxide (molar ratio of NaOH to oil=0.124) at 80° C. and under agitation. After the addition of the coconut oil was complete, the reaction mixture was maintained at reaction temperatures for an hour and then cooled. The amide-ester content (all esters calculated as amide-ester and determined by infrared analysis) of the product was found to be 3%. The product was essentially odorless and very light (pale yellow) in color.

EXAMPLES 2–6

The same procedure as in Example 1 was used except that the catalyst level was varied as follows:

	Molar Ratio of NaOH To Coconut Oil	Percent Amide-Ester In Product
Example No.:		
2	0.03	20
3	0.05	11
4	0.08	5.5
5	0.15	3
6	0.20	3

The results show that the molar ratio of catalyst to ester group must be above a minimum level in order to obtain a product having an acceptable amide-ester content.

EXAMPLE 7

The same procedure as in Example 5 was followed except that the reaction temperature was 70° C. The amide-ester content of the product was only 2%. The product was essentially odorless and pale yellow in color.

EXAMPLE 8

The same procedure as in Example 5 was followed except that the reaction temperature was 65° C. The amide-ester content of the product was only 2%. The product was essentially odorless and pale yellow in color.

EXAMPLE 9

The same procedure as in Example 5 was followed except that the molar ratio of diethanolamine to coconut oil was 3.3 to 1.0 (i.e., 1.1 moles of diethanolamine per ester group in the glyceride). The amide-ester content of the product was 7%. The product was essentially odorless and pale yellow in color.

EXAMPLE 10

The procedure employed in Example 5 was followed except that the reaction temperature was 85° C. The amide-ester content of the hot reaction product was 4%. The product was then slowly cooled over a 3 hr. period. The amide-ester level remained at 4% showing that a slow cooling step is unnecessary to obtain a product having a low amide-ester content.

EXAMPLE 11

The procedure of Example 5 was again followed employing a reaction temperature of 100° C. The amide-ester content of the product was 7%. The product was odorless and pale yellow although the color was slightly darker than the product of Example 10.

When the process was repeated using a reaction temperature of 115° C., the product had a relatively high amide-ester content of 12%. The product was also darker in color than the products obtained by using reaction temperatures of 85° C. and 100° C.

EXAMPLE 12

A mixture of coconut mono- and di-glycerides was first prepared by reacting 658 g. (1 mole) of refined, bleached and deodorized coconut oil with 184 g. (2.0 moles) of glycerol at 80° C. for three hours in the presence of 4 g. (0.1 mole) of powdered sodium hydroxide and under agitation. The mixed glycerides, 846 g., were then gradually added to a mixture of 405 g. (3.85 moles) of diethanolamine (molar ratio of amine to ester groups, 1.3) and 4 g. (0.1 mole) of powdered sodium hydroxide (molar ratio of total NaOH per ester group 0.07) at 80° C. and under agitation. After the addition of the glyceride mixture was complete, the reaction mixture was maintained at reaction temperatures for an hour and then cooled. The amide-ester content of the product was 6%. The product was essentially odorless and very light (pale yellow) in color.

It will be observed from the above disclosure that the invention involves a novel combination of several critical features to provide surprising and unexpected results. Thus, a fatty acid ester of glycerol and a dihydroxyalkyl amine are reacted under the following critical conditions:

(a) Using an alkali metal hydroxide catalyst;

(b) Using a reaction temperature of between about 65° to 100° C.;

(c) Employing an excess of amine relative to the glyceride;

(d) Employing at least about 0.02 mole of alkali metal hydroxide per mole of ester group.

By following these conditions, fatty acid dihydroxyalkyl amides are obtained which are essentially odorless, light in color and exhibit low amide-ester levels without the necessity of using holding periods or a slow cooling step.

Products made with sodium methoxide as the catalyst according to the above procedure were characterized by a sweet ester odor which rendered the products unsuitable for many applications. This compares unfavorably with the results obtained by the procedure of the present invention wherein an essentially odorless product was produced which also had an acceptable amide-ester content.

As additional evidence of the unexpected nature of the invention, products have been prepared using NaOH as a catalyst and methyl esters of coconut oil (lauric-myristic acids in ratio of 80:20) as reactants at 80° C. These products had a very high amide-ester level (about 12%) in comparison to amides obtained in accordance with the principles of the present invention.

While the working examples all disclose the preferred embodiment of operating the process batch-wise, it should be realized that the method of the invention can be operated continuously. The particular operating conditions to be employed in a continuous operation can be readily determined by those skilled in the art bearing in mind that the critical conditions of temperature, type and level of catalyst and excess amine as discussed above must be observed.

It will occur to those skilled in the art that there are many modifications to the invention as specifically described herein. It is intended to include all such modifications within the scope of the appended claims.

I claim:

1. A method for the production of fatty acid dihydroxyalkyl amides which comprises reacting a higher fatty acid ester of glycerol containing fatty acids of about 8 to 18 carbon atoms and mixtures thereof and a secondary dihydroxy lower alkyl amine at temperatures of about 65° C. to about 100° C. in the presence of at least about 0.02 mole of an alkali metal hydroxide catalyst per mole of ester group, with an upper limit of 0.2 mole of catalyst per mole of ester group in addition to the amount required to neutralize any free fatty acid present in the glycerol ester, the total mole proportions of amine to ester group being at least 1.1 to 1.0 respectively, the reaction conditions being maintained so that at all times

there exists in the reaction medium an excess of amine relative to the fatty acid glycerol ester.

2. A process according to claim 1 in which the ester of glycerol is a triglyceride.

3. A process according to claim 2 in which the triglyceride is coconut oil.

4. The process of claim 1 in which the catalyst is sodium hydroxide.

5. The process of claim 1 in which the reaction temperature is about 80° C. to 90° C.

6. A method for the production of fatty acid dihydroxyalkyl amides which comprises gradually adding refined coconut oil to diethanolamine in a molar proportion of about 1 to 3.85 at a temperature of about 80° C. in the presence of about 0.15 to 0.20 mole of sodium hydroxide per mole of coconut oil, the reaction conditions being maintained so that at all times there exists

in the reaction medium an excess of amine relative to coconut oil, to obtain coconut oil diethanolamine free of substantial amounts of interfering by-products.

References Cited

UNITED STATES PATENTS

2,844,609	7/1958	Tesoro	260—404
2,863,888	12/1958	Schurman	260—404
3,040,075	6/1962	Lohr	260—404

FOREIGN PATENTS

781,549	8/1957	Great Britain.

NICHOLAS S. RIZZO, *Primary Examiner.*

F. A. MIKA, *Assistant Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,395,162 July 30, 1968

Vincent Lamberti

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, line 10, insert the following reference:

3,107,258 10/1963 Lamberti et al.

Signed and sealed this 13th day of January 1970.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents