PREPARATION OF AMIDES OF HIGHER FATTY ACIDS

FIG. 1

ESTER WATER NH₃

1

ALCOHOL WATER

2

ALCOHOL NH₃ WATER

3

4

5

NH₃

AMIDE

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FIG. 2

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THE EFFECT OF TEMPERATURE ON PRODUCT COMPOSITION AT 30 and 75 min. REACTION TIME

FIG. 3

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PREPARATION OF AMIDES OF HIGHER FATTY ACIDS

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This application is a continuation-in-part of my application Serial No. 159,836, filed December 18, 1961, and now abandoned.

This invention relates to the preparation of normal amides of fatty acids having from eight to eighteen carbon atoms. In particular it relates to a commercially desirable method of synthesis for such amides.

The preparation of fatty acid amides can be accomplished by a variety of known methods. In general it can be said that the usual methods possess at least one of three serious drawbacks. Either the method requires a long reaction time, the method gives low percentage yields, or the method requires the synthesis of an expensive intermediate compound. For example, the common method of synthesis is to allow ammonia and fatty acid to react under anhydrous conditions. This permits almost complete conversion, but requires a reaction time of as much as several days. Similarly, other methods have used expensive intermediates such as acid halides which react with ammonia to form corrosive inorganic acids as well as the desired amide.

Accordingly, it is an object of this invention to provide an efficient method of synthesis for normal amides of fatty acids.

It is a further object of this invention to provide such a method of synthesis which will give a high percentage yield of amide with a short reaction time.

It is a still further object of this invention to provide such a method of synthesis that does not require the use of expensive intermediate compounds.

It is another object of this invention to provide a commercially desirable, continuous process for the production of normal amides of fatty acids.

The process of this invention involves reacting each (1) a fatty acid having from eight to eighteen carbon atoms, (2) an ester of said fatty acid with an alcohol having from one to four carbon atoms, or (3) an anhydride of said fatty acid, with ammonia in the presence of water in an amount from 50% to 200% by weight of the amount of water needed to saturate the equilibrium reaction mixture. The reaction is maintained at a temperature in the range of from about 320°F. to about 550°F., preferably 420°F. to 470°F., and the reaction is conducted in a closed vessel at a pressure which is maintained above 1000 pounds per square inch gauge, preferably above 2000 pounds per square inch gauge, for a reaction time of 30 to 120 minutes.

FIGURE 1 of the drawing is a block flow diagram of the process of this invention in its preferred aspects of a continuous process, as hereinafter more fully described.

FIGURE 2 of the drawing is a plot of the percentage yield of ammonia amide against varying water-ester ratios for a reaction of the methyl ester of middle cut coconut fatty acids, hereinafter defined, with ammonia at a temperature of 425°F. and a pressure of about 2,000 pounds per square inch, for varying water-ester ratios.

FIGURE 3 of the drawing is a plot of the percentage yields of total amide and methyl amide against temperature for the reaction of FIGURE 2 at a constant water-ester ratio of 0.977.

It will be understood that within the aforementioned ranges there will be optimum conditions depending upon the particular reactants used and the practical limitations imposed by economic considerations. The choice of such reactants and conditions can be made in accordance with the following considerations.

The choice of which reactant to use as a source of fatty acid radicals may depend to a great extent upon availability. The preferred reactant of applicant is the methyl ester of a fraction derived from coconut oil having an approximate composition such that 2% of the fatty acids have 10 carbon atoms, 66% have 12 carbon atoms, 23% have 14 carbon atoms and 9% have 16 carbon atoms. The fatty acids are fractionated by distillation most easily when in the form of their methyl esters.

The fatty acid groups can be either saturated or unsaturated. Examples of suitable fatty acid groups include the groups from caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, palmitoleic acid, oleic acid, linoleic acid, and mixtures of the fatty acids derived from natural fats and oils such as coconut oil, tallow, palm kernel oil, soybean oil, whale oil, fish oil, tall oil, and other natural oils whether derived from animal, vegetable or marine sources.

Sufficient ammonia (NH₃) is used in the reaction to achieve and maintain the partial pressure hereinafter more fully described.

The optimum water level, which is highly critical to the process of the invention, is that amount which will just exactly saturate the equilibrium mixture, and desirable results are achieved when 50% to 200% of this amount is employed. Although it is not desired to be bound by theory, it is believed that the reaction under these conditions proceeds as follows, using fatty acid as an example. (The other possible reactants (e.g., monohydric alcohol esters or anhydrides) will hydrolyze in water to form the fatty acid and, in the case of fatty acid esters, some impurities (e.g., the alcohol).)

\[
\begin{align*}
0 & \quad \text{NH}_3 \quad \text{(Vapor phase)} \\
\text{(R—OH + \text{NH}_3 + \text{H}_2\text{O})} & \quad \text{R—\text{ONH}_2 + \text{H}_2\text{O}} \\
\text{NH}_3 \quad \text{(Liquid phase)} & \quad \text{R—OH} \\
\text{R—ONH}_2 + \text{H}_2\text{O} & \quad \text{R—NH}_2 + \text{H}_2\text{O} \\
\text{(R—C having from 8 to 18 carbon atoms)} & \quad \text{R—\text{CN} + \text{H}_2\text{O}}
\end{align*}
\]

The first step in the reaction is the formation of ammonium soap which quickly changes to either fatty acid and ammonia or fatty acid amide and water. These latter two changes are competing reversible reactions. The ammonia in the liquid phase is also in equilibrium with the ammonia in the vapor phase. The amide can also be dehydrated to form a nitrile.

By means of these theoretical equations it is possible to explain many of the effects of changing the important independent variables of temperature, pressure, water concentration, and the effect of the mixing of the reactants.

The reaction vessel will ideally contain only two phases, one vapor and one liquid. The vapor phase will contain ammonia, water vapor, and any volatile alcohol which is present as a result of using esters as raw materials. The liquid phase will contain the raw material (e.g., fatty acid, ester, and/or anhydride), free fatty acid or ammonium soap, the desired amide, water, alcohol when esters are used as raw materials, ammonia, and impurities such as nitriles and substituted amides. When more than the amount of water necessary to saturate this fatty phase is used, a second aqueous phase forms containing a major amount of ammonium soap, as will hereinafter be dis-
discussed, and minor amounts of the other materials in the fatty phase.

The concentration of ammonia in the liquid fatty phase is important since by the presence of an excess of ammonia the formation of fatty acid from ammonium soap is desirably kept at a minimum. Since ammonia is formed at the same time as the fatty acid in the decomposition of ammonium soap, a large concentration of ammonia in the liquid fatty phase will drive the reaction in the opposite direction to form ammonium soap. This is desirable since this ammonium soap will then change to fatty acid amide and water. Only the ammonium soap in the lipide fatty phase is effective in this portion of the reaction.

The water catalyzes the reaction in which the ammonium soap is dehydrated to form amide. The variation of amide production with reaction-mixture water content is shown in FIGURE 2. Increasing water content increases the production of amide up to a certain point and thereafter an increase in water content causes a gradual decline in the amount of amide produced. The rate of this soap-dehydration reaction is increased relative to the rate of the reaction in which the amide is dehydrated to form the nitrile to such an extent that nitrile formation can be minimized while maintaining a high yield of amide. Nitriles are highly reactive and may react with such minor ingredients in a detergent composition as perfumes or optical brighteners. Consequently, they are a highly undesirable by-product in an amide which is to be used in a detergent composition. Also, since nitriles are responsible to a large extent for undesirably coloring amide, the product of the process of this invention is much whiter than an amide product prepared without observing the essential water requirements. It is impossible to form amides without forming nitriles; the process of this invention, however, minimizes this inevitable nitrile formation.

The presence of water in the liquid fatty phase also promotes the solubility of ammonia in the liquid fatty phase. Therefore, the use, in the reaction, of the maximum amount of water which is soluble in the liquid fatty phase is desirable. However, water in excess of that needed to saturate the liquid fatty phase will form a new liquid aqueous phase which will become saturated with ammonium soap. This ammonium soap in such a new liquid aqueous phase does not form amide and thus excess water in the reaction is to be avoided.

The amount of water needed to saturate the reaction mixture can be determined fairly closely by determining the separation points of the major constituents (ammonium fatty acid, etc.). This can be done by injecting various amounts of water into the fatty material in a closed, pressurized container with agitation until the point where an increase in the amount of water present does not give a corresponding increase in pressure, thereby indicating the formation of a separate aqueous phase. The amount of water in the fatty liquid phase at that point can then be determined by analysis.

The reaction of this invention can be conducted at a temperature in the range of about 320° F. to about 550° F. and within this range is an optimum temperature. An increase in reaction temperature from a temperature below the optimum temperature initially permits an increase in the equilibrium ratio of fatty amide to fatty acid by increasing the amount of water which can be dissolved in the liquid fatty phase which in turn permits a greater amount of NH₃ to dissolve in the liquid fatty phase. This increases the solubility of ammonia in water (at a higher temperature) soon counteracts the effect of the increase in amount of water present in the liquid fatty phase and, consequently, an increase in temperature then lowers the equilibrium concentration of ammonia in the liquid fatty phase. This in turn lowers the equilibrium concentration (and yield) of fatty amide. Also, additional factors to be considered are (1) that increasing temperature promotes the formation of undesirable products such as nitriles and contributes to a coloration of the product (temperatures above about 550° are bad for this reason), and (2) that the equilibrium constant for formation of amide appears to decrease with increasing temperature (according to proposed theory).

Therefore, at a given pressure there is an optimum temperature, within the range of about 320° to 550° F., because of the equilibrium constant, and these water and ammonia solubility considerations. The optimum temperature is primarily determined by the solubility of ammonia in the liquid fatty phase which in turn results in the maximum yield of amide. For a pressure of about 2000 pounds per square inch gauge, for example, the optimum temperature is about 425° F. when the reactants are the methyl esters of fatty acids derived from coconut oil and ammonia. The variation of amide yield with temperature is shown in FIGURE 3. There is a temperature at which a maximum yield occurs and temperatures above and below this temperature result in poorer yields when the same pressure and water content are used.

The reaction pressure at any given reaction temperature is proportional to the partial pressure of ammonia vapor present in the reaction mixture. Therefore, increasing reaction pressure increases ammonia concentration in the liquid phase which increases the fatty amide yield. As noted above, the reaction pressure should be more than 1000 pounds per square inch. There is a pressure for given reactants where a subsequent increase in pressure does not give a corresponding increase in percentage yield of amide. This optimum pressure is preferably above about 2000 pounds per square inch gauge. Higher pressures can be used but are not necessary.

The effect of thorough mixing is to promote the rate of solution of the ammonia gas by mixing the vapor into the liquid fatty phase. This is very important since reaction time is lengthened by inadequate mixing and formation of undesirable side products is promoted. Thus, the reaction mixture should be agitated to achieve optimum results. The reaction of this invention usually takes from about 30 minutes to about 75 minutes.

The volatile impurities (e.g., methyl alcohol, water and ammonia) in the reaction product can be removed by known methods such as flash distillation after first cooling the mixture to prevent hydrolysis of the amide to ammonium soap and/or fatty acid. The method of purification chosen will depend to a certain extent upon the size of the operation and whether the process is a continuous or batch type operation. The type of purification is in general not critical, however, due to the low percentage conversion of fatty acid to fatty amide which can be achieved with the process of this invention.

When the basic reactant is an ester of the fatty acid with an alcohol containing one to four carbon atoms such as methyl ester (all alcohols herein are monohydroric alcohols), another reaction, in addition to those described above, must be considered. This reaction is postulated to be:

This N-methyl (or N-alkyl) amide, although technically a by-product, is useful as a Suds and detergent builder for anionic detergents. Therefore, the product of the instant process when a methyl ester is a fatty material, consisting of a major amount of ammonia amide and a minor amount of N-methyl amide, is extremely useful as a detergent builder. Due to its relative lack of color and the small amount of nitrile present, this mixture is extremely desirable. FIGURE 3 shows the relationship of N-methyl amide production to temperature. The amount of N-methyl amide increases with an increase
in temperature if the other variables such as pressure and water content are held constant. The speed with which the instant reaction occurs makes it relatively easy to adapt it to a continuous process. Referring to FIG. 1, the basic reactants are mixed and run through a preheater 1 which raises the temperature of the mixture to the reaction temperature. The reaction mixture is then run through a tubular reactor 2 at a rate which will provide sufficient turbulence to the reactor. The reactor should be long enough to give a sufficiently long reaction time to achieve equilibrium. The tubular reactor 2 can be baffled to prevent back mixing if the flow rate is not sufficiently fast. The reaction mixture is then run through a cooler 3 and subsequently the amide is substantially separated from the reaction mixture in a stripper 4 by flash distillation of the volatile components (e.g., ammonia, water, and other organic volatiles, if any). If desired, the volatiles may then be subjected to distillation in a still 5 to recover the ammonia and other valuable by-products of the reaction.

The process and its advantages are demonstrated by the following examples.

**EXAMPLE I**

In Example I, all runs were made with the methyl esters of fatty acids derived from mustard oil and having an approximate distribution of carbon chain lengths as follows: C₁₀₂--2%; C₁₄--66%; C₁₆--23%; and C₁₈--9%. 291 grams of this methyl ester and alternately either 45 or 114 grams of water were charged to a one liter autoclave. The 45 grams represents theoretical saturation of the reaction mixture at 450° F, and the 114 grams represents theoretical saturation at 550° F. The reaction mixture was heated to the desired temperature, sufficient anhydrous ammonia was added to produce the indicated pressures, and the reaction mixture was stirred by means of a turbine agitator in the baffled autoclave. The following table summarizes the results of runs under varying conditions of water level, temperature, pressure, and time. The abbreviation FA stands for fatty acid and the abbreviation A stands for the amides of the fatty acid. The percentages are by weight of the organic portion of the reaction mixture. The balance of the organic portion in each run is unreacted methyl ester, impurities which were in the methyl ester, and fatty nitrile, the dehydration product of amide. These impurities are generally less than one percent of the methyl ester as charged to the autoclave.

<table>
<thead>
<tr>
<th>Reaction Time, min.</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>450° F.</td>
<td>65° F.</td>
</tr>
<tr>
<td>Water content</td>
<td></td>
</tr>
<tr>
<td>45 grams</td>
<td>114 grams</td>
</tr>
<tr>
<td>85% FA</td>
<td>85% FA</td>
</tr>
<tr>
<td>80% FA</td>
<td>80% FA</td>
</tr>
<tr>
<td>60% FA</td>
<td>60% FA</td>
</tr>
</tbody>
</table>

As can be seen from the preceding data, operation at a water level near the saturation point of the reaction mixture gave generally higher percentage yields of amide. Both too much and too little water gave generally decreased yields. An increase in temperature above 450° F. also led to a decrease in percentage yield of amide and an increase in pressure above 1800 pounds per square inch gauge gave essentially no increase in percentage yield under optimum conditions of water content and temperature. A similar run was made at 1800 pounds per square inch gauge, 45 grams of water, 425° F., and 60 minutes reaction time. This run had an organic portion of the reaction product which was 91% by weight fatty amide and 5% by weight fatty acid. As can be readily seen, there is little difference between 425° F. and 450° F. and, therefore, about 425° F. is preferred for economic reasons.

When caprylic, capric, lauric, myristic, palmitic, stearic, oleic, linoleic acids or their ethyl esters, propyl esters, butyl esters, anhydrides or mixtures thereof are substituted in the previous reactions (in molar equivalent amounts based on fatty acid), substantially equivalent results are obtained. Also, when the methyl esters of the pure fatty acids hereinbefore mentioned or mixtures of these are used derived from coconut oil are substituted in the previous reactions (in molar equivalent amounts based on fatty acid), substantially equivalent results are obtained.

**EXAMPLE II**

A 3½-inch diameter thermally insulated tube was used as a reactor in conjunction with a preheater. A continuous reaction was run in which 750 parts by weight of the methyl ester of Example I, 125 parts by weight of anhydrous ammonia, and 125 parts by weight water were pumped through the reactor at a rate of 1340 pounds/ hour-square foot. The temperature in the reactor was about 430° F. and the pressure was about 2000 pounds per square inch gauge. A sample of the reaction mixture taken after the reactants had traversed eight feet of the reactor yielded 79% amides and 5% fatty acid, all percentages being by weight of the organic portion of the reaction mixture. A sample taken after the reactants had traversed 10.5 feet of the reactor yielded 87% amides and 5% fatty acid, all percentages again being by weight of the organic portion of the reaction mixture. Since even the larger reactor length corresponds to a reactor time of only about 15 minutes in a batch process, the product from longer reactors will approach the equilibrium yields of Example I under optimum conditions.

**EXAMPLE III**

Into the reactor of Example II, a mixture of 800 parts of the methyl ester of Example I, 70 parts anhydrous ammonia, and 130 parts water were charged at a rate of 1130/pound/hr-square feet at a temperature of 430° F., and a pressure of 2000 pounds per square inch gauge. Samples taken after eight feet and 10.5 feet of the reactor had traversed gave respectively 74% amides and 3% fatty acid, and 85% amides and 4% fatty acid. Although not wishing to be bound by theory, it is felt that the slightly lower yields under these conditions are due to the difference in mixing. The faster flow rate of Example II gave better mixing and consequently better yields.

The products prepared by the reactions of Examples I, III and III, were found to be outstanding as such enhancing and such stabilizing agents when used at a 2% level in a granular detergent composition containing 17.5% of a mixture of sodium dodecyl benzene sulfonate and sodium tallow alkyl sulfate as active detergent ingredients and 50% sodium tripolyphosphate. Fatty acid amides prepared by the reaction of this invention can also be used as water proofing agents and as intermediates in preparing amines or sulfonated amines. The latter compounds are used as wetting, detergent and emulsifying agents.

What is claimed is:

1. The process of preparing a normal amide of a fatty acid having from eight to eighteen carbon atoms comprising the step of reacting, with agitation, a material selected from the group consisting of (1) fatty acids having from eight to eighteen carbon atoms, (2) the anhydrides of said fatty acids and (3) the esters of said fatty acids with alcohols selected from the group consisting of methyl, ethyl, propyl and butyl alcohols with ammonia in the presence of water in an amount from
about 50% to about 200% of the amount of water needed to saturate the equilibrium reaction mixture, at a temperature of from about 320° F. to about 550° F. and a pressure of more than 1000 pounds per square inch gauge, the temperature and pressure being adjusted to provide a maximum concentration of ammonia in the liquid fatty phase of the reaction mixture.

2. The process of claim 1 wherein the reactants are the methyl esters of fatty acids derived from coconut oil.

3. The process of claim 1 wherein the temperature is about 425° F. and the pressure is about 2000 pounds per square inch gauge.

4. The process of claim 1 wherein the equilibrium mixture is just saturated with water.

5. A continuous process for preparing a normal amide of a fatty acid having from eight to eighteen carbon atoms comprising the steps of (I) forming a reaction mixture by mixing a material selected from the group consisting of (fatty acids having from eight to eighteen carbon atoms, (2) the anhydrides of said fatty acids, and (3) the esters of said fatty acids with alcohols selected from the group consisting of methyl, ethyl, propyl and butyl alcohols with ammonia and water in an amount from about 50% to about 200% of the amount of water needed to saturate the equilibrium reaction mixture; (II) preheating the mixture to a temperature of from about 320° F. to about 550° F. with a pressure of more than 1000 pounds per square inch gauge; (III) passing the hot mixture through a tubular reactor of sufficient length to allow the reaction to reach essentially equilibrium; (IV) cooling said reaction mixture; and (V) separating the volatile components from said reaction mixture.

6. The process of preparing a normal amide of a fatty acid having from eight to eighteen carbon atoms comprising the step of reacting, with agitation, a material selected from the group consisting of (1) fatty acids having from eight to eighteen carbon atoms, (2) the anhydrides of said fatty acids and (3) the esters of said fatty acids with alcohols selected from the group consisting of methyl, ethyl, propyl and butyl alcohols with ammonia in the presence of water in an amount from about 50% to about 200% of the amount of water needed to saturate the equilibrium reaction mixture, at a temperature of from about 320° F. to about 550° F. and a pressure of more than 1000 pounds per square inch gauge.

7. The process of preparing a normal amide of a fatty acid having from eight to eighteen carbon atoms comprising the step of reacting, with agitation, the esters of fatty acids having from eight to eighteen carbon atoms with alcohols selected from the group consisting of methyl, ethyl, propyl and butyl alcohols with ammonia in the presence of water in an amount from about 50% to about 200% of the amount of water needed to saturate the equilibrium reaction mixture, at a temperature of from about 320° F. to about 550° F. and a pressure of more than 1000 pounds per square inch gauge, the temperature and pressure being adjusted to provide a maximum concentration of ammonia in the liquid fatty phase of the reaction mixture.

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