

1

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PROCESS FOR THE PREPARATION OF FATTY ACID DIHYDROXYALKYL AMIDES

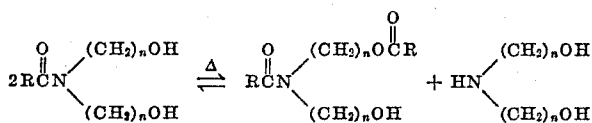
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4 Claims. (Cl. 260—404)

The present invention relates to a process for the production of fatty acid dihydroxyalkyl amides in high purity and in a form especially suitable for incorporation in liquid detergent concentrates. The amides of the present process are characterized by low contents of fatty acid esters and free amines.

As set forth in my previously filed application Serial Number 458,754 (of which this is a continuation-in-part), fatty acid dihydroxyalkyl amides exist in equilibrium with a fatty acid mono ester of the fatty acid dihydroxyalkyl amide (referred to hereinafter as ester-amide) and dihydroxyalkyl amide in accordance with the following equation:



where



is a fatty acyl radical, and n is an integer.

As is apparent, the equilibrium is such as to favor formation of the ester-amide at elevated temperatures (e. g. the equilibrium ester-amide level at 74° C. is 15%). Moreover, the rate of reaction characterizing this equilibrium is quite high at the elevated temperatures (such as 100° C. and higher) at which fatty acid dihydroxyalkyl amides are prepared from fatty esters and dihydroxyalkyl amines, but is almost negligible at temperatures below about 55° C. Thus amides which are prepared at or heated to elevated temperatures (as in the course of melting a large quantity of material) frequently contain the high level of ester-amide characterizing high temperatures because on cooling, the equilibrium condition characterizing the lower temperature is approached only at a negligible rate.

In my previously filed application I have also disclosed that it is desirable that fatty acid dihydroxyalkyl amides which are incorporated in substantial proportions in liquid detergent concentrates be of high purity, especially as regards freedom from substantial amounts of the ester-amide which is very deleterious to the foaming ability of detergent compositions containing the amide. It is also desirable to maintain a low level of free or non-esterified dihydroxyalkyl amine.

Fatty acid dihydroxyalkyl amides which are to be incorporated in concentrated liquid detergent composition should be in molten or liquefied form in order to avoid the long delay required for complete dissolution of the solid material in the solvent, such as aqueous alcohol, employed in liquid detergent concentrates in which the amides are used (as exemplified by Vitale and Leonard, U. S. Re. 23,480). However, in melting solidified fatty acid dihydroxyalkyl amides, especially in commercial operations wherein a large quantity of amide must be melted within a reasonable time, the amide is likely to

2

be heated, at least locally, to temperatures at which it rearranges to form a substantial proportion of ester-amide and free dihydroxyalkyl amine in accordance with the above equation. For instance, it has been found that a fatty acid dihydroxyalkyl amide heated to 105° C. (as may be experienced when steam is used to melt the solid amide) never reaches an equilibrium ester-amide level, as removal of dihydroxyalkyl amine from the system by formation of non-reactive tertiary amines results in continuous conversion of the desired amide to the undesirable ester-amide.

In accordance with the present invention, a process for the preparation of fatty acid dihydroxyalkyl amides having a low content of the fatty acid monoester of said amide normally associated therewith and being in a molten form suitable for incorporation in liquid detergent concentrates comprises holding a fatty acid dihydroxyalkyl amide molten at a temperature below 55° C. for at least about two days in the presence of free dihydroxyalkyl amine and in the presence of at least 0.05% of an alkali metal catalyst selected from the group consisting of alkali metal, alkali metal alkoxides, and alkali metal amides to produce a molten product containing at least 85% fatty acid dihydroxyalkyl amide. Preferably the present process is carried out immediately following preparation of fatty acid dihydroxyalkyl amide by amidation of a fatty acid ester with dihydroxy alkyl amine at an elevated temperature suitable for this reaction, i. e. 70°–175° C.

The amides employed in the present process melt at temperatures between about 30° C. and about 50° C., and may in some instances be supercooled several degrees below their melting point without solidifying. (Thus the diethanolamide of coconut oil fatty acids which has a melting point of about 30° C. normally remains liquid at room temperature.) It is preferred to carry out the aging of the molten amide at a temperature lower than 10° C. above the melting point of the product being treated. This shifts the equilibrium between the amide and the ester-amide most favorably toward the amide. It has been found that in the presence of the alkali metal catalyst, approach to equilibrium is initially very rapid and then tapers off asymptotically, a contacting period of from 2 to 4 days normally sufficing to enable a substantial approach to the equilibrium ratio of amide to ester-amide and to reach a state wherein a further shift toward the equilibrium condition occurs at a substantially reduced rate. Normally, on aging for about two days at the preferred temperature, a major portion of that amount of ester-amide which is present over and above the equilibrium content at the temperature of aging is converted to the desired dihydroxyalkyl amide, provided of course, that the required active catalyst and free dihydroxyalkyl amine are present in the product being aged. Typically, the amount of ester-amide (above the equilibrium value) in such a product drops on the order of 75% of the way to the equilibrium value during the first 2 to 4 days of treatment. Such products contain not more than about 8% and preferably less than about 5% of ester-amide. The total free amine content of the instant products is less than 10%, preferably less than 5% with the result that the aged product contains at least 85%–87% of the desired amide. A small amount (up to 3%) of alkali metal soap may also be present, but the product is essentially free of tertiary amines and other degradation products characterizing exposure to elevated temperatures for any substantial period of time. An amide product prepared from a fatty acid ester of a non-volatile alcohol may also contain on the order of 10% of the alcohol, and each of the foregoing figures will be decreased correspondingly to the proportion of the innocuous alcohol that is present.

The diminution of the ester-amide content of amide products being aged in accordance with the present process may conveniently be evaluated either by infra-red analysis or by observing the decrease in the total basicity of the product by titration to an acid end point, e. g. a pH of 4.5, with standardized strong mineral acid. The diminution in total basicity, when expressed in terms of dihydroxyalkyl amine, represents the amount of dihydroxyalkyl amine consumed by reaction with the ester-amide to form two moles of amide for each mole of ester-amide.

The fatty acid radical of the instant amides contain about 10 to 18 carbon atoms. Fatty acids representative of such radicals are lauric, myristic, palmitic, stearic, linoleic and oleic acids and mixtures thereof. These acids may be derived from naturally occurring products such as coconut, palm kernel, babassu, palm, fish, linseed, sperm, soy bean, olive, and cottonseed oils, grease tallow, and their hydrogenation products. Especially preferred are mixtures of higher fatty acids wherein the resulting fatty acid dihydroxyalkyl amide exhibits a low melting eutectic e. g. mixtures of lauric and myristic acids, such as occur almost in the eutectic proportion in coconut oil and which on amidation with diethanolamine, produce an amide product which melts at 30° C., but which on cooling, readily supercools to room temperature.

The mixtures of amide and ester-amide which are treated according to the present process may be prepared from fatty acid esters such as esters of the foregoing fatty acids with alcohols containing up to about 5 carbon atoms, e. g. the fatty acid esters of mono- and polyhydric alcohols such as methanol, ethanol, isopropanol, 1-butanol, ethylene glycol, propylene glycol and glycerol. By using esters of volatile alcohols, such as the lower monohydric alcohols containing up to 3 carbon atoms, e. g. methanol and ethanol, and carrying out the amidation reaction under vacuum, the alcohol liberated during the course of the amidation reaction may be distilled out of the reaction mass, thus providing an alcohol free product. Operating pressures employed for such a reaction are dependent on the particular reactants involved, being generally within the range of 1 to 20 inches of mercury absolute.

Dihydroxyalkyl amines suitable as a source of the dihydroxyalkyl amine radical of the instant amides are those dihydroxyalkyl amines which have two alkyl groups each joining an esterifiable hydroxy group to a common nitrogen atom, this nitrogen atom also having attached thereto a replaceable hydrogen atom. Among representative dihydroxyalkyl amines which may be used are, for examples, diethanolamine, diisopropanolamine, dibutanolamine, dipentanolamine and the like. It is a preferred embodiment of the invention, however, to use those fatty acid dihydroxyalkyl amides having up to 4 carbon atoms in each alkyl radical and more particularly it is preferred to employ those derived from diethanolamine. In general, in order to insure the presence of an amount of amine adequate to conversion of the ester-amide to the amide without producing a product containing more than 10% by weight of free amine, the free amine should be present in the product to be aged in a molar proportion of from 1 to 1.1 moles per mole of ester-amide therein.

The catalyst employed in the process of the present invention is selected from the group consisting of alkali metals, alkali metal alkoxides and alkali metal amides. It is of course, within the scope of the invention to employ materials capable of reacting with hydroxyl-alkyl amines to form alkali metal alkoxides and/or amides. Thus the catalyst may conveniently be prepared by mixing a highly concentrated aqueous alkali metal hydroxide, such as potassium hydroxide, with the dihydroxyalkyl amine present in the final product and subjecting the mixture to heat and high vacuum so as to distill off

water, or by simply using solid anhydrous alkali metal hydroxide per se, e. g. lithium hydroxide.

The catalyst may be added directly to the amide product which is to be treated in accordance with the present process, or it may be carried over from an initial amidation reaction between the aforesaid fatty esters of lower alcohols and dihydroxyalkyl amine, provided that the initial reaction has been carried out under such conditions that the product to be aged contains adequate free catalyst. The amount used during the instant heat-treating process is at least 0.05% by weight free catalyst calculated as alkali metal. Where contamination of the product by soap is not objectionable, relatively large amounts of catalyst may be employed, e. g. up to about 1% by weight of the reactants, but it is normally desirable to use on the order of from 0.05% to .3% by weight free alkali metal catalyst in carrying out the present process. Where the catalyst is to be carried over from an initial amidation reaction between a fatty ester of a lower alcohol and a dihydroxyalkyl amine, the necessary initial catalyst concentrations vary depending upon processing conditions, the particular materials involved in the reaction, the water content thereof, the concentrating effect of the removal of volatile reaction products, and other factors. Thus, as set forth in my previous application, it has been found that under certain conditions including extremely short reaction time, the removal of a volatile product such as methanol, and immediate cooling of the reacted materials, an amidation process may be operated with as little as about 0.05% catalyst calculated as alkali metal based on the reactants, and that as a result of the concentrating effect of the removal of the methanol, a cooled product may be produced containing as much as 0.05% by weight of active catalyst (based on the product) in addition to the soap which has formed during the reaction.

Example I

Diethanolamine is reacted with the methyl esters of coconut oil fatty acids at 114° C. and 100 to 125 millimeters of mercury absolute in the presence of a potassium catalyst. The weight ratio of diethanolamine to methyl esters is 17.5:32. Methanol distills off in the stoichiometric quantity, indicating completion of the reaction.

The reaction product, which has a melting point of about 30° C., is cooled to 35° C. Initially the cooled liquid product contains 0.2% free potassium catalyst (remaining from the original amidation reaction) and 10% of the coconut oil fatty acid monoester of the N bis(2-hydroxy ethyl) amide of coconut oil fatty acids. After being held at 35° C. for three days, the product has a total ester-amide content of less than 3%, a free diethanolamine content of about 5.5%, an alkali metal soap content to about 2%, and the rest is substantially all the N bis(2-hydroxy ethyl) amide of coconut oil fatty acid (also known as coconut oil fatty acid diethanolamide). This liquid product readily forms clear, single phase liquid detergent concentrates (e. g. in admixture with a triethanolamine salt of a higher alkyl benzene sulfonate, water and alcohol) having a high level of foaming and detergent power.

The methyl esters of coconut oil fatty acids used in the foregoing example may be replaced by a mixture of methyl laurate and methyl myristate in the proportion of 74:26 to form a low melting mixture of lauric and myristic diethanolamides.

Example II

Diethanolamine is reacted with the methyl ester of coconut oil fatty acids at 110° C. and 100 millimeters of mercury absolute in the presence of a sodium catalyst. The methanol liberated is distilled off. The mole ratio of diethanolamine to methyl ester employed is 1.1:1.

On being cooled to room temperature, the product,

5

which readily supercools, is titrated with standardized dilute mineral acid to a pH of 4.5. It is found to contain 7.14% of basic material expressed as diethanolamine. After aging at room temperature for about 90 days, in the presence of from .05 to .11% free sodium catalyst, the product is still liquid and the ester-amide content is less than 5%. Titration of the product shows that the content of basic material expressed as diethanolamine has diminished to 4.32%. This diminution in free diethanolamine represents a decrease in ester-amide of 13.1 parts parts per 100 parts of product.

Unless otherwise indicated, the proportions expressed herein are based on percentage by weight. Thus free catalyst is referred to in terms of alkali metal regardless of the free form in which it exists, e. g. as alkali metal per se or as alkali metal amide, but does not include that alkali metal which has been converted to catalytically inactive fatty acid soap.

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 dihydroxy alkyl amides having a low content of the fatty acid monoester of said amide normally associated therewith and being in a molten form suitable for incorporation in liquid detergent concentrates which comprises holding a fatty acid dihydroxy alkyl amide molten at a temperature below 55° C. for at least about two days in the pres-

6

sence of free dihydroxy alkyl amine and in the presence of at least 0.05% of an alkali metal catalyst selected from the group consisting of alkali metal, alkali metal alkoxides, and alkali metal amides to produce a molten product containing at least 85% fatty acid dihydroxy alkyl amide.

2. A process for the preparation of dihydroxy alkyl amides of mixed higher fatty acids having a low content of the fatty acid monoester of said amide normally associated therewith and being in a molten form suitable for incorporation in liquid detergent concentrates which comprises reacting a lower monohydric alcohol ester of mixed higher fatty acids with diethanolamine in the presence of a catalyst selected from the group consisting of alkali metal, alkali metal alkoxides and alkali metal amides at a temperature within the range of about 70° C. to 175° C. to produce a liquid reaction product, and thereafter holding said product in a molten condition at a temperature below 55° C. and lower than 10° C. above its melting point for at least two days in the presence of free dihydroxy alkyl amine and of at least about 0.05% of said catalyst to produce a molten product containing at least 85% fatty acid dihydroxy alkyl amide.

3. A process for the preparation of dihydroxy alkyl amides of mixed higher fatty acids as set forth in claim 2 wherein said higher fatty acids are lauric and myristic acids.

4. A process for the preparation of dihydroxy alkyl amides of mixed higher fatty acids as set forth in claim 2 wherein said higher fatty acids are coconut oil fatty acids.

No references cited.