

1

3,244,734

MANUFACTURE OF FATTY ACID AMIDE COMPOUNDS

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No Drawing. Filed May 31, 1963, Ser. No. 284,336
6 Claims. (Cl. 260-404)

The present invention relates generally to the manufacture of long carbon chain amide compounds, and more particularly, the present invention relates to the manufacture of such amide compounds from esters of short carbon chain alcohols and long carbon chain fatty acids.

This application is a continuation-in-part of Serial No. 80,049, filed January 3, 1961, now abandoned.

Long chain amide compounds are commercially available and are used for many purposes in various operations. For example, stearamides are used in the rubber industry for vulcanizing and molding, and are used as additives to aid in adhesion, anti-block, anti-tack, and viscosity control in printing inks. Stearamides are also used as organosols, plastisols, and in vinyl coatings, and as intermediates in the manufacture of N-methylol stearamide, a water-proofing compound, and in other reactions. Palmitamide can be used as a textile processing and finishing chemical, paper or cardboard coating compound, and as an additive to plastics and plastisols. Oleamide also has many and varied uses, such as components of waxed paper coatings, specialty lubricants and dye solubilizers.

There are various known processes for manufacturing these long carbon chain amides and a conventionally used process employs ammoniation and dehydration of a long carbon chain fatty acid. Another known process involves taking a long carbon chain fatty acid and, in the presence of phosphorous trichloride, effecting ammonolysis. These processes are not always most satisfactory, and in the case of ammoniation and dehydration, large scale production and heavy investment in capital equipment is required for economic operation, whereas the use of phosphorous trichloride presents difficult handling problems.

Another known process for making amides involves the ammonolysis of esters of long chain fatty acids and short chain fatty acids. However, it has been found, in accordance with this invention, to provide satisfactory results, this reaction must be carried out under particular conditions to provide the desired end product.

In accordance with the process of this invention, an ester of a long carbon chain fatty acid having a carbon chain of from 12 to 30 carbon atoms and of a short carbon chain alcohol having a carbon chain of from 1 to 2 carbon atoms is subjected to ammonolysis under particular conditions. The term "long carbon chain fatty acids" is meant to include both saturated and unsaturated fatty acid chains which may or may not have branched chains.

The ester is introduced into a reaction zone which is maintained at a pressure above about 100 p.s.i.g., and preferably above about 350 p.s.i.g., at a temperature between about 275 degrees F. and about 375 degrees F. If these conditions are not maintained, substantial side reactions occur and above 375 degrees F. substantial amounts of nitriles are formed. The reaction should be carried out for at least 7 hours under these conditions and the nitrile content of the end product should be less than 1.5 percent.

An important feature of the process of this invention is the provision of a fatty acid catalyst with the ester during ammonolysis. The catalyst is preferably present

2

in an amount of between about .5 percent and about 5 percent, although the catalyst may be present in an amount of up to 10 percent of the fatty acid or higher. At lower percentages of fatty acid, the reaction is not catalyzed to an appreciable degree. The process is not materially enhanced by the use of a fatty acid catalyst within the range of 5 to 10 percent or higher and, in general, it becomes impractical to employ an amount of catalyst that is substantially in excess of 10 percent. Further, when the catalyst is employed in excess of 10 percent, the end product may be contaminated with fatty acid to an undesired degree.

The fatty acid employed as a catalyst is desirably the same fatty acid as the long carbon chain radical of the ester to thereby provide a high purity product. It will be understood, however, that the fatty acid catalyst may have short chain length. Thus, the fatty acid catalyst may have a chain length of from 8 to 30 carbon atoms.

EXAMPLE I

In the manufacture of high quality stearamide, in accordance with this invention, commercial methyl stearate, comprising 85 percent methyl stearate and 15 percent methyl palmitate, is used and, in this connection, 6,000 pounds of the commercial methyl stearate is employed and is charged into a sealed vessel. A pressure of about 500 pounds per square inch is established in the vessel and a reaction temperature of about 310 degrees F. is provided. Ammonia gas is introduced into the vessel during the treatment. There is present at the commencement of the reaction about 5 percent of stearic acid which provides the necessary catalyst for the reaction. The reaction is carried out for a period of about ten hours, and, at the completion of the reaction, the product is filtered and flaked or otherwise treated, in accordance with usual procedures.

The product comprises about 93 percent stearamide and has improved color over that which is commercially available. The product is of such purity that its melting point exceeds 100 degrees C. The product has an acid number, measured as milligrams of potassium hydroxide per gram, of 2.0, and has a soap number, measured as milligrams of potassium hydroxide per gram, of .6. It has a saponification number, also measured as milligrams of potassium hydroxide per gram, of 16. The nitrile content of the product is less than .2 percent.

EXAMPLE II

In another example of the manufacture of stearamide, the same raw materials are utilized as in the previous example and the reaction is carried out in the same manner and in the same time, except that a pressure of 600 pounds per square inch is established and the reaction temperature is 280 degrees F. The fatty acids are present in an amount of about 3 percent, the fatty acid being stearic acid. The nitrile content of the end product is less than .1 percent and stearamide comprises about 91 percent of the end product.

EXAMPLE III

In still another example of the manufacture of stearamide, the same methyl stearate as in the previous examples is utilized and a pressure of 600 pounds per square inch is established and a temperature of 375 degrees F. is utilized for a ten hour period of ammonolysis. The resulting product comprises about 1.3 percent of nitriles and has a stearamide content of about 91 percent.

EXAMPLE IV

In the manufacture of oleamide, about 6000 pounds of methyl oleate (67 percent pure) is introduced into a pressure vessel and subjected to ammonolysis over a pe-

ried of about ten hours at a temperature of about 320 degrees F. Oleic acid is present in an amount of about 2½ percent at the start of the reaction and the end product has the following characteristics:

Physical constants

Melting point, ° C.	69-72.
(Fischer-Johns) -----	2.3R-0.4Y.
Color, 1" Lovibond -----	Almost white,
Physical appearance -----	flowable powder.

Chemical constants

Acid number, mg. KOH/gm. -----	3.16
Saponification number, mg. KOH/gm. -----	15.9
Ester number, mg. KOH/gm. -----	12.7
Soap number, mg. KOH/gm. -----	0.96
Iodine value, Wijs -----	94.6
Percent N, Kjeldahl -----	4.78

The product has a nitrile content of less than about .6 percent and has an oleamide content of about 95 percent.

The product is dried and packaged in a 200 pound carton. The product has good flowability. The product has excellent color and is substantially improved over competitive oleamide compounds.

EXAMPLE V

Palmitamide is made from methylpalmitate (83.4 percent pure), in accordance with this invention. In this connection, methyl palmitate is reacted with ammonia at a pressure of about 600 pounds per square inch for about ten hours at a temperature of about 335 degrees F. The reaction is carried out in the presence of about 3 percent fatty acid and, in this run, palmitic acid is utilized as the acid in the reaction. The resulting product comprises less than about .6 percent nitriles and about 95.3 percent palmitamide, and has excellent color.

EXAMPLE VI

In the manufacture of behenamide, methyl behenate (65 percent pure) is taken in presence of about 2½ percent fatty acid, behenic acid being the fatty acid, and is reacted in a sealed vessel at 400 pounds per square inch at a temperature of about 365 degrees F. for about ten hours. At the end of the reaction time, the product comprises about 90 percent behenamide, has excellent color characteristics, and nitriles comprise less than about 0.3 percent of the product.

EXAMPLE VII

In another example of the practice of this invention, oleamide is manufactured from ethyl oleate and, in this connection, ethyl oleate is introduced into a pressure vessel and a pressure of about 475 pounds per square inch is established in the vessel. Oleic acid is present in an amount of 2.5 percent to catalyze the reaction. Ammonia is introduced over a period of about eighteen hours and, at the end of this period, the reaction is 61.7 percent complete. At a pressure of 1000 pounds per square inch the reaction is about 95 percent complete.

EXAMPLE VIII

Stearamide is manufactured from methyl stearate and, in this connection 576 grams of methyl stearate is introduced into a pressure vessel. The temperature of the vessel is raised to 150 degrees C. and pressure of about 550 pounds p.s.i.g. is established within the vessel. The methyl stearate contains 5.75 percent of stearic acid which is employed to catalyze the reaction. Ammonia is introduced into the pressure vessel over a period of about 14¼ hours during which time the vessel is agitated by shaking. At the end of this period, the stearamide product contains 95.9 percent stearamide and 0.44 percent nitrile. The stearamide has a saponification number of 13.4, an acid number of 4.3 and has excellent color characteristics.

EXAMPLE IX

In a further example of the invention, stearamide is manufactured from methyl stearate utilizing 10 percent of stearic acid as a catalyst. The mixture of stearic acid and methyl stearate is introduced into a pressure vessel and a pressure of about 550 pounds per square inch at 150 degrees C. is established in the vessel. Ammonia is introduced into the vessel over a period of about 14¼ hours. At the end of this time, a stearamide product is obtained which contains 95.9 percent stearamide and 0.36 percent nitrile. The product has an excellent color, a saponification number of 11.2 and an acid number of 5.2.

EXAMPLE X

In another example of the practice of the present invention, oleamide is manufactured from methyl oleate and, in this connection, methyl oleate is introduced into a pressure vessel and a pressure of about 650 pounds per square inch is established in the vessel. Stearic acid is present at a level of about 0.8 percent to catalyze the reaction. Ammonia is introduced over a period of about nine hours while the temperature is maintained at about 320 degrees F. At the end of this period, the reaction is 93.3 percent complete. At a reaction time of ten hours, the reaction is about 95 percent complete.

In each of the foregoing examples, methanol or ethanol is condensed in the vessel during the reaction period and removed as a by-product from the reaction zone.

It will be understood that the reaction can be carried out under a blanket of nitrogen or other inert gas in order to minimize any oxidation of the product.

The various features of the invention which are believed new are set forth in the following claims.

What is claimed is:

1. A process for the manufacture of amides comprising the steps of reacting an ester of a short carbon chain alcohol and a long carbon chain fatty acid with ammonia, the short carbon chain radical of said ester having a chain length of from 1 to 2 carbon atoms and the fatty acid radical of said ester having a chain length of from 12 to 30 carbon atoms, introducing into said reaction a fatty acid as a catalyst at a level of at least about .5 percent by weight of said ester, said fatty acid having a chain length of from 8 to 30 carbon atoms, maintaining during the reaction a temperature of from about 275° F. to about 375° F. and a pressure of at least 100 pounds per square inch gauge, said reaction providing a product having a nitrile content of less than about 1.5 percent.
2. A process for the manufacture of amides comprising the steps of reacting an ester of a short carbon chain alcohol and a long carbon chain fatty acid with ammonia, the short carbon chain radical of said ester having a chain length of from 1 to 2 carbon atoms and the fatty acid radical of said ester having a chain length of from 12 to 30 carbon atoms, introducing into said reaction a fatty acid as a catalyst at a level of from about .5 to about 10 percent by weight of said ester, said fatty acid having a chain length of from 8 to 30 carbon atoms, maintaining during the reaction a temperature of from about 275° F. to about 375° F. and a pressure of at least 100 pounds per square inch gauge, said reaction providing a product having a nitrile content of less than about 1.5 percent.
3. A process for the manufacture of amides comprising the steps of reacting an ester of a short carbon chain alcohol and a long carbon chain fatty acid with ammonia, the short carbon chain radical of said ester having a chain length of from 1 to 2 carbon atoms and the fatty acid radical of said ester having a chain length of from 12 to 30 carbon atoms, introducing into said reaction a fatty acid as a catalyst at a level of from about .5 to about 10 percent by weight of said ester, said fatty acid having a chain length of from 8 to 30 carbon atoms, maintaining during the reaction a temperature of from about 275° F. to about 375° F. and a pressure of at least 100 pounds

5

per square inch gauge, said reaction being continued for at least 7 hours.

4. A process for the manufacture of amides comprising the steps of reacting an ester of a short carbon chain alcohol and a long carbon chain fatty acid with ammonia, the short carbon chain radical of said ester having a chain length of from 1 to 2 carbon atoms and the fatty acid radical of said ester having a chain length of from 12 to 30 carbon atoms, introducing into said reaction a fatty acid as a catalyst at a level of from about .5 to about 5 percent by weight of said ester, said fatty acid having a chain length of from 8 to 30 carbon atoms, maintaining during the reaction a temperature of from about 275° F. to about 375° F. and a pressure of at least 350 pounds per square inch gauge, said reaction being continued for at least 7 hours.

5. A process for the manufacture of amides comprising the steps of reacting an ester of methyl alcohol and a long carbon chain fatty acid with ammonia, the fatty acid radical of said ester having a chain length of from 12 to 30 carbon atoms, introducing into said reaction a fatty acid as a catalyst at a level of from about .5 to about 10 percent by weight of said ester, said fatty acid having

6

a chain length of from 8 to 30 carbon atoms, maintaining during the reaction a temperature of from about 275° F. to about 375° F. and a pressure of at least 350 pounds per square inch gauge, said reaction being continued for at least 7 hours.

6. A process for the manufacture of amides comprising the steps of reacting an ester of methyl alcohol and a long carbon chain fatty acid with ammonia, the fatty acid radical of said ester having a chain length of from 12 to 30 carbon atoms, introducing into said reaction a fatty acid as a catalyst at a level of from about .5 to about 10 percent by weight of said ester, said fatty acid having a chain length corresponding to the fatty acid radical of said ester, maintaining during the reaction a temperature of from about 275° F. to about 375° F. and a pressure of at least 350 pounds per square inch gauge, said reaction being continued for at least 7 hours.

No references cited.

CHARLES B. PARKER, *Primary Examiner*.

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